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Expert Committee Chemistry

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Method for the determination of 2-naphthylamine

Method tested and recommended by the Berufsgenossenschaften for the determination of 2-naphthylamine in working areas after discontinuous sampling.
For the assessment of working areas, both personal and stationary sampling are possible.

1 Sampling with a pump and absorption in sulfuric acid,
thin layer chromatography
Canceled April 2002

2 Sampling with a pump and adsorption on impregnated silica gel,
gas chromatography after desorption.

Sampling can also be carried out with an evacuated gas collection vessel to find leaks in industrial systems or for control determinations during cleaning and repair work, and for orientation purposes.

2 Sampling with a pump and adsorption on impregnated silica gel, gas chromatographic determination after desorption

Principle: With a pump a measured air volume is drawn through a glass tube filled with impregnated silica gel. The adsorbed 2-naphthylamine is desorbed with a mixture of dichloromethane and 2-aminoethanol and determined by gas chromatography.

Technical data:

Quantification limit: absolute: 2 ng 2-naphthylamine,
relative: 0.05 mg/m^3 = 0.009 ml/m^3 (ppm) 2-naphthylamine for a 40-litre air sample.

Selectivity: The selectivity of the procedure must be checked in each individual case. Interference can generally be eliminated by selecting a different column.

Advantages: Personal sampling, selective determination possible.

Disadvantages: No indication of peak concentrations, time-consuming.

Apparatus: Pump,
gas meter or flow meter,
adsorption tubes with impregnated silica gel,
gas chromatograph with flame ionisation detector (FID) or phosphorus/nitrogen detector (PND).

Detailed description of the method

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Summary

This method permits the determination of 2-naphthylamine concentrations in working areas averaged over the sampling time after personal or stationary sampling.

With a pump carried by a person or used in a stationary position, a measured air volume is drawn through an adsorption tube filled with silica gel. After desorption with a mixture of dichloromethane and 2-aminoethanol, the 2-naphthylamine is determined by gas chromatography.

The absolute quantification limit is 2 ng 2-naphthylamine.

The relative quantification limit is 0.05 mg/m^3 = 0.009 ml/m^3 (ppm) 2-naphthylamine for a 40-litre air sample.

2 Equipment, chemicals and solutions

2.1 Equipment

For sampling:
Pump
Sampling tube: Glass tube 10 cm in length, with about 6 mm internal diameter and about 8 mm external diameter, which at one end is drawn out to a pipette-like point. This tube consists of two zones with about 0,8 g impregnated silica gel (preparation see Section 2.3) and separated by PTFE*-wool (5 mm).

For sample preparation and analysis:
Sample vial: 5 ml or 10 ml with septum and aluminium cap
Crimper
Gas chromatograph with flame ionisation detector.
If a phosphorus/nitrogen detector is used, the procedure described here can be followed, but methanol must be used as the desorption agent.

2.2 Chemicals

2-Naphthylamine, ultrapure
Silica gel from Grace, type 12
Amidosulfuric acid, analytical grade
Dichloromethane, analytical grade
2-Aminoethanol, purity 99%
Gases for gas chromatography: Nitrogen
Hydrogen
Synthetic air

2.3 Solutions

Desorption solution:	50 ml 2-aminoethanol is placed in a 1000 ml volumetric flask which is then filled to the mark with dichloromethane.
Preparation of the impregnated silica gel:	For each 10 g of silica gel from Grace, type 12, 0.5 g amidosulfuric acid is dissolved in 5 ml methanol/water (1 : 1) and added to the silica gel. The mixture is left to stand for one hour, is occasionally shaken, and the solvent is evaporated to dryness on a rotary evaporator at room temperature.
2-Naphthylamine stock solution I:	Solution with 5 mg 2-naphthylamine per ml. 50 mg 2-naphthylamine is placed in a 10 ml volumetric flask which is then filled with desorption solution to the mark.

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* Polytetrafluoroethylene

2-Naphthylamine stock solution II: Solution with 500 µg 2-naphthylamine per ml. e.g. 1 ml 2-naphthylamine stock solution I is pipetted into a 10 ml volumetric flask which is then filled with desorption solution to the mark.

Calibration solutions: By diluting stock solution II, solutions of 2-naphthylamine in desorption solution are prepared which contain e.g. 3, 5, 10, 15, 20 and 30 µg 2-naphthylamine in 1 ml.

3 Sampling

With a pump a measured air volume is drawn through the sampling tube at a rate of 40 l/hour.

