Lacquer aerosols

Method number	2
Application	Air analysis
Analytical principle	Gas chromatography (solvent desorption)
Completed in	January 2001

Summary

The sampling of lacquer aerosols is carried out in such a way that simultaneously both the particulate components and the solvent vapour of the lacquer aerosols are collected. A measured air volume is drawn through a glass fibre filter at the inlet of the sampling system. The particulate components of the lacquer aerosol are deposited as the inhalable fraction according to EN 481 [1].

The air containing the solvent vapour is drawn further through the sampling system and the solvent vapour is adsorbed by the activated carbon contained in the cartridge. After sampling, clean air is drawn through the sampling system. This guarantees that the solvent vapour adhering to the particles, which is released during the drying process, is also collected. Determination of the particles collected as the inhalable fraction is carried out gravimetrically. To determine the collected solvent vapour, a suitable desorption solvent is added to the collection phase (activated carbon). Separation and quantification is then carried out by gas chromatography.

Precision:

Inhalable particles

Standard deviation (rel.): $s = 4.3\%$
Mean variation: $u = 10.1\%$
in the concentration range of 20–220 mg/m^3 and for 7 duplicate determinations

Solvent vapour

Standard deviation (rel.): $s = 3.6–8.0\%$
Mean variation: $u = 8.6–19.0\%$
in the concentration range of 0.4–60 mg/m^3 and for 7 duplicate determinations

Limit of quantification:	*Inhalable particles*	
	absolute	0.3 mg
	relative	2.9 mg/m^3 with sampling for 30 minutes
	Solvent vapour	
	absolute	0.04 mg
	relative	0.2–0.5 mg/m^3 with sampling for 30 minutes
Recovery:	η = 0.9−1.0 (90−100%) for the solvents	
Sampling recommendation:	Sampling time:	0.5−1 hour
	Sampled air volume:	up to 210−420 L
	Flow rate:	(3.5 L/min)

Lacquer aerosols

Unlike during the brushing and rolling of paints and lacquers, or similar activities, during spray lacquering, not only solvent vapour but also particles are set free which contain solid components such as pigments, fillers etc. as well as solvents. The solvent vapour adhering to these particles, which is only released during the drying process, is not determined when the particulate components and the solvent vapour of the aerosol are sampled separately. For the complete determination of all solvent vapour, it is therefore imperative that the particles and the solvent vapour are collected simultaneously with one sampling system, as it can only then be guaranteed that the solvent vapour released during drying is determined together with the free solvent vapour of the aerosol.

Toxicological evaluation of exposure to solvent vapour at the workplace is carried out with reference to the threshold values in the air. There is, at present, no way of evaluating the aerosol fraction. The sub-committee V “Grenzwerte“ (“Threshold Values“) of the Ausschuss für Gefahrstoffe (AGS: Committee for Hazardous Substances) is currently investigating whether it is possible to set a threshold value in air on the basis of what is technically possible, in analogy to the concept of the Technical Exposure Limits (TRK).

In the procedure described in the present method “Lacquer aerosols“ the main emphasis is on the simultaneous sampling of the particles and free solvent vapour together with that released during drying.

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Contents

1 General principles

The particles and the solvent vapour of the lacquer aerosols are collected simultaneously with one sampling system. The workplace air is drawn through a sampling system for the personal sampling of total inhalable dust and gas. Behind the air inlet of the sampling system is placed a glass fibre filter onto which the particles are deposited as the inhalable fraction [1]. After it has passed the filter, the workplace air is drawn through a cartridge filled with activated carbon. The solvent vapour is deposited on the activated carbon by adsorption.

After sampling, solvent-free air is drawn through the sampling system for about a further 5 minutes. It is thus guaranteed that the residual solvent evaporating from the particles is completely collected and is included in the analysis of the workplace air.

The particles deposited on the filter are determined gravimetrically. The collected solvent vapour is desorbed with a ternary mixture of 60% v/v dichloromethane, 35% v/v carbon disulfide and 5% v/v methanol. After gas chromatographic separation, the components are quantified with a flame ionization detector. To check that the peaks are assigned correctly to the substances, a mass spectrometric detector is used if needed.

