

Indium – Determination of indium and its compounds in workplace air using mass spectrometry with inductively coupled plasma (ICP-MS)

Air Monitoring Method – Translation of the German version from 2021

Keywords

indium; hazardous substances; air analyses; workplace measurement; inductively coupled plasma mass spectrometry; ICP-MS; acid digestion; membrane filter

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Abstract

This analytical method is a validated measurement procedure for the determination of indium [7440-74-6] and its compounds in workplace air in an concentration range of one tenth up to twice the currently valid German OEL of 0.0001 mg/m³ R (respirable fraction). For sampling a defined volume of air is drawn through a membrane filter (cellulose nitrate). The flow rate is set to 10 l/min and sampling is performed over 2 hours (which correspond to a sampling volume of 1200 l). Indium and its compounds deposited as dust on the filter is treated with acid and afterwards analysed using inductively coupled plasma mass spectrometry (ICP-MS). The quantitative determination is based on a calibration function, whereby the indium concentration of the calibration standard is plotted against the intensities, calculated over the internal lutetium standard. The limit of quantification is 0.0000022 mg/m³ based on an air sample volume of 1200 l. The mean recovery is 105% and the expanded uncertainty for the validation range of 0.00001 to 0.0002 mg/m³ is 26.5 to 26.9%.

Method number	1
Application	Air analysis
Analytical principle	Mass spectrometry with inductively coupled plasma (ICP-MS)

1 Characteristics of the method

Precision:	Standard deviation (rel.): $s = 0.50$ to 1.54% Expanded uncertainty: $U = 26.5$ to 26.9% in the concentration range of $c = 0.01$ to $0.2 \mu\text{g}/\text{m}^3$ and for $n = 6$ determinations
Limit of quantification:	$0.0000022 \text{ mg}/\text{m}^3$ for an air sample volume of 1200 l and a sampling period of 2 h
Recovery:	$\eta = 0.963$ to 1.05 (96.3 – 105%)
Sampling recommendations:	Sampling period: 2 h Air sample volume: 1200 l Flow rate: $10 \text{ l}/\text{min}$
Short-term exposure limit:	Sampling period: 0.25 h Flow rate: $10 \text{ l}/\text{min}$ Air sample volume: 150 l

2 Description of the substance

Indium [7440-74-6]

Indium with the chemical symbol In (relative atomic mass 114.818 u , melting point $156.6 \text{ }^\circ\text{C}$, boiling point $2,000 \text{ }^\circ\text{C}$, density $7.31 \text{ g}/\text{cm}^3$) is a silvery-white, intensely shiny, very soft metal that melts at a low temperature.

Indium is very rare and is produced as a byproduct during the processing of zinc and lead ores. Industrially indium is produced by electrolysis. Due to its versatile properties, indium is predominantly used in the electrical industry as a soldering material and for low melting alloys. Furthermore, it is used for the production of III-V compound semiconductors as well as a semiconductor dopant. In the aviation industry it is used as a melted-down, galvanic indium coating on lead for bearings e.g. in aircraft engines. These are also used in high-performance automotive engines (Formula 1) and in turbo-diesel HGV engines. The industrial use of indium compounds, for example indium phosphide or indium tin oxide, has become increasingly interesting in recent years. The development of liquid-crystal display (LCD) and their use in electronic devices (e.g. consumer electronics, mobile phones, touchscreens or measurement devices) has greatly increased the demand for the electricity-conducting indium tin oxide, which is transparent in thin layers.

Indium and indium hydroxide [20661-21-6], [55326-87-9] have an Occupational Exposure Limit (OEL) of $0.0001 \text{ mg In}/\text{m}^3$ for the respirable dust fraction; the short-term exposure limit is assigned to Peak Limitation Category II with an excursion factor of 8 (AGS 2021). In the TRGS 900 guidelines indium phosphide is listed as a Category 1A or 1B carcinogenic substance or a carcinogenic activity or process according to Section 2, Paragraph 3 No. 4 of the German Hazardous Substances Ordinance (Gefahrstoffverordnung), additionally Section 10 of the German Hazardous Substances Ordinance should be taken into consideration (AGS 2021). In the “Justification for indium phosphide in TRGS 900“ a threshold concentration for indium phosphide is also stated as $0.0001 \text{ mg In}/\text{m}^3$ for the respirable dust fraction in order to protect from its carcinogenic effects (AGS 2017). The Occupational Exposure Limits are based on the element content of indium (AGS 2021). No MAK value is specified for indium phosphide [22398-80-7], but it is assigned to Carcinogen Category 2 in the List of MAK and BAT Values. Please refer to the documentation for these substances in the TRGS 900 guidelines (AGS 2021) for details on the toxicity and carcinogenicity of indium and the indium compounds described in this method.

