Nickel – Method for the determination of nickel and its compounds in workplace air using graphite furnace atomic absorption spectrometry (GF-AAS) after high-pressure microwave digestion

Air Monitoring Method

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Abstract

This analytical method is a validated measurement procedure for the determination of nickel [7440-02-0] and nickel compounds in workplace air after personal or stationary sampling. Sampling is performed by drawing a defined volume of air through a quartz fibre filter using a suitable flow-regulated pump. After high-pressure microwave digestion, the respirable and inhalable fraction of nickel retained on the filter is analysed using an atomic absorption spectrometer with the graphite furnace technique. The relative limit of quantification (LOQ) is 0.098 µg nickel/m³ for an air sample volume of 1.2 m³. Sampling is performed over 2 h at flow rate of 10 l/min, a measurement solution

volume of 25 ml and an injection volume of 20 µl. It is not possible to differentiate between the individual nickel compounds. The mean recovery for nickel was 87%. The concentration-dependent expanded uncertainty was between 25% and 26% and the concentration-dependent uncertainty for the determination of nickel in the inhalable fraction was 25 to 26%, too. This analytical method has been accredited by the accident insurance companies for the detection in workplace air of substances that are carcinogenic, mutagenic or toxic to reproduction. This method has been tested and recommended for the determination of nickel in work areas by the German Social Accident Insurance (DGUV). Both personal and stationary sampling can be performed for measurements in order to evaluate work areas.

Name	CAS-Nr.	Molar mass [g/mol]	Formula	Substance-specific concentration values [µg Ni/m³]
Nickel compounds (as nickel), classified as C1A and C1B	7440-02-0	58.69	Ni	TC 6.0 (R) EF 8 (AGS 2022 b) AC 6.0 (R) (AGS 2022 b)
Nickel and nickel compounds (as nickel)	7440-02-0	58.69	Ni	OELV 30 (I) EF 8 (II) (AGS 2022 a)
Nickel metal	7440-02-0	58.69	Ni	OELV 6.0 (R) EF 8 (II) (AGS 2022 a)

AC: acceptable concentration; EF: excursion factor, short-term value in parentheses; I: inhalable fraction; OELV: occupational exposure limit value; R: respirable fraction; TC: tolerable concentration

1 Summary

The mean concentration of nickel and its compounds (as nickel) at the workplace over the sampling period can be determined with this method using personal or stationary sampling.

Measurement principle: A pump is used to draw a defined volume of air through a quartz fibre filter. After high-pressure microwave digestion, the respirable and inhalable particle fraction retained on the filter is analysed for nickel using an atomic absorption spectrometer with graphite furnace technique.

Limit of quantification (calculated as Ni):

Absolute: 82 pg of nickel
0.10 µg of nickel per sample carrier

Relative: 0.098 µg/m³ for an air sample volume of 1.2 m³ (a sampling period of 2 h at 10 l/min, a measurement solution volume of 25 ml and an injection volume of 20 µl)

Measurement range: 0.10 to 19 µg/m³ based on an air sample volume of 1.2 m³ and 0.29 to 283 µg/m³ based on an air sample volume of 420 l.

Selectivity: Interference by other components was not observed. Possible matrix effects can be corrected by measurement with Zeeman correction and by calibration of the sample in accordance with the standard addition method. It is not possible to differentiate between the individual nickel compounds.

Advantages: It is possible to perform personal sampling with great sensitivity and determinate other analytes in the sample solution with atomic spectrometric parameters adapted accordingly.

Disadvantages: No indication of concentration peaks, requires great technological resources.

