Method for the determination of nickel and its inorganic compounds

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German Social Accident Insurance
Deutsche Gesetzliche Unfallversicherung
Analytical Subcommittee of the Chemistry Board of Experts*

Carcinogenic substances	Order number:	BGI 505-10-3
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This method has been tested and recommended by the German Social Accident Insurance for the determination of nickel and its inorganic compounds at workplaces.
Both personal and stationary sampling can be performed for the assessment of workplaces.

Sampling is carried out with a pump and collection on a membrane filter. Analysis is performed by graphite furnace atomic absorption spectrometry (GFAAS) after acid digestion.

Chemical name:	Nickel
CAS number:	7440-02-0
Symbol:	Ni
Atomic mass:	58.69 g/mol

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Summary

This method can be used with personal or stationary sampling to determine the mean concentration of nickel and its inorganic compounds at workplaces over the sampling time.

Principle: A pump draws a defined volume of air through a membrane filter. The nickel contained in the collected aerosol is determined by means of graphite furnace atomic absorption spectrometry after acid digestion.

Limit of quantification: Absolute: 0.22 ng of nickel
Relative: 0.47 µg/m^3 for an air sample of 1.2 m^3, a sample solution of 20 mL (dilution factor 4) and an injection volume of 16 µL.

Selectivity: The selectivity of the method depends above all on the wavelength selected, the absence of spectral interference and the minimization of non-spectral interference. The conditions stated here have proved successful in practice.

Advantages: Personal measurements with high sensitivity are possible; can be used for short-term measurements.

Disadvantages: Time-consuming, requires highly sophisticated apparatus.

Apparatus: Sampling system consisting of a pump, volumetric flow meter, filter holder with membrane filter, digestion apparatus, atomic absorption spectrometer with graphite furnace.

Detailed description of the method

Contents

1

Equipment, chemicals and solutions

1.1

Equipment

For sampling:

- Sampling device suitable for collecting the inhalable aerosol fraction, GSP 10 sampling head (PGP according to BGIA), e.g. from GSM Gesellschaft für Schadstoffmesstechnik GmbH, 41469 Neuss, Germany
- Pump for sampling with a nominal flow rate of 10 L/min, GSM/SG10, e.g. from Leschke Messtechnik GmbH, 15230 Frankfurt (Oder), Germany
- Membrane filter, diameter 37 mm, pore size 8.0 µm, cellulose nitrate, if possible with a test certificate stating the content of metals, e.g. from Sartorius AG, 37075 Göttingen, Germany
- Volumetric flow meter

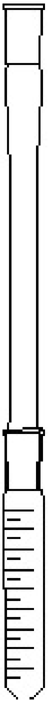

Fig. 1 Schematic illustration of a digestion vessel with attached cooler.

For sample preparation:

- Aluminum heating block thermostat with external time/temperature control, operating range up to 200 °C, e.g. from Gebr. Liebisch GmbH & Co, 33649 Bielefeld, Germany
- Graduated digestion vessels with air cooler (see Fig. 1) made of quartz glass (diameter 19 mm, maximum volume 25 mL) with ground connections (NS 19/26), acid-proof 0.2 mL graduation from 15 to 25 mL, e.g. from VWR International GmbH, 40764 Langenfeld, Germany
- Polyethylene stoppers for the digestion vessels (NS 19/26), e.g. from Pöppelmann GmbH & Co, 49378 Lohne, Germany
- Quartz glass rods (diameter approx. 4 mm), with fitted replaceable endpieces of PTFE tube [1]), e.g. from VWR International GmbH
- 5 L bottle made of perfluoroalkoxy copolymer (PFA) with PTFE dispenser for rinsing the air cooler or preparing dilutions, e.g. Optifix HF Dispenser, 30 mL, from Poulten & Graf GmbH (Fortuna), 97877 Wertheim, Germany
- Measuring cylinders made of PFA, 500 mL, 100 mL, 50 mL, e.g. from VIT-LAB GmbH, 64332 Seeheim-Jugenheim, Germany

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1) Normal boiling glass capillaries cannot be cleaned without leaving residues.

- Pair of ceramic tweezers to transfer the membrane filters to the digestion vessels, e.g. PLANO, from W. Plannet GmbH, 35578 Wetzlar, Germany

For the analytical determination:

- Atomic absorption spectrometer with equipment for graphite furnace technique and autosampler
- Volumetric flasks made of PFA for standard and calibration solutions with screw caps and ring marks, 500 mL, 100 mL, 50 mL, e.g. from VIT-LAB GmbH
- Disposable polystyrene vessels, volume approx. 1.5 mL for the autosampler, e.g. from Greiner Bio One GmbH, 72636 Frickenhausen, Germany
- Adjustable piston pipettes with the following volume ranges: 2 to 20 µL, 20 to 100 µL, 30 to 200 µL, 200 to 1000 µL, 1000 to 5000 µL, e.g. Pipetman Ultra, from Gilson International B.V., 65555 Limburg-Offheim, Germany
- Ultrapure water unit, e.g. from Wilhelm Werner GmbH, 51381 Leverkusen, Germany