2 Equipment, chemicals and solutions

2.1 Equipment

Sampling pump for personal air sampling, flow rate 3.5 L/min (e.g. PP5 ex, from Gilian)
Sampling system: System for the personal sampling of total inhalable dust and gas with glass cartridge for the activated carbon (Fig. 1)
Glass fibre filter: Diameter 37 mm, (e.g. MN 85/90 BF, from Macherey und Nagel)
Gasmeter or soap bubble flowmeter and stop clock
Gas chromatograph with two flame ionization detectors (HP 6890 from Hewlett-Packard)
Various microlitre syringes
Capillary columns of different polarity (e.g. DB-5, and DB-Wax: each 60 m, 0.25 µm film thickness, 0.25 mm internal diameter, from J&W)
Various screw-top and crimp-top vials with PTFE-coated septa and aluminium crimp caps
Crimping tongs for sealing and opening the vials
Various pipettes
Analytical balance: mean variation max. 0.1 mg
Barometer
Hygrometer
Thermometer
Desiccator

Rack for thin-layer chromatography plates
Glass cutter
Tweezers

2.2 Chemicals

The substances to be determined, analytical grade
n-Undecane (internal standard for DB-Wax), for GC
2-Methylheptane (internal standard for DB-5), for GC
Carbon disulfide (benzene-free, e. g. Promochem 9056)
Dichloromethane (Merck, analytical grade)
Methanol (Merck, analytical grade)
Helium, purity 99.996%
Hydrogen, purity 99.999%
Synthetic air (free of hydrocarbons)
Nitrogen, purity 99.999%
Dessicant
Activated carbon (e. g. Dräger coconut carbon, particle size 0.4–1.2 mm)

2.3 Solutions

Ternary mixture (60% v/v dichloromethane, 35% v/v carbon disulfide, 5% v/v methanol)
Mixture of 2-methylheptane and *n*-undecane in equal volume parts (internal standard)

2.4 Calibration standards

For calibration of the gas chromatographic system, six calibration standards of each substance to be analysed are prepared which cover at least the range of 0.1 times to twice the threshold value.
If this is not possible because the curve is not linear, calibration is carried out within the linear range and the samples are diluted accordingly.

Stock solution:
From the components to be analysed a stock solution is prepared which contains the substances in 10 mL ternary mixture. Determination of the amount of substance used can be carried out gravimetrically or volumetrically. The procedure for the determination of a solvent mixture made up of ethyl acetate, *n*-hexane and toluene is described below.

Table 1. Preparation of the stock solution of the components.

Substance	Added volumes µL	Weighed amount mg	Final volume mL	Concentration g/L
Ethyl acetate	300	270.2	10	27.02
n-Hexane	400	264.1	10	26.41
Toluene	300	258.9	10	25.89

Calibration standards:

The calibration standards are prepared from the stock solutions. Ternary mixture is placed in 10 mL volumetric flasks, the volumes of the stock solution listed in Table 2 are added and the flasks are then filled to the mark with ternary mixture. 5 µL of a mixture of 2-methyl heptane and *n*-undecane (equal volume parts) is added to each calibration standard as internal standard.

The concentrations of the calibration solutions are shown in Table 2.

Table 2. Concentration in mg/10 mL of the calibration solutions.

Calibration solution	Volume of the stock solution µL	Ethyl acetate mg/10 mL	*n*-Hexane mg/10 mL	Toluene mg/10 mL
1	1.5	0.041	0.040	0.039
2	120	3.24	3.17	3.11
3	240	6.48	6.34	6.21
4	360	9.73	9.51	9.32
5	480	12.97	12.68	12.43
6	600	16.21	15.85	15.53

3 Sample collection and preparation

3.1 Preparing the sampling tubes

3.1.1 Pretreatment of the filters

The glass fibre filters are conditioned before sampling for at least 12 hours in the desiccator, then left to stand uncovered next to the scales for an hour and weighed. For conditioning, the filters are placed e.g. in a rack for thin-layer chromatography plates in the desiccator, which is filled with dessicant. Tweezers must always be used when handling the conditioned filters.

3.1.2 Filling the cartridges

The cartridges are filled with two separate layers of activated carbon each weighing about 1.5 g (Section 2.2). The activated carbon is held in place with PTFE sieves and O rings.

3.2 Sample collection

Sample collection can be performed as static sampling or as personal air sampling. For sampling, a conditioned filter and a glass cartridge filled with activated carbon are placed in the sampling system. The parameters which are important for the determination of the concentrations in air (volume of the air sample, temperature, atmospheric pressure and relative humidity) are recorded in a sampling protocol.

With personal air sampling it must be ensured that the inlet of the sampling system is not obstructed during work. In particular, care must be taken that the sampling system is attached in the breathing zone of the employee on the side of the body opposite the arm used for working, i.e. on the left for lacquer spraying with the right hand, and vice versa. Intermittent obstruction of the sampling system by the arm movements of the worker is thus avoided.

