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

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Method for the determination of acrylamide

Method tested and recommended by the German Social Accident Insurance for the determination of acrylamide in work areas.
Both personal and stationary sampling can be conducted for the assessment of work areas.

Sampling is carried out by means of a pump and collection on a charcoal filter.

Analysis is performed by gas chromatography with mass selective detector (GC/MS) after elution.

Chemical names:	Acrylamide, 2-Propenamide, Acrylic acid amide
CAS-No.:	79-06-1
Molecular formula:	C_3H_5NO
Molar mass:	71.08 g/mol

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Summary

This method permits the determination of acrylamide concentrations in work areas averaged over the sampling time after personal or stationary sampling.

Principle: A pump is used to draw a measured volume of air through a GSP-sampling system equipped with a charcoal filter. The inhalable dust fraction of acrylamide is collected on the GSP-sampling system according to EN 481, whereas gaseous acrylamide is adsorbed on a charcoal filter. The collected acrylamide is eluted with a mixture of dichloromethane and methanol (9 + 1 v/v) and determined by gas chromatography with mass selective detector.

Technical data:

Limit of quantification: absolute: 0.1 ng acrylamide,
relative: 1 µg/m^3 acrylamide for a 210-litre air sample, 2 mL elution solution and an injection volume of 2 µL.

Selectivity: The method is selective due to the combination of separation by gas chromatography and mass selective detection.

Advantages: Personal sampling and selective determination possible.

Disadvantages: No indication of peak concentrations.

Apparatus: Pump
Gas meter or volumetric flow meter
GSP-sampling system with charcoal filter
Gas chromatograph with mass selective detector (GC/MS)

Detailed description of the method

Content

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:

Pump suitable for flow rates of 1000 mL/min, e.g. PP5 from Gilian, suppliers in Germany: DEHA Haan & Wittmer, D-71296 Heimsheim

Soap bubble flow meter, e.g. Gilibrator from Gilian

GSP-sampling system with flow rates of 1 L/min, e.g. from GSM, D-41469 Neuss

Charcoal filter, e.g. charcoal paper, type 508, diameter 37 mm (special size) from Whatman, D-37586 Dassel

For sample preparation and analysis:

Volumetric flasks, 10 mL, 100 mL, and 250 mL

Glass vials, 10 mL, with screw caps and PTFE-coated septa

Microlitre syringes, 10 µL, 50 µL, and 100 µL

Adjustable piston pipette, e.g. Multipette pro from Eppendorf, D-22366 Hamburg

Glass autosampler vials with crimp caps

Analytical balance, sensitivity 0.1 mg

Mechanical shaker

Gas chromatograph with mass selective detector (MSD)

1.2 Chemicals and solutions

Acrylamide, 99%, e.g. from Sigma-Aldrich, D-82024 Taufkirchen
β-Citronellol, 95% (internal standard), e.g. from Sigma-Aldrich, D-82024 Taufkirchen
Dichloromethane, p.a., e.g. from Merck, D-64271 Darmstadt
Methanol, p.a., e.g. from Merck, D-64271 Darmstadt
Helium, purity 99.999% (operating gas for the GC)

Eluent: Mixture of dichloromethane/methanol (9 + 1 v/v).

Eluent solution: Solution of approx. 17 µg β-citronellol/mL eluent.
5 µL β-citronellol (density 0,857 g/mL) is pipetted into a 250 mL volumetric flask, which has been almost completely filled with eluent. The flask is then filled to the mark with eluent and shaken.

Stock solution: Solution of approx. 0.35 mg acrylamide/mL eluent solution.
35 mg of acrylamide is weighed to the nearest 0.1 mg and transferred to a 10 mL volumetric flask. The flask is then filled with eluent solution to the mark and shaken.

Calibration solutions: Solutions of 0.17 µg/mL, 0.87 µg/mL, 1.73 µg/mL, 2.60 µg/mL, 3.47 µg/mL, and 4.33 µg/mL acrylamide in eluent solution.
Volumes of 5 µL, 25 µL, 50 µL, 75 µL, 100 µL and 125 µL of the stock solution are pipetted into separate 10 mL volumetric flasks, each containing a few millilitres of eluent solution. The flasks are filled to the mark with eluent solution and shaken.
For an air sample volume of 120 L and 2 mL sample solution, these solutions cover an acrylamide concentration range from 2.0 µg/m^3 to 41.3 µg/m^3 air.

2 Sampling

For sampling, the GSP-sampling system equipped with the charcoal filter is connected to the pump. Pump and GSP-sampling system are carried by a person during working hours or used in a stationary position. The flow rate is set at 1.0 L/min. Under these conditions sampling is in accordance with the definition of inhalable dust fraction [1].
A sampling time of 3.5 hours then corresponds to an air sample volume of 210 L. After sampling the volume flow is to be checked for constancy. If the deviation from the volume flow is above ± 5% it is recommended to reject the sample.