3 General principles

This analytical method permits the simultaneous determination of indium and indium compounds in the workplace air in a concentration range of one tenths up to twice the currently valid Occupational Exposure Limit (OEL) of 0.0001 mg/m³ (respirable dust fraction) (AGS 2021; DIN 2015, 2020).

A suitable pump draws a defined volume of air through a membrane filter (nitrocellulose) for sampling. The indium deposited on the filter is determined using an inductively coupled plasma mass spectrometer after acid digestion. The quantitative evaluation is based on a calibration function, whereby the concentrations of indium in the calibration standards are plotted versus the intensities obtained, these intensities are calculated based on the internal standard lutetium.

4 Equipment, chemicals and solutions

4.1 Equipment

For sampling:

- Sampling pump, for personal or stationary sampling (sufficiently independent from the reduction in pressure caused by the sample carriers to be used) suitable for a flow rate of 10 l/min, e.g. SG 10-2, from GSA Messgerätebau GmbH, Ratingen, Germany
- FSP-10 sampling head with cyclone separator, e.g. from GSA Messgerätebau GmbH, 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, Ratingen, Germany
- Membrane filter, diameter 37 mm, pore size 8.0 µm, cellulose ester, accompanied by a test certificate stating the content of metals, e.g. nitrocellulose membrane filter, from Sartorius AG, Göttingen, Germany (or similar quality)
- Gas meter or volumetric flow meter

For sample preparation:

- Heating block thermostat made of metal or graphite with time/temperature control, e.g. from Gebr. Liebisch GmbH & Co, Bielefeld, Germany
- Digestion vessels preferably made of quartz glass or similar quality in accordance with the requirements for reaction vessels stipulated in DIN 12353 (DIN 1981), graduated (do = 19 mm, maximum volume = 25 ml) with standard outer ground glass joints (NS 19/26), 0.2-ml graduation at least in the range of 15 to 25 ml, e.g. from Merck Eurolab GmbH, Lohmar, Germany
- Air cooler preferably made of quartz glass with standard inner and outer ground glass joints for mounting onto a digestion vessel (or of comparable quality) in accordance with the requirements stipulated in DIN 12353 (DIN 1981) and DIN 12242 (DIN 1980), e.g. from Merck Eurolab GmbH, Lohmar, Germany
- Glass rods preferably made of quartz glass with replaceable endpieces (e.g. PTFE tube), e.g. from Merck Eurolab GmbH, Lohmar, Germany
- Litre bottle made of PFA with PTFE (“hydrofluoric acid”) dispenser for ultra-pure water, e.g. for PFA vessels: from VIT-LAB GmbH, Seeheim-Jugenheim, Germany and for the dispenser: “Optifix HF Dispenser 30 ml“, from Poulten & Graf GmbH (Fortuna), Wertheim, Germany
Application: rinsing the air cooler, resulting in the primary dilution after digestion

- Measuring cylinder made of PFA, maximum nominal volume 500, 100, 50 ml Application: measurement of acid aliquots for the preparation of standard acid mixtures, e.g. from Vitlab GmbH, Großostheim, Germany
- PTFE (hydrofluoric acid) dispenser “Optifix HF Dispenser 30 ml“, from Poulten & Graf GmbH (Fortuna), Wertheim, Germany
- 2.5 litre quartz bottle with lateral filler neck (NS 29/32), sealable with air-permeable PTFE ground-glass stopper and PTFE (“hydrofluoric acid“) dispenser as a bottle attachment, specially made, e.g. from Merck Eurolab GmbH, Lohmar, Germany
Application: dispensing of recently prepared standard acid mixtures into the digestion vessels
- Stoppers made of polyethylene for the above mentioned digestion vessels (NS 19/26), e.g. from Pöppelmann GmbH & Co KG, Lohne, Germany
- Ceramic tweezers, e.g. from Plano W. Plannet GmbH, Wetzlar, Germany
Application: transfer of the membrane filters into the digestion vessels

For the analytical determination:

- Quadrupole ICP mass spectrometer with cell technology to minimise interference, e.g.: NexION 350D, from PerkinElmer LAS GmbH, Rodgau, Germany
- 7900 ICP-MS, from Agilent Technologies Deutschland GmbH, Waldbronn, Germany
- Autosampler, e.g. ESI SC-8 DXS FAST, from Elemental Scientific Inc., Omaha, USA
- Peltier-cooled cyclonic spray chamber made of quartz glass with inner tube, e.g. from Elemental Scientific, Omaha, USA
- Concentric PFA nebuliser, e.g. Micro-Flow PFA-ST Nebulizer, low pressure, from Elemental Scientific Inc., Omaha, USA
- Vessels for the matrix adjustment
- PFA vessels with a screw-cap (tested for blank values), volume: 2 l, e.g. from Vitlab GmbH, Großostheim, Germany
- Vessels for standard solutions/calibration solutions
- Polypropylene vessels with a screw-cap (tested for blank values), graduated, 2.5 ml increments, maximum volume: 50 ml, for the autosampler, e.g. from Greiner Bio One GmbH, Frickenhausen, Germany
- Sample vials for the ICP-MS
- Polypropylene vessels with a screw-cap (tested for blank values), graduated, 0.5 ml increments, maximum volume: 15 ml, for the autosampler, e.g. from Greiner Bio One GmbH, Frickenhausen, Germany
- Various adjustable piston pipettes to cover a volume range of 2 µl to 10 ml, air displacement: for aqueous solutions and suspensions at a density and viscosity similar to water; e.g.: Socorex Acura 825[®] (2 to 1000 µl), Socorex Acura 835[®] (500 to 5000 µl) & Socorex Acura 835[®] (1000 to 10000 µl), from Socorex Isba S.A., Ecublens, Switzerland
- Electronic precision balance, e.g. L 610D Type, from Sartorius AG, (weighing range: a) 60 g, b) 606 g, readability: a) 1 mg, b) 10 mg), from Sartorius AG, Göttingen, Germany
- Ultra-pure water unit with reverse osmosis device and GenPure ultra-pure water system with xCAD, for the preparation of ultra-pure water ($\rho \geq 18.2 \text{ M}\Omega \times \text{cm}$ at 25 °C), reduction of the general metal content, in particular for the production of water that is low in boron and alkalis, e.g. from Wilhelm Werner GmbH, Leverkusen, Germany

4.2 Chemicals

- Ultra-pure water ($\rho \geq 18.2 \text{ M}\Omega \times \text{cm}$ at 25 °C), low metal content and specifically low in boron and alkalis, e.g. GenPure xCAD ultra-pure water purification system, from Fisher Scientific GmbH, Schwerte, Germany
- Nitric acid, low metal content, contents certified by the manufacturer for each batch, e.g. 65% nitric acid, Suprapur[®], from Merck KGaA, Darmstadt, Germany
- Nitric acid, low metal content, contents certified by the manufacturer for each batch, e.g. 67 to 70% nitric acid, INSTRA-ANALYZED[®] Plus for the trace analysis of metals, J.T. Baker[®], from VWR International GmbH, Darmstadt, Germany
- Hydrochloric acid, low metal content, contents certified by the manufacturer for each batch, e.g. 30% hydrochloric acid, Suprapur[®], from Merck KGaA, Darmstadt, Germany
- Indium plasma standard solution 1000 mg/l, Specpure[®], traceable to SRM from NIST, indium in 5% of HNO₃, e.g. from Alfa Aesar, Thermo Fisher (Kandel) GmbH, Karlsruhe, Germany, Order No. 13846
- Indium(III)chloride, anhydrous, 99.999% of indium (metal basis), e.g. from Alfa Aesar, Thermo Fisher (Kandel) GmbH, Karlsruhe, Germany, Order No. 11856
- Indium antimonide, 99.999% of indium (metal basis), e.g. from Alfa Aesar, Thermo Fisher (Kandel) GmbH, Karlsruhe, Germany, Order No. 14626
- Multi-Element Calibration Standard 3, 10 mg/l, matrix per volume: 5% of HNO₃ per 125 ml, e.g. from PerkinElmer LAS, Rodgau-Jügesheim, Germany, Order No. N9301720
- Lutetium ICP Standard 1000 mg/l, Certipur[®], traceable to SRM from NIST, Lu₂O₃ in HNO₃ 2% to 3%, e.g. from Merck, Darmstadt, Germany, Order No. 1.703300100
- Multi-Element Quality Control Standard, 100 mg/l for 33 elements, ARISTAR[®] for ICP, traceable to SRM from NIST, including analysis certificate, e.g. from VWR International GmbH, Darmstadt, Germany
- Multi-Element Calibration Standard 4, 10 mg/l, matrix per volume: 10% of HCl per 125 ml, e.g. from PerkinElmer LAS, Rodgau-Jügesheim, Germany, Order No. N9300234
- Argon 5.0 (purity 99.999%)

4.3 Solutions

The following solutions are prepared using the chemicals listed in [Section 4.2](#):

Acidic digestion mixture: 2 parts by volume of 65% nitric acid (HNO₃) and 1 part by volume of 25% hydrochloric acid (HCl)

2 parts by volume of 65% nitric acid and 1 part by volume of 25% hydrochloric acid are carefully mixed in a 2.5-l quartz bottle.

Acid mixture for the preparation of the calibration, quality control and sample solutions:

20 ml of 70% nitric acid are added to a 2-litre PFA vessel into which approx. 1.5 l of ultra-pure water have been previously placed, the vessel is then filled to 2 l with ultra-pure water.