Apparatus:	Sampling devices:
	Pump and sampling head, filter holder with quartz fibre filter and supporting sieve
	Flow meter
	High-pressure microwave digestion system
	Atomic absorption spectrometer with graphite furnace technique

2   Equipment and chemicals

2.1   Equipment

For sampling:

- Pump, suitable for a flow rate of 3.5 to 10 l/min (e.g. SG10-2, from GSA, Gesellschaft für Schadstoffanalytik mbH, 40880 Ratingen, Germany)
- PGP system with FSP 10 sampling head, suitable for a flow rate of 10 l/min, from DEHA, Haan & Wittmer, 71296 Heimsheim, Germany
- GSP sampling head, suitable for a flow rate of 3.5 l/min, from DEHA Haan & Wittmer, 71296 Heimsheim, Germany
- Filter holder and cap made of PTFE with supporting sieve
- Quartz fibre filter, diameter 37 mm (e.g. QM-A from Whatman, supplied by VWR, 64295 Darmstadt, Germany)
- Gas flow meter (e.g. rotameter flow meter, influx 1 to 13 litres, from DEHA Haan & Wittmer, 71296 Heimsheim, Germany)

For the sample preparation and the analytical determination:

- Atomic absorption spectrometer with graphite furnace technique, autosampler and nickel hollow cathode lamp
- High-pressure microwave digestion system (e.g. MarsXpress with digestion vessels and seals made of PTFE, from CEM, 47475 Kamp-Lintford, Germany)
- Analytical balance
- Plastic tweezers
- Variable piston pipettes 1 to 50 000 µl (e.g. Multipette pro, from Eppendorf, 22339 Hamburg, Germany)
- Volumetric flasks, 10 ml, 25 ml and 50 ml, made of DURAN glass
- Glass funnel (e.g. 55 mm diameter)
- Wide-necked flasks, 50 ml made of PE
- Disposable syringes, 5 ml made of PE
- Syringe filters made of regenerated cellulose, pore width 0.45 µm, diameter 30 mm (e.g. from Roth, 76185 Karlsruhe, Germany)
- Autosampler vials made of PE or PTFE

2.2   Chemicals

- Nitric acid, 65%, with a low metal content (e.g. Suprapur, from Merck KGaA, 64293 Darmstadt, Germany)
- Hydrochloric acid, 30%, with a low metal content (e.g. Suprapur, from Merck KGaA, 64293 Darmstadt, Germany)
- Water for trace analysis, with a low metal content (e.g. Tracepur, from Merck KGaA, 64293 Darmstadt, Germany)

- Nickel standard for the AAS with a certified nickel content of 1000 mg/l in dilute nitric acid, traceable to a standard reference material (e. g. from Merck KGaA, 64293 Darmstadt, Germany, Order No. 1.19792)
- Multi-element Standard Solution 4 for ICP, with a certified nickel content of 20 mg/l in dilute nitric acid, traceable to a standard reference material (e. g. from Merck KGaA, 64293 Darmstadt, Germany, Order No. 51844)
- Argon 5.0 (purity at least 99.999%)

2.3 Solutions

Note: Before use, all glassware must be pre-rinsed with dilute nitric acid and then rinsed with water for trace analysis, in order to ensure that all vessels are free of any metal traces.

Blank value solution: Solution of 0.65% nitric acid in water

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

Calibration Solution 1: Solution of 40 mg nickel/l water

Water is placed into a 50 ml volumetric flask. 2 ml of the nickel standard (1000 mg Ni/l) are pipetted into the volumetric flask, which is then filled to the mark with water and shaken.

Calibration Solution 2: Solution of 2 mg nickel/l water

Water is placed into a 25 ml volumetric flask. 1.25 ml of Calibration Solution 1 are pipetted into the volumetric flask, which is then filled to the mark with water and shaken.

Calibration Solution 3: Solution of 40 µg nickel/l water

In order to stabilise the dilution, 0.25 ml of nitric acid (65%) is pipetted into a 25 ml volumetric flask, into which water has been previously placed. Then 500 µl of Calibration Solution 2 are pipetted into the volumetric flask, which is then filled to the mark with water and shaken. This solution is stable for a period of at least three weeks.

Control Solution 1: Solution of 400 µg nickel/l water

Water is placed into a 25 ml volumetric flask. 0.5 ml of Multi-element Standard Solution 4 (20 mg Ni/l) are pipetted into the volumetric flask, which is then filled to the mark with water and shaken.