4 Analytical determination

4.1 Sample preparation and analysis

After sampling, the first and second adsorption layers of the sampling tube are placed in separate 5 ml sampling vials. After the addition of exactly 1 ml of the desorption solution, the vial is closed and left for about 48 hours (sample solution). 1 µl of this solution is then injected into the gas chromatograph. The area or height of the 2-naphthylamine peak is determined.

4.2 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

Apparatus: Perkin Elmer, model F 22, with flame ionisation detector
Operating conditions A: Packed column, isothermal
Column: Material: glass
Length: 2 m
Internal diameter: 3 mm
Stationary phase: SP 2250 (1,5%) + SP 2401(1,95%) on Supelcoport (100–120 mesh)
Temperatures: Injection block: 280 °C
Column: 160 °C, isothermal
Detector: 300 °C
Carrier gas: Nitrogen, 25 ml/min
Detector gases: Hydrogen, 42 ml/min
Synthetic air, 420 ml/min

Operating conditions B:	Capillary column, with temperature programme, on-column injection	
Column:	Material:	Glass capillary
	Length:	50 m
	Stationary phase:	SE 54
Temperatures:	Injection block:	on-column injection
	Column:	programmed; 5 minutes at 80 °C, then heated to 280 °C at 5 °C/min
	Detector:	300 °C
Carrier gas:	Nitrogen (column inlet pressure 1.0 bar)	

5 Evaluation

5.1 Calibration

1 µl of each of the calibration solutions, which contain e.g. 3, 5, 10, 15, 20 and 30 µg 2-naphthylamine in 1 ml, is injected into the gas chromatograph. The calibration curve is prepared by plotting the peak areas or peak heights determined against the amount of 2-naphthylamine in µg contained in 1 ml of each calibration solution.
The calibration solutions and the sample solution must be analysed in sequence.

5.2 Calculation of the analytical result

With the calibration curve, the amount of 2-naphthylamine in the sample is determined from the peak area or peak height of the sample solution.
The 2-naphthylamine concentration by weight in the air sample is calculated in mg/m^3 according to the equation (1).

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

For 20 °C and 1013 mbar the concentration by volume in ml/m^3 is calculated according to the equation (2):

$$c_v = 0.17 \cdot c_w \tag{2}$$

Where:
c_w Concentration of 2-naphthylamine in the air sample in mg/m^3
c_v Concentration of 2-naphthylamine in the air sample in ml/m^3 (ppm)
w Weight of 2-naphthylamine in the sample solution in µg taken from the calibration curve
V Air sample volume in l

6 Reliability of the method

6.1 Accuracy

The relative standard deviation for the analytical procedure is ±6%, evaluated from 6 individual determinations in which calibration solutions each with 18 µg 2-naphthylamine were loaded onto silica gel. The range of scatter was calculated from this to be ±15%.

6.2 Quantification limit

The absolute quantification limit is 2 ng 2-naphthylamine.
The relative quantification limit is 0.05 mg/m^3 = 0.009 ml/m^3 (ppm) 2-naphthylamine for a 40-litre air sample, 1 ml sample solution and 1 µl injection volume.

6.3 Selectivity

The selectivity of the procedure must be checked in each individual case. It depends in particular on the type and quality of the column used.
Under the gas chromatographic conditions described, 2-naphthylamine is separated from 1-naphthylamine.
As a result of interference, the flame ionisation detector can produce too high values. Interference can generally be eliminated by selecting a different column. If interfering factors cannot be eliminated, selectivity can be increased by using a phosphorous/nitrogen-specific detector (PND).

6.4 Recovery

The recovery was 87%. If sulfur dioxide, nitrogen oxides, hydrogen chloride gas or carbonyl compounds are present in concentrations above their threshold values, the recovery of 2-naphthylamine can be considerably reduced.

7 Suppliers

Pump:	Du Pont Instruments, Supplier in Germany: DEHA-Haan & Wittmer GmbH, Friolzheim
Silica gel tubes:	e. g. Grace GmbH, Worms
Gas chromatograph:	e. g. Bodenseewerk Perkin Elmer & Co GmbH, Überlingen

Carlo Erba
Supplier in Germany:
Erba Science, Hofheim/Ts
Siemens AG, Karlsruhe
Varian GmbH, Darmstadt

8 References

Blome H, Thielen RG, Hennig H (1983) Untersuchungen über die Belastung von Kokereiarbeitern durch 2-Naphthylamin. Staub-Reinhalt. Luft 12