1.2
Chemicals and solutions

Ultrapure water (specific resistance ≥ 17 MΩ × cm at 25 °C)
Nitric acid (65%), with low metal content, e.g. Suprapur, from Merck KGaA, 64271, Darmstadt, Germany
Hydrochloric acid (30%), with low metal content, e.g. Suprapur, from Merck KGaA
Standard acid digestion mixture according to the DFG [1], prepared from 1400 mL of nitric acid, 570 mL of hydrochloric acid and 130 mL of ultrapure water (equivalent to 2 parts by volume of nitric acid (65%) and 1 part by volume of hydrochloric acid (25%))
Nickel Stock Solution 1: c = 1000 µg/mL, e.g. Product No. 13839 from Alfa Aesar GmbH & Co. KG, 76185 Karlsruhe, Germany
Nickel Stock Solution 2: c = 50 µg/L (25 µL of Stock Solution 1 are placed in a 500 mL volumetric flask and the flask is filled to the mark with ultrapure water)
Calibration solutions (see Section 4.1)
Argon 4.6 (purity at least 99.996%)

2
Sampling procedure

A membrane filter is inserted into the filter holder, and then placed in the GSP sampling head, which is connected to the pump. Stationary or personal sampling can be carried out. The flow rate is initially adjusted to 10 L/min. The definition of the inhalable dust is fulfilled by this flow rate [2]. At a sampling time of 2 hours, this corresponds to an air sample volume of 1.2 m^3. After sampling, the flow rate must be checked for constancy. If the deviation from the adjusted flow rate is greater than ± 5%, it is advisable to discount the measurement (see BGI 505-0 “General Part”, Section 3).

3
Analytical determination

3.1
Sample preparation and analysis

The loaded filter is folded using a pair of ceramic tweezers, transferred to the 25 mL digestion vessel and pressed down to the bottom of the vessel by means of a quartz glass rod (see Section 1.1). Then 10 mL of the standard acid digestion mixture are added.

An air cooler is attached to the vessel, which is then placed in the aluminum heating block thermostat for two hours under reflux (block temperature: approx. 125 °C). After cooling down to approx. 50 °C, 10 mL of ultrapure water are carefully added through the air cooler to rinse the cooler and also to dilute the viscous solution.

A brief heating phase follows to achieve homogenization. After cooling, the air cooler and the quartz glass rod are removed, the digestion vessel is sealed with a polyethylene stopper and the volume of the solution (sample solution) is read off. Before analysis, the sample solution must be diluted (see Section 3.2).

A current blank value $\bar{c}_{\mathrm{Bl(current)}}$ is determined for each series of samples. For this purpose a filter that has not been used for sampling is subjected to the entire sample preparation and analyzed. This blank value must be within three times the standard deviation of the mean blank value determined in the course of the method development. If this is not the case, then the mean blank value must be determined anew as stipulated in Section 5.2.

3.2

Operating conditions for atomic absorption spectrometry

The characteristics of the method stated in Section 5 were obtained under the following experimental conditions:

Apparatus:	Atomic absorption spectrometer with equipment for the graphite furnace technique “AAS vario 6 EA” from Analytik Jena, “MPE 50 Mikropipettiereinheit” (micropipetting unit), integrated circulation cooler
Absorption:	231.1 nm
Slit width:	0.2 nm
Lamp current:	5 mA
Background compensation:	Deuterium lamp
Measuring solution:	An aliquot of the sample solution (see Section 3.1) is diluted with three parts of ultrapure water[2]
Injection volume:	16 µL of the measuring solution Injection is performed by the micropipetting unit

Table 1 Temperature/time program.

Program step	Explanation	Heating rate [°C/s]	Furnace temperature [°C]	Holding time [s]	Argon purging gas
1	Injection	15	90	10	Max.
2	Drying	5	105	15	Max.
3	Drying	15	120	15	Max.
4	Pyrolysis	15	1000	15	Max.
5	Zero adjustment	0	1000	6	Min.
6	Atomization/ measurement	3000	2200	5	Min.
7	Heating	3000	2600	3	Max.

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[2] As a rule a dilution of 1:4 is sufficient for a measurement free of interference. If the matrix of the measuring solution is still too concentrated or the nickel content too high, then it must be further diluted.

4
Evaluation

4.1
Calibration

In order to obtain the calibration function, the MPE 50 micropipetting unit of the autosampler is used to prepare the following dilutions from Nickel Stock Solution 2 (see Section 1.2). Dilution with ultrapure water is performed automatically.

The measurement is performed with a constant injection volume of 16 µL. The absorbances are determined from the peak heights and recorded versus the concentrations. Under the conditions stated here the calibration function is linear.