After sampling, clean air is drawn through the sampling system for about a further 5 minutes. This can be carried out by drawing air through the system from a work area without solvents.

The filter holder with the loaded filter is then removed and closed with the appropriate caps. The cartridge is removed from the sampling apparatus and closed with plastic caps.

3.3 Sample preparation

The samples should be analysed immediately, if possible. With storage for more than 14 days, the shelf-life of the substances to be analysed must be checked.

For analytical determination the solvent components adsorbed on the activated carbon must be desorbed. This is carried out by adding a ternary mixture of 60% v/v dichloromethane, 35% v/v carbon disulfide and 5% v/v methanol [2]. The two activated carbon layers in the glass cartridge are transferred separately to two 10 mL sample vials. Then 10 mL of the ternary mixture is added to each and the vials are closed. After desorption is complete, 5 µL of the internal standard mixture (Section 2.3) is added to each solution. 1 µL of this solution is injected into the gas chromatograph.

To determine the blank value, unused cartridges must be prepared in the same way as the samples. Desorption is complete after treatment for half an hour with gentle shaking.

The filters loaded with the particles are evaluated gravimetrically. Before weighing, the filters are conditioned in the desiccator over a dessicant for at least 12 hours.

4 Operating conditions for gas chromatography

Column:	Capillary column:	fused silica
	Length:	60 m
	Internal diameter:	0.25 mm
	Stationary phase:	Poly (5% diphenyl- 95% dimethyl-)siloxane, bound, and polyethylene glycol, from Agilent
	Film thickness:	0.25 µm
Detector:	Flame ionization detector (FID)	
Temperatures:	Injector:	200 °C
	Detector:	250 °C
	Furnace:	5 min at 50 °C isothermal, 2.5 °C/min up to 120 °C
Sample injection:	Automatic, split	
Split flow:	32 mL/min	
Split ratio:	20 : 1	
Septum purge flow:	1 mL/min	
Carrier gas:	Helium (1.6 mL/min)	
Detector gases:	Hydrogen (30 mL/min) Synthetic air (400 mL/min)	
Detector make-up gas:	Nitrogen (30 mL/min)	
Injection volume:	1 µL	

5 Analytical determination

5.1 Determination of the particles

Determination of the collected lacquer particles is carried out gravimetrically.
The loaded filters are conditioned for at least 12 hours in the desiccator, and then left uncovered next to the scales for an hour. The scales should be in an air-conditioned room. Evaluation is carried out as described in Section 7.1.

5.2 Calibration

Calibration is necessary only for the solvents. For calibration, 1 µL of each of the calibration standards is injected three times into the gas chromatograph. The calibration curves are linear in the concentration ranges given here for the substances tested. The calibration curves must be checked in routine analysis by checking at least one point on the curve.

5.3 Determination of the solvents

1 µL of each of the desorption solutions from the activated carbon collection and control phases prepared as described in Section 3.3 are injected into the GC port. The sample is analysed in parallel on two columns of different polarity (Section 4).
The analysed component weights from the collection and control phases are added together. If >25% of the concentration of the components on the collection phase is found on the control phase, the sample must be discarded as breakthrough of the solvent cannot be excluded.

6 Calculation of the analytical result

6.1 Calculation of the concentration of the particles

The weight of the collected particles m_v is calculated from:

$$X_P = m_n - m_v \qquad (1)$$

where:

$$k = m_{Rn}/m_{Rv} \qquad (2)$$

where:
X_P is the weight of the collected inhalable lacquer particles in mg
m_n is the weight of the conditioned filter after sampling in mg
m_v is the weight of the conditioned filter before sampling in mg

The concentration of the inhalable particles is then calculated from:

$$\rho_{\mathrm{P}} = X_P/V \qquad (3)$$

where:
ρ_{P} is the concentration of the inhalable particles in mg/m^3
V is the collected air sample volume in m^3

6.2 Calculation of the concentration of the solvent vapour

The concentration of the individual solvents in the workplace air is determined using the peak areas found for these solvents. For this purpose, the ratio of the peak area for the internal standard and that for the component to be determined is calculated. With this quotient the weight of each component is calculated using the appropriate analytical function or response factor. This procedure can be used for all the components for

which a linear calibration curve was determined during calibration. The results obtained from the two columns of different polarity are averaged.
The weight of the components to be determined is then calculated from:

$$X_A = (X_{is} \times F_A)/(F_{is} \times R_A