4.4 Calibration solutions, internal standards and reference standards

4.4.1 Calibration solution

Calibration standards are prepared by diluting Multi-Element Calibration Standard 3 (10 mg/l) as follows:

Multi-Element Calibration Standard 3 Stock Solution 1: Dilution 1:100 \approx 100 $\mu\text{g/l}$

1 ml of the Multi-Element Calibration Standard 3 is pipetted into a 100 ml volumetric flask into which approx. 50 ml of the acid mixture have been previously placed. The volumetric flask is then filled to the mark with acid mixture and shaken.

Multi-Element Calibration Standard 3 Stock Solution 2 from Stock Solution 1: Dilution 1:100 \approx 1 $\mu\text{g/l}$

1 ml of Multi-Element Calibration Standard 3 is pipetted into a 100 ml volumetric flask into which approx. 50 ml of the acid mixture have been previously placed. The volumetric flask is then filled to the mark with acid mixture and shaken.

Calibration standards:

Calibration standards with indium concentrations of 0.1, 0.5, 1 and 5 $\mu\text{g/l}$ in 10 ml volumetric flasks are prepared from the Multi-Element Calibration Standard 3 Stock Solution 1 (100 $\mu\text{g/l}$). The volumetric flasks are subsequently filled to the mark with acid mixture.

Calibration standards with indium concentrations of 0.01, 0.05 $\mu\text{g/l}$ are prepared in 10 ml volumetric flasks from the Multi-Element Calibration Standard 3 Stock Solution 2 (1 $\mu\text{g/l}$). The volumetric flasks are subsequently filled to the mark with acid mixture.

The dosing scheme for the preparation of the calibration solutions is shown in [Table 1](#).

Tab. 1 Concentrations of indium in the calibration solutions

Calibration solution [μg of indium/l]	Volume of Stock Solution 1 [μl]	Volume of Stock Solution 2 [μl]	Addition of the internal standard solution [μl]	Total volume [ml]
0.01	–	100	100	10
0.05	–	500	100	10
0.1	10	–	100	10
0.5	50	–	100	10
1	100	–	100	10
5	500	–	100	10

4.4.2 Internal standards

The internal standard is prepared from Lutetium ICP Standard Solution (1000 mg/l) and added to the blank solution, the calibration solutions, the sample solutions as well as to the quality control samples. A stock solution with a concentration of 0.2 mg/l of lutetium is prepared from the 1000 mg/l Lutetium ICP Standard Solution. For this purpose, 100 μl of the Lutetium ICP Standard Solution (1000 mg/l) are added to a 500 ml volumetric flask into which approx. 450 ml of the acid mixture have been previously placed, the flask is then filled to the mark with acid mixture and shaken.

Then 0.1 ml of the internal standard stock solution is added to all the solutions (to 10 ml). This is equivalent to a lutetium concentration of 2 $\mu\text{g/l}$ in all the measurement solutions.

4.4.3 Reference standards

Quality control samples are prepared as reference standards by dilution of the Multi-Element Quality Control Standard in concentrations of 0.1, 1 and 10 µg/l and checked periodically in the analytical run. The quality control samples are prepared as follows:

Multi-Element Quality Control Standard Stock Solution: Dilution 1:1000 \approx 100 µg/l

0.01 ml of the Multi-Element Quality Control Standard is pipetted into a 10 ml volumetric flask into which approx. 9 ml of the acid mixture have been previously placed. The volumetric flask is then filled to the mark with acid mixture and shaken.

The reference standards with various concentrations are then prepared from this stock solution; the dosing scheme for the preparation of the quality control samples is listed in Table 2.

Tab. 2 Concentrations of indium in the quality control solutions

Quality control solution [µg of indium/l]	Volume of stock solution [µl]	Addition of internal standard solution [µl]	Total volume [ml]
0.1	10	100	10
1	100	100	10
10	1000	100	10

5 Sampling and sample preparation

5.1 Sampling

Sampling can be carried out as stationary or personal sampling. Measurements are taken in the breathing zone in the case of personal sampling. It is important to ensure that the inlet of the sampling head is freely accessible.

The membrane filter is inserted into the sampling head of the fine dust collection device (FSP), and a pump is connected. The air sample is drawn through the membrane filter by means of a flow-regulated pump at a flow rate of 10 l/min. After 2 hours of sampling, this is equivalent to an air sample volume of 1.2 m³. The important parameters for the determination of the concentration in air (air sample volume, temperature, air pressure and relative humidity) are documented in the sampling record.

After sampling, the flow rate must be tested for constancy. If the deviation from the adjusted flow rate is $\geq \pm 5\%$, it is advisable to repeat the measurement (DIN 2014). The loaded sample carriers are then removed from the sampling head, sealed with the pertinent caps and transported to the laboratory for analysis with as little vibration as possible.