Control Solution 2: Solution of 20 µg nickel/l water

In order to stabilise the dilution, 0.25 ml of nitric acid (65%) is pipetted into a 25 ml volumetric flask, into which water has been previously placed. Then, 1.25 ml of Control Solution 1 are pipetted into the volumetric flask, which is then filled to the mark with water and shaken. This solution is stable for a period of at least three weeks.

Nickel Solution 1: Solution of 0.18 g nickel/l water

In order to stabilise the dilution, 0.1 ml of nitric acid (65%) is pipetted into a 10 ml volumetric flask, into which water has been previously placed. 100 µl of the nickel standard (1000 mg Ni/l) are pipetted into the volumetric flask, the flask is then filled to the mark with water and shaken.

3 Sampling

The filter batch used must be checked for its suitability before the measurements (see Section 5.2).

Sampling can be carried out as stationary or personal sampling. The caps of the filter transport capsules are removed and a quartz fibre filter (Ø 37 mm) with a supporting sieve is placed into the FSP sampling system. A membrane filter is also suitable for use. 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 checked for constancy. If the deviation from

the adjusted flow rate is greater than ± 5%, it is advisable to repeat the measurement (see DGUV Information 213-500 "General Part", Section 3 (DGUV 2015)).

The GSP sampling head with a flow rate of 3.5 l/min can also collect the inhalable particle fraction in the same manner as the respirable particle fraction. This is equivalent to an air sample volume of 420 l for a sampling period of 2 hours. Alternatively, the sampling head can also be used with a suitable intake cone for a flow rate of 10 l/min.

A blank sample (field blank value) is included in addition to the samples. This serves as a transport check and differs from the analytical sample in that no sample air is drawn through the filter.

The loaded filters are then removed from the sampling system and sealed with the caps of the transport capsules.

4 Analytical determination

4.1 Sample preparation

The loaded filters and the field blank are each transferred into a separate digestion vessel using plastic tweezers and 6 ml of nitric acid (65%) and 3 ml of hydrochloric acid (30%) are added to each vessel. The vessels are covered with the caps and sealed with the screwcaps. These are then evenly distributed on the sample turntable of the microwave digestion device and the dust deposited on the filters is digested.

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 sample has been digested, it is left to cool in the microwave device. The quartz fibre filter is not digested completely.

Water with a low metal content is used to quantitatively transfer the digestion solution into a 25 ml volumetric flask through a previously cleaned glass funnel. The volumetric flask is filled to the mark and shaken. The sample solution is transferred to a 50 ml wide-necked flask made of PE for storage. If precipitation occurs or there are non-soluble components, then the sample solution is filtered using a disposable syringe filter. Immediately before analysis, part of the sample solution is transferred into an autosampler vial. A suitable pre-dilution is carried out, if required.

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

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

4.2 Operating conditions

AAS parameters:	Graphite furnace AAS with autosampler (Perkin Elmer PinAAcle 900Z with Zeeman background compensation and transversely heated graphite tube including a L'vov platform) Nickel hollow cathode lamp, warm-up period at least 15 minutes
Wavelength:	232 nm
Slit width:	0.2 nm
Injection:	20 µl of the sample solution + 5 µl of the modification solution + 5 µl of the blank value solution (injection in duplicate in each case)

Tab. 1   Oven program

Step	Temperature	Heating period	Dwell time	Gas flow rate
	[°C]	[s]	[sec]	[ml/min]
Drying 1	120	1	30	250
Drying 2	140	15	40	250
Pyrolysis	1100	10	20	250
Atomisation	2150	0	4	0
Heating	2450	1	3	250

The prepared samples, the field blank value, a reagent blank value consisting of nitric acid and hydrochloric acid at a ratio of 2 : 1 (analogous to the digestion), the blank value solution and, if necessary, a filter batch blank value are analysed in the AAS. For this purpose, 20 µl each of the solution to be investigated with 5 µl of the blank value solution are injected into the AAS using the autosampler and analysed under the specified AAS operating conditions. Each sample is analysed in duplicate and the mean value is used for calculating the result.