3 Analytical determination

3.1 Sample preparation and analysis

The loaded charcoal filter is placed in a 10 mL volumetric flask. After addition of 2 mL eluent solution, the flask is sealed and shaken for 15 min on a mechanical shaker. The supernatant solution is than removed by means of a pipette and an aliquot of it is transferred to an autosampler vial.
In order to make sure that the used elution solution and the charcoal filter do not contain any interfering impurities, a filter of each new batch is eluted with 2 mL elution solution and a volume of 2 µL is injected into the gas chromatograph (blank value).
Quantitative analysis of the chromatograms is performed by the internal standard method.

3.2 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Gas chromatograph HP 5890 with mass selective detector MSD HP 5870, split/splitless injector, and autosampler			
Column:	Quartz capillary DB-WAX (polyethylene glycol), length 30 m, internal diameter 0.25 mm, film thickness 0.25 µm			
Temperatures:	Injector: 220 °C Oven: Initial temperature: 65 °C, 0.5 minutes isothermal Heating rate: 10 °C/min Final temperature: 220 °C, 5 minutes isothermal Transfer line: 280 °C			
Injection:	Splitless, 1 min			
Carrier gas:	Helium, pre-pressure at 65°C: 69 kPa, constant flow			
Injection volume:	2 µL			
Ionization:	Electron impact ionization (EI) (70 eV)			
Measurement mode:	Selected ion monitoring (SIM)			
Registered masses (m/z in amu):		*Quantification* / Qualification		
	β-Citronellol:	*69*	81	156
	Acrylamide:	*71*	55	
Dwell time:	100 ms/registration mass for acrylamide 100 ms/registration mass for β-citronellol			

4 Calculations

4.1 Calibration

Aliquots of 2 µL of each of the calibration standard solutions described in Section 1.2 are injected into the gas chromatograph and chromatograms are recorded. The calibration graph is obtained by plotting the peak area ratios determined for acrylamide and β-citronellol (used as internal standard) against the ratio of acrylamide and β-citronellol concentrations of the individual calibration standard solutions. The calibration graph is linear under the described conditions.

4.2 Calculation of the analytical result

The peak areas of acrylamide and β-citronellol are determined, the quotient formed and the corresponding weight of acrylamide in the elution solution in µg is read from the calibration graph.
The concentration by weight of acrylamide in the air sample in mg/m^3 is calculated according to equation (1):

$$c_w = \frac{w}{V \cdot \eta} \tag{1}$$

Where:
c_w is the concentration by weight of acrylamide in the air sample in mg/m^3
w is the weight of acrylamide in the sample solution in µg
V is the air sample volume in litres
η is the recovery

5 Reliability of the method

5.1 Accuracy and recovery

The accuracy in the minimum measurement range according to EN 482 [2] and the recovery were determined for four different concentrations of acrylamide. The results are shown in Table 1. For this, the following spiking solutions were prepared:

Spiking solution I:
Solution of 0.13 mg acrylamide/mL dichloromethane.
13.0 mg of acrylamide is weighed into a 10 ml volumetric flask. The flask is then filled to the mark with dichloromethane and shaken.

Spiking solution II:
Solution of 0.34 mg acrylamide/mL dichloromethane.
3.4 mg of acrylamide is weighed into a 10 mL volumetric flask. The flask is then filled to the mark with dichloromethane and shaken.
Four separate charcoal filters were spiked with 5 µL of the spiking solution I and 4 µL, 40 µL and 80 µL of the spiking solution II. Afterwards, laboratory air (30–50% relative humidity) was drawn for three and a half hours through the GSP-sampling system at a flow rate of 1 L/min. After elution, the obtained solutions were injected into the gas chromatograph. This procedure covers the air concentrations given in Table 1.

Table 1. Relative standard deviation and recovery for n = 4 determinations.

Concentration [mg/m^3]	Relative standard deviation [%]	Recovery
0.003	7.4	0.87
0.006	5.7	0.85
0.064	7.9	0.86
0.128	4.2	0.84

Based on this, the mean recovery is 0.86.

5.2 Limit of quantification

The limit of quantification was determined from the signal/background noise ratio of the chromatogram. Calculation of the quantification limit based on the tenfold of the background noise.
The absolute limit of quantification is 0.1 ng acrylamide.
The relative limit of quantification is 1 µg/m^3 acrylamide for a 120-litre air sample, 2 mL elution solution and 2 µL injection volume.

5.3 Selectivity

The method is selective due to the combination of gas chromatographic separation and mass selective detection.

6 Discussion

The loaded charcoal filter can be stored for 14 days at room temperature without any loss of adsorbed acrylamide. At higher flow rates during sampling (e. g. GSP 3.5), a breakthrough through the sampling system occurs.
At workplace areas (e. g. safety glass manufacturing) where besides of acrylamide, also *N*-methylol acrylamide is present, false-positive results can be obtained. In such cases, an analysis by HPLC is recommended.
The method also permits the determination of ε-caprolactam in the air of work areas.

7 References

[1] EN 481, Workplace atmospheres – Size fraction definitions for measurement of airborne particles, European Standard, Issue: September 1993.
[2] EN 482, Workplace atmospheres – General requirements for the performance of procedures for the measurement of chemical agents, European Standard, Issue: October 2006.

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