5.2 Sample preparation

Ceramic tweezers are used to transfer the loaded membrane filter to a 25 ml digestion vessel made of quartz glass and a glass rod is used to push it down to the bottom of the vessel. Then 10 ml of the acidic digestion mixture are added, an air cooler is mounted on the vessel and the solution is boiled for two hours in an heating block thermostat at 135 °C under reflux. After cooling, 10 ml of ultra-pure water are carefully added via the reflux cooler and the mixture is briefly brought to the boiling point again. 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 analysed by ICP-MS.

A blank value determination is performed with each sample series. For this purpose at least two filters from the same batch that have not been used for sampling are subjected to the entire sample preparation and analysed.

To prepare the sample dilutions for the quantitative analysis, a few millilitres of the acid mixture are placed into suitable graduated 15 ml polypropylene vessels, a pipette is used to add an aliquot of the acid digestion mixture as well as the internal standard and the vessels are filled to 10 ml with acid mixture.

6 Operational parameters for ICP-MS

Apparatus:	Quadrupole ICP mass spectrometer with cell technology to minimise interference, NexION ICP-MS 350D with autosampler ESI SC-8 DXS FAST, from PerkinElmer LAS GmbH	
Plasma parameters:	Plasma gas flow:	15 l/min
	Auxiliary gas flow rate:	1.2 l/min
	Nebuliser gas flow rate:	0.96 l/min
	RF power:	1500 Watt
Flow rate (sample):	0.4 ml/min	
Nebuliser system:	Nebuliser chamber:	Cyclonic spray chamber made of quartz glass with inner tube, peltier-cooled
	Nebuliser:	Micro-Flow PFA-ST nebuliser e.g. ST-5660
Injector:	Material:	Sapphire
	Inner diameter:	1.8 mm
Isotope:	Indium 115 amu	
Interference correction:	The isobar interference by ^{115}Sn is corrected by „ $-0.014038 \times ^{118}\text{Sn}^c$ “.	
Internal standard isotope:	Lutetium 175 amu	
Measured solutions:	An aliquot of the sample solution is diluted to at least 1:10 (v/v). Lutetium is added to each measurement solution so that each measurement solution has a lutetium concentration of 2 µg/l. If the measurement result is outside the linear range of the calibration function, further dilutions, e.g. 1:100 and 1:1000 (v/v) must be prepared.	

7 Analytical determination

An autosampler transfers the prepared sample at a flow rate of 0.40 ml/min into the ICP mass spectrometer and analysis is performed under the conditions stated in [Section 6](#).

Note:

All solutions must be freshly prepared every working day, in particular this includes the calibration solutions and the quality control samples.

8 Calibration

The calibration solutions described in [Section 4.4.1](#) are used to obtain the calibration functions.

The calibration solutions are introduced into the ICP mass spectrometer at a flow rate of 0.40 ml/min and analysis is carried out under the operating conditions stipulated in [Section 6](#). The intensities are determined from the mass/charge ratio (m/z), which are plotted versus the corresponding concentrations. The net Intensity is obtained by means of division of the indium intensities by the intensities of the internal standard lutetium, on which the entire calculation of the concentrations is based. The calibration curves are linear in the investigated concentration ranges.