The sample solutions are diluted with water and nitric acid (65%), if the nickel concentrations are above the range of the calibration curve, so that there is an acid level of at least 0.65% in the dilution for the purpose of stabilisation. The dilution factor can be estimated by means of pre-analyses.

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

Control Solution 2 is analysed before the analysis of the sample solution and at the end of the sequence. The concentration must fall within defined limits (in this case ± 10%), otherwise the calibration must be checked and the analysis of the sample solution must be repeated. This serves to check the stability of the analytical devices and the accuracy of the results. In the case of larger sample series, it is advisable to carry out further periodic measurements of Control Solution 2.

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 blank value solution is replaced by 5 µl of Calibration Solution 3. The recovery is calculated from the nickel concentration of the original sample in relation to the spiked nickel concentration. 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 range of the calibration curve.

Example: A nickel concentration of the sample solution of 16 µg/l, a nickel concentration of the spiked sample of 27.5 µg/l and a spiked nickel concentration of 10 µg/l results in a recovery of 106% (calculated from: 27.5 / (16 + 10) × 100).

If the matrix of the sample has a significant influence, evaluation using the standard addition method with the sample solution is required.

5 Evaluation

5.1 Calibration

5.1.1 External calibration

The calibration must be performed every working day. Calibration Solution 3 with a nickel concentration of 40 µg/l is diluted by the autosampler as specified in the following scheme (Table 2) to yield the five calibration standards. The standards are analysed under the AAS operating conditions described in Section 4.2 and a linear calibration function is created.

Tab. 2   Calibration standards for external calibration

	Concentration	Blank value solution	Calibration Solution 3
	[µg Ni/l]	[µl]	[µl]
Nickel blank value	0	25	0
Calibration Standard 1	8	21	4
Calibration Standard 2	16	17	8
Calibration Standard 3	24	13	12
Calibration Standard 4	32	9	16
Calibration Standard 5	40	5	20

Control Solution 2 is analysed in order to check the calibration (see Section 4.2).

5.1.2   Standard addition calibration

In order to eliminate a possible matrix effect, the sample must undergo a standard addition calibration. The nickel concentration of the sample should be between 15 and 40 µg/l. The calibration standards are obtained by addition of different concentrations of Calibration Solution 3 to the sample (see Table 3). All standards and solutions are analysed in duplicate.

Otherwise, the AAS operating conditions remain unaltered.

The intercept of the calibration curve with the x-axis is equivalent to the nickel concentration of the sample solution.

Tab. 3   Standard addition calibration

	Concentration	Blank value solution	Sample solution	Calibration Solution 3
	[µg Ni/l]	[µl]	[µl]	[µl]
Nickel blank value	0	25	0	0
Sample		15	10	0
Calibration Standard 1	16	11	10	4
Calibration Standard 2	28	8	10	7
Calibration Standard 3	40	5	10	10

5.2   Calculation of the analytical result

The nickel concentration c in the air sample in µg/m³ is obtained as follows (see Equation 1):

$$c = \frac{((c_{SOL} \times F) - c_{FB}) \times V_{SOL}}{1000 \times \eta \times V} \tag{1}$$

where:

c is the mass concentration of nickel in the air sample in µg/m³

c_{SOL} is the concentration of nickel in the measurement solution in µg/l obtained from the calibration curve

c_{FB} is the concentration of nickel in the measurement solution of the field blank value in µg/l obtained from the calibration curve

F is the dilution factor

V_{SOL} is the volume of the prepared sample solution in ml (= 25)

V is the air sample volume in m³

η is the recovery (0.87, see Section 6.2)

6   Reliability of the method

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

6.1   Repeatability

The repeatability was determined by analysing one standard solution (prepared from Nickel Solution 1) and one prepared sample on six different days. Calibration was carried out every working day for quantification. The nickel concentration of both solutions was 29 µg/l. The repeatability of the standard solution was 1.4% and that of the sample 2.1%.