Based on an air sample volume of 1.2 m^3, a concentration range from approx. 0.4 to 3.4 µg/m^3 is covered by the dilutions stated in Table 2. The measurement range can be extended by appropriate dilution steps or the use of less sensitive wavelengths (e.g. at 341.5 nm or 346.2 nm). Spectral interference may occur in some cases when multiple-element lamps are used. Therefore lines and signals must always be critically checked.

Table 2 Dilutions for the determination of the calibration function.

Stock Solution 2 [µL]	2	4	6	8	10	12	14	16
Ultrapure water [µL]	14	12	10	8	6	4	2	0
Mass (nickel) [ng]	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Nickel concentration [µg/L]	6.3	12.5	18.8	25.0	31.3	37.5	43.8	50.0

4.2
Calculation of the analytical result

The corresponding value for the mass in the measuring solution is obtained from the absorbance in the calibration function, and the nickel mass in the sample is then calculated according to equation (1).

$$m = (c - \bar{c}_{\mathrm{Bl(current)}}) \times V \times f \tag{1}$$

The concentration by weight of nickel in the air sample in µg/m^3 is calculated according to equation (2).

$$c_{\mathrm{m}} = \frac{m}{V_{\mathrm{Air}}} \tag{2}$$

where:

m	is the mass of nickel in the sample in µg
c	is the nickel concentration in the measuring solution in µg/L

$\bar{c}_{Bl(current)}$ is the current mean value for the nickel concentration in the blank solution in µg/L (see Section 3.1)
V is the volume of the sample solution in L
f is the dilution factor (f = 4, see Section 3.2)
c_m is the nickel concentration by weight in the air sample in µg/m^3
V_{Air} is the air sample volume in m^3

5
Reliability of the method

5.1
Precision and recovery

Six filters were each spiked with three solutions of different nickel concentrations and then subjected to the entire analytical procedure.

Nickel Stock Solution 1 (see Section 1.2) served as the starting solution for spiking the filters (see Table 3).

As a result of the different chemical composition and the different physical properties of the aerosols in various work areas, it is impossible to make generally a valid statement on the recovery for the entire procedure.

On the basis of the sample preparation described above, the analytical recovery is defined as 100% according to DIN EN 13890 (restricted to those metals and compounds that are soluble in the stated system) [3, 4].

The described sample preparation procedure was checked with elemental nickel and one of its defined compounds. For this purpose three samples of approx. 2 mg of nickel powder and three samples of approx. 0.6 mg of nickel(II) oxide were each subjected to the digestion procedure in 80 mL of the standard acid digestion mixture (see Section 3.1). Solutions without any visible particles were obtained in every case. The subsequent analysis resulted in 98 or 96% respectively of the calculated nickel concentration.

Table 3 Determination of the relative standard deviation.

Spiked mass of nickel [µg]	Air concentration* [µg/m^3]	Relative standard deviation [%]
6	5	4.0
60	50	3.5
120	100	2.9

* The concentration is calculated on the basis of an air sample volume of 1.2 m^3 (2-hour sampling period at a flow rate of 10 L/min)

5.2

Limit of quantification

During development of the method the limit of quantification was determined according to the blank value method as stipulated in DIN 32645 [5]. For this purpose ten filters that were not used for sampling were subjected to the entire sample preparation procedure, the mean for the blank value ($\bar{c}_{\mathrm{Bl}}$), which is caused by the filters, reagents and vessels used, as well as the corresponding standard deviation were determined and inserted into equation (3) to calculate the limit of quantification.

$$X_{\mathrm{LQ}} = \bar{c}_{\mathrm{Bl}} + 10 \times s \tag{3}$$

After subtraction of the mean blank value, the lowest determinable concentration in the air sample is only dependent on ten times the standard deviation (see Table 4).

Table 4 Limit of quantification and blank value.

Limit of quantification [X_{LQ}] in the measuring solution	14 µg/L
Mean blank value [$\bar{c}_{\mathrm{Bl}}$] in the measuring solution	6.9 µg/L
Standard deviation [s] of the blank values in the measuring solution	0.71 µg/L
Absolute limit of quantification	0.22 µg
Lowest determinable concentration in the air sample*	0.47 µg/m^3

* For an air sample volume of 1.2 m^3, a sample solution of 20 mL and a dilution factor of 4

5.3

Selectivity

The selectivity of the method depends above all on the wavelength selected, and on the absence of spectral interference due to iron and chromium. In the case of non--spectral interference, such as more complex matrix effects, it is advisable to use the addition procedure. The stated conditions have proved successful in practice [6].

The described sampling procedure is not suitable for vaporous or liquid nickel compounds, such as tetracarbonylnickel.

If compounds that can occur both as vapor and particles in the air at workplaces, the method must be adapted to the requirements of simultaneous sampling by modifying the sampling system (e.g. varying the filter material or combining different collection phases).

6
Remarks

The analytical procedures for the determination of nickel that have been published in this series [7, 8] are now superseded by the present method.

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