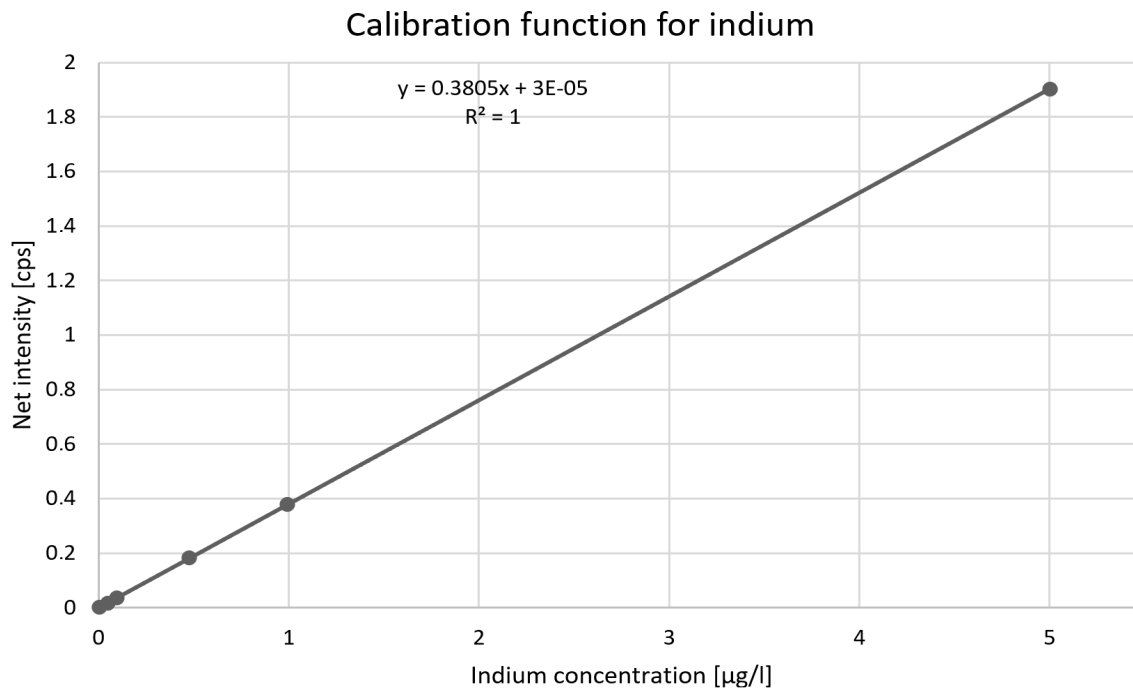


Fig. 1 Calibration function for indium

9 Calculation of the analytical result

The indium concentration in the workplace air is obtained from the concentration of indium in the measured solution calculated by the data evaluation unit. The data evaluation unit uses the calculated calibration function for this purpose. The concentrations of indium in the workplace air are calculated from the indium concentrations, taking the corresponding dilutions and the air sample volume into account.

The concentration by mass of the analyte is calculated using [Equation 1](#):

$$\rho = \frac{(C - C_{Blank}) \times 0.001 \times f_D \times V}{V_{Air}} \quad (1)$$

where:

- ρ is the mass concentration of indium in the air sample in mg/m^3
- C is the concentration of indium in the measured solution in $\mu\text{g}/\text{l}$
- C_{Blank} is the concentration of the blank value (mean value) in $\mu\text{g}/\text{l}$
- 0.001 is the conversion factor [$\mu\text{g} \rightarrow \text{mg}$]
- f_D is the dilution factor (as a rule the dilution is 1:10)
- V is the volume of the sample solution in l
- V_{Air} is the air sample volume in m^3

10 Reliability of the method

The characteristics of the method were determined as stipulated in DIN EN 482, DIN EN ISO 21832 and DIN 32645 (DIN 2008, 2015, 2020).

10.1 Precision and expanded uncertainty

In order to determine the precision and expanded uncertainty, six membrane filters in each case are spiked with different masses of indium (12 ng, 120 ng, 240 ng), dried and subjected to all the steps of the sample preparation and analysis as described in Sections 5.2, 6 and 7. A blank value correction was carried out as described in Section 9.

For this purpose a spiking stock solution with an indium concentration of 120 µg/l was prepared from the indium standard solution of 1000 mg/l via an intermediate dilution with a concentration of 6 mg/l. Six filters were spiked with 100 µl each (equivalent to an In content of 12 ng) using this spiking stock solution. A further spiking stock solution containing 2.4 mg/l was also prepared from the intermediate dilution with a concentration of 6 mg/l. Six filters were spiked with 50 µl each (equivalent to an In content of 120 ng) and six filters with 100 µl each (equivalent to an In content of 240 ng) using this spiking stock solution. The filters thus spiked were prepared and analysed in the same manner as the sample solutions. For an air sample volume of 1200 l these spiked masses are equivalent to indium concentrations in air of 10 ng/m³, 100 ng/m³ and 200 ng/m³.

The digestion solutions with the spiked masses of 12 ng, 120 ng and 240 ng were diluted with the acid mixture by a factor of 10 and the internal standard was added before analysis by means of ICP-MS. Furthermore, two unused filters (blank filters) were subjected to the complete analytical method. The precision data shown in Table 3 were calculated from these results.

Tab. 3 Standard deviation (rel.) and expanded uncertainty *U* for *n* = 6 determinations

Spiked mass of indium [ng]	Concentration of indium) ^{a)} [ng/m ³]	Standard deviation (rel.) [%]	Expanded uncertainty <i>U</i> [%]
12	10	1.54	26.7
120	100	0.57	26.5
240	200	0.50	26.9

^{a)} The concentration is calculated based on a 2-hour sampling period at a flow rate of 10 l/min

The expanded uncertainty is obtained by estimation of all the relevant influencing parameters. The uncertainty of the result consists of two important steps, the uncertainty components for sampling and for analysis.

In order to estimate the uncertainty components of sampling the uncertainty associated with the air sample volume and the sampling effectiveness for respirable dusts were determined according to Appendix C of DIN EN ISO 21832 (DIN 2020). The combination of random and non-random uncertainty components results in an uncertainty of 11.7% when respirable dusts are sampled for two hours.

The uncertainty components of the analysis encompasses the entire analytical preparation including digestion, dilution, calibration, recovery and precision. The concentration-dependent uncertainties of the analysis by this method for the mean value of the spiked masses of indium are 6.4% for 12 ng, 6.2% for 120 ng and 6.6% for 240 ng.