6.2   Reproducibility and recovery

As a result of the different chemical compositions and the different physical properties of the aerosols in different work areas, it is impossible to provide generally valid data on the recovery for the entire procedure.

The recovery was determined by spiking 12 quartz fibre filters each with 40 µl of Nickel Solution 1 (0.18 g/l). Six filters were prepared and analysed as described in Section 4.1 and 4.2. Laboratory air was drawn through the other six filters over a time period of 2 hours at a flow rate of 10 l/min. The samples were then also prepared and analysed.

In order to obtain reference values, a pipette was used to add 40 µl of Nickel Solution 1 (0.18 g/l) each into six 25 ml volumetric flasks, into which water and 0.25 ml of 65% nitric acid had been previously placed. The solutions were filled to the mark with water, shaken and analysed according to Section 4.2.

The nickel concentrations of the spiked filters were calculated in relation to the reference values and on this basis the analytical recovery (conversion) and the recovery for air sampling were determined. The analytical recoveries thus obtained as well as the recovery with sampling determined were statistically not significantly different from the reference values according to the *t*-test and are taken into account for calculating the result with $\eta = 0.87$.

The spiked amount of nickel was equivalent to the concentration in the air sample listed in Table 4 for an air sample volume of 1.2 m^3. The reproducibility, expressed as relative standard deviation, was determined from the six spiked filters with sampling and was around 2.4%.

Tab. 4   Characteristics of the validation

Spiked volume per filter	Spiked mass per filter	Concentration in the air sample	Conversion	Recovery	Relative standard deviation
[µl]	[µg]	[µg/m^3]			[%]
40	7.2	6.0	0.89	0.87	2.4

Recovery experiments with a spiked mass of 100 µl of the nickel standard (1000 mg/l) and an air sample volume of 420 l resulted in a statistically significantly lower recovery of 0.84 according to the *t*-test and a reproducibility of 7.1%, thus a correction of the recovery should be carried out (see Table 5).

Tab. 5   Characteristics of the validation at high concentrations

Spiked volume per filter	Spiked mass per filter	Concentration in the air sample	Conversion	Recovery	Relative standard deviation
[µl]	[µg]	[µg/m^3]			[%]
100	100	238	0.85	0.84	7.1

The recovery is defined as 87% on the basis of the sample preparation described above according to DIN EN ISO 21832 (DIN 2020) (restricted to those metals and compounds that are soluble in the stated system).

6.3   Limit of quantification

The absolute limit of quantification according to DIN 32645 (DIN 2008) was determined using six filter blank values from two batches. For this purpose, the six filters were prepared and analysed according to Section 4.1 and Section 4.2. The absolute limit of quantification as stipulated in DIN 32645 according to the blank value method is 4.1 µg/l of nickel or 82 pg of nickel per injection for a statistical certainty of 95% and a relative uncertainty of the result of 33% or k = 3.33. A relative limit of quantification of 0.098 µg/m^3 of nickel or of 0.10 µg of nickel per sample carrier is obtained for an air sample volume of 1.2 m^3, a sample solution volume of 25 ml and an injection volume of 20 µl.

The limit of quantification must be determined again if a new batch of filters is used.

6.4   Storage stability

Nickel deposited on a filter can be stored at room temperature without losses for at least 22 days. Storage stability of a prepared sample solution with a concentration of approx. 29 µg/l of nickel is at least 40 days at room temperature.

6.5   Selectivity

High concentrations of other elements and compounds can lead to interferences. In principle, for samples of unknown composition, the measurement results must be checked for possible interferences and, if necessary, a suitable dilution step must be chosen in order to achieve a valid result. Non-spectral interferences and matrix effects can be reduced by means of a suitable dilution. Non-spectral matrix effects can also be effectively eliminated by use of the Zeeman correction.

To date, interferences due to other components, in particular at high concentrations, have not been observed, however, these cannot be ruled out. Possible matrix effects can be eliminated by calibration of the sample solution in accordance with the standard addition method. It is not possible to differentiate between the individual nickel compounds.

6.6   Uncertainty

The expanded uncertainty is obtained by estimation of all the relevant influencing parameters (bottom-up method). The uncertainty of the result consists principally of the uncertainty contributions of sampling u_S and the analytical preparation (preparation volume u_V, recovery and storage losses u_R, concentration-dependent influences of the measurement values u_{MV} attributable to the scatter of the calibration function, uncertainty of the calibration solution and the laboratory's own reproducibility).

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

The estimation of the sampling-dependent components of the uncertainty is based on the following factors according to Annex B of DIN EN ISO 21832 (DIN 2020) for sampling respirable dusts:

Calibration of the test system:	1%
Estimation of the aggregated concentration:	1%
Systematic deviation from the sampling convention:	8%
Deviation from the nominal flow of the cyclone:	3%

Individual variability of the sampling device: 7%

This results in a combined uncertainty for the sampling system of 11.1%.

A combined uncertainty for sampling respirable dusts u_S of 11.7% is obtained taking a sampling period of 120 minutes into account.

The individual uncertainty contributions and the resulting combined uncertainties are summarised in Table 6.

Tab. 6   Uncertainty contributions in % for nickel determination in the respirable particle fraction

u_S	u_V	u_D	u_R	u_{MV}		u_{comb}	
				C₁ (20 µg Ni/l)	C₂ (40 µg Ni/l)	C₁	C₂
11.7	0.1	3.0	4.4	3.9	12.8	12.7	11.7

Table 7 lists the concentration-dependent expanded uncertainties u_{exp} with the corresponding nickel concentrations of the sample solution and the relevant nickel concentrations in the air at an air sample volume of 1.2 m³ with and without dilution. Only the uncertainties for the medium to higher calibration range were taken into account, as at higher nickel concentrations in the air the samples in this calibration range are diluted.

Tab. 7   Expanded concentration-dependent uncertainties

	C₁	C₂
Expanded uncertainty [%]	**26**	**25**
Nickel concentration in the sample solution [µg/l]	20	40
Nickel concentration in the air [µg/m³]	0.48	0.96
Nickel concentration in the air with a sample diluted by a factor of 20 [µg/m³]	9.6	19

In order to calculate the expanded uncertainty for the determination of nickel in the inhalable particle fraction, the uncertainty components of sampling were estimated according to Appendix B in DIN EN ISO 21832 (DIN 2020).

Calibration of the test system: 0.5%

Estimation of the aggregated concentration: 4%

Systematic deviation from the sampling convention: 7.5%

This results in a combined uncertainty for the sampling system of 8.5%.

The results of the recovery with the high spiked quantity and additionally the uncertainty of the dilution of the sample solution were taken into account to calculate the combined uncertainty. Table 8 lists the concentration-dependent expanded uncertainties u_{exp} with the corresponding nickel concentrations of the sample solution and the respective nickel concentrations in the air at an air sample volume of 0.42 m³ with and without dilution.

Tab. 8   Expanded concentration-dependent uncertainties for the determination of nickel in the inhalable particle fraction

	C₁	C₂
Expanded uncertainty [%]	**26**	**25**
Nickel concentration in the sample solution [µg/l]	20	40
Nickel concentration in the air [µg/m³]	1.4	2.8
Nickel concentration in the air with a sample diluted by a factor of 50 [µg/m³]	71	142

6.7   Comparative measurement

In 2017, as part of an interlaboratory comparability experiment, the high-pressure microwave digestion described here was compared to an open digestion method published by the MAK Commission (Pitzke et al. 2020). For this purpose, a grinding dust was weighed onto a nitrocellulose filter, prepared and analysed. The nickel concentration of the dust for the open digestion were 0.31% on average and 0.099% with relative standard deviation of 9.2% and 10.7% for six participating laboratories. Concentrations of 0.28% and 0.11% were determined with the analytical method described here. Comparability between the high-pressure microwave digestion described here and the open digestion is thus confirmed.

Notes

Competing interests

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

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