The combination of all uncertainty contributions results in the concentration-dependent combined uncertainties of the entire method. The values for the expanded uncertainty of the entire method listed in Table 3 are obtained by multiplication with the expansion factor *k* = 2.

10.2 Recovery

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

Certified indium and indium compounds (see Section 4.2) were used to check this sample preparation method with regard to the analytical recovery and the reproducibility of the method.

As the indium concentrations to be examined are in the ultratrace range and therefore reliable weighing of reference materials is difficult, the following procedure was selected.

Two amounts of approx. 10 mg were weighed onto a nitrocellulose filter in a 100 ml digestion vessel. Four additional nitrocellulose filters were added per vessel and boiled for two hours under reflux in 50 ml of the digestion solution (see Sections 4.3 und 5.2). After digestion, 50 ml of ultra-pure water were added via the reflux cooler and again heated to the boiling point. The solutions prepared in this manner were visually free of particles. Two intermediate dilutions in each case are prepared from the reference material solutions thus obtained. The second intermediate dilution, which has an indium concentration of 12 µg/l, was diluted six times in each case to yield indium concentrations of 10 ng/m³, 100 ng/m³ and 200 ng/m³ using the acid mixture for the preparation of the sample solutions and was diluted and analysed (see Section 4.4.3) in the same manner as the air samples. Furthermore, at least two unused filters (blank filters) were subjected to the entire analytical method. A blank value correction was carried out in order to calculate the results.

Mean recoveries for indium from indium(III)chloride of $\eta = 0.989$ and for indium from indium antimonide of $\eta = 0.980$ were determined in the quantitative analysis. The results are listed in Table 4.

The results for the recovery obtained from the measurements to determine the precision (Section 10.1) are also shown in Table 4, whereby the mean recovery was 105%.

Tab. 4 Recovery of indium for n = 6 determinations

Reference standard	Mass of indium on the filter [ng]	Concentration of indium [ng/m ³]	Recovery [%]	Standard deviation (rel.) [%]
Indium	12	10	105	1.5
Indium	120	100	105	0.57
Indium	240	200	105	0.50
Indium(III)chloride	12	10	99.7	1.6
Indium(III)chloride	120	100	98.6	1.0
Indium(III)chloride	240	200	98.5	0.84
Indium antimonide	12	10	101	1.2
Indium antimonide	120	100	96.6	1.1
Indium antimonide	240	200	96.3	0.27

10.3 Limit of quantification

During the development of the method the limit of quantification was calculated as stipulated in DIN 32645 according to the blank value method (DIN 2008).

For this purpose twelve unused membrane filters were subjected to the complete analytical method and ten measurement values are used for the determination of the limit of quantification (outlier exclusion). The mean, which is calculated from the blank values resulting from the filters, reagents and vessels used, as well as the corresponding

standard deviation were determined and inserted in Equation 2 to calculate the limit of quantification:

$$X_{LQ} = \bar{X}_{BL} + k \times s \quad (2)$$

where:

- X_{LQ} is the limit of quantification in ng/l
- \bar{X}_{BL} is the mean value for the blank value measurements in ng/l
- s Standard deviation
- k is the selected factor ($k = 10$)

Table 5 shows the limit of quantification for indium.

Tab. 5 Limit of quantification for indium

Mean blank value in the digestion solution \bar{X}_{BL}	Standard deviation of the blank values in the digestion solution	Limit of quantification in the digestion solution X_{LQ}	Limit of quantification in the air sample (1.2 m ³)
[ng/l]	[ng/l]	[ng/l]	[ng/m ³]
16.1	11.2	128	2.2

The air sample volume is 1.2 m³ for a sampling period of 120 minutes as well as a sample volume of 20 ml and a dilution factor of 10. When taking these factors into account the limit of detection for indium is 0.57 ng/m³ ($k = 3$).

When sampling is carried out for 15 minutes, the air sample volume is 0.15 m³ at a sample volume of 20 ml and a dilution factor of 10. The limit of quantification for indium in this case is 17.1 ng/m³

The instrumental limit of detection was determined by measuring twelve calibration blank value solutions. For this purpose, the stock solution of the internal standard lutetium (see Section 4.4.3) was added twelve times to the acid mixture for the preparation of the calibration solution (see Section 4.3) and analysed. Three times the standard deviation of the measurement values yields an instrumental limit of detection of 0.22 ng/l for indium for the ICP mass spectrometric analysis method.

10.4 Storage stability

The storage period of the loaded membrane filters at room temperature should generally not exceed one month. For the purpose of checking this 24 filters were each spiked with 12 ng and 240 ng of indium and dried. Three filters in each case were subjected to the entire sample preparation on two measurement days within four weeks and analysed using ICP-MS.

It has been shown that when the filters are spiked with 12 ng of indium (equivalent to 10 ng/m³ of indium) the recovery is stable over a time period of two weeks. The recovery is reduced by approx. 20% after a storage period of more than two weeks. The recovery is stable for four weeks when the filter is spiked with 240 ng.

It is recommended that a storage period of two weeks is not exceeded before carrying out the digestion and analysis of membrane filters loaded with indium.

10.5 Selectivity

Non-spectral and spectral interferences influence the analysis by means of ICP-MS. Non-spectral interferences can be divided into physical interferences and problems that can be caused by transport of the samples and their physical characteristics as well as by chemical reactions of the sample with parts of the apparatus, in der sample during sample preparation or the transfer of sample to the nebuliser. For these reasons, with regard to the analysis in the ultratrace range it is particularly important to use the most pure reagents and inert materials.

Furthermore, spectral interferences affect the analysis result significantly. The greatest influencing factors in this case are isobaric interferences caused by the occurrence of different elements of the same mass in the sample matrix. Most elements have several naturally occurring isotopes.

The selectivity of the method depends largely on the selected isotope and thus on spectral interference. The indium isotope with a mass of 115 amu has a relative frequency of 95.7%. At a mass of 115 tin has a relative frequency of 0.34%. This interference must be taken into account. The isobaric interference for indium due to ^{115}Sn is corrected arithmetically by “ $-0.014038 \times ^{118}\text{Sn}$ ”.

In order to check the correction factor, solutions with a constant indium concentration (prepared from indium antimonide, [Section 4.2](#)) and different tin concentrations (Multi-Element Calibration Standard 4, [Section 4.2](#)) were prepared and measured. The indium concentration was consistently at the level of the OEL value (0.6 $\mu\text{g/l}$ of indium in the measurement solution); the different tin concentrations were in a concentration range of 10 $\mu\text{g/l}$ to 5 mg/l . The indium concentration of 0.6 $\mu\text{g/l}$ in the measurement solution is equivalent to the OEL value of 0.0001 mg/m^3 at a dilution of 1:10, a digestion volume of 20 ml and an air sample volume of 1.2 m^3 . Additionally, tin solutions in a concentration range of 10 $\mu\text{g/l}$ to 5 mg/l were analysed in order to check the correction factor.

Experience has shown that the arithmetically calculated correction factor for the isobaric interference for indium due to tin yields correct results up to a tin concentration of 500 $\mu\text{g/l}$. In the case of a tin concentration greater than 500 $\mu\text{g/l}$, the arithmetic correction leads to an over-correction of the indium concentration. Therefore, the concentration of tin in the sample must also be considered when analysing indium using ICP-MS.

Additional spectral interference can be caused by polyatomic interference (molecule ions in the measurement solution). The intensity of isotopes with low masses can be diminished by the presence of elements with high masses. In the case of samples with a high salt concentration it is advisable to adjust the nebuliser to the sample input. A higher limit of quantification may occur in cases like these.

In order to check the comparability of the preparation method for dusts described in the chapter “Sampling and determining of aerosols and their chemical components“ for the determination of the total metal content, 24 samples were taken in parallel at three different indium concentrations in each case in a dust chamber (Giesen et al. 2016, 2018; Pitzke et al. 2020). Loading is achieved by pyrolytic decomposition of an indium acetate solution. The desired concentrations of indium should simulate the OEL, twice the OEL and 20 times the OEL. Twelve digestions in each case of each indium concentration are prepared using the open digestion procedure and high-pressure microwave digestion and the indium concentrations are quantitatively analysed using the ICP-MS. The relative standard deviations of each of the twelve measured values of an indium concentration and of a digestion procedure were consistently under 5%. The results of the quantitative analyses show very good agreement of all indium concentrations with both the different digestion procedures. The results are shown in [Table 6](#).

Tab. 6 Comparability of open digestion and digestion using high-pressure microwave technology for indium with $n = 12$ determinations in each case

	Desired concentration of indium	Mean value of the indium concentrations [$\mu\text{g/m}^3$]	Standard deviation (rel.) of the indium-concentrations [%]
Open digestion	OEL	0.103	4.2
High-pressure microwave digestion	OEL	0.099	2.4
Open digestion	2 × OEL	0.174	2.5
High-pressure microwave digestion	2 × OEL	0.171	1.7
Open digestion	20 × OEL	1.31	2.1
High-pressure microwave digestion	20 × OEL	1.30	1.4

11 Discussion

The analytical procedure described here permits the determination of indium and its compounds in the workplace air in a concentration range from a tenth to twice the currently valid OEL of 0.0001 mg/m³ in the respirable fraction. The analytical method is suitable for monitoring compliance with the short-term value.

Principally all working conditions, in particular sample preparation and analysis conditions, must be adapted to the respective ICP-MS device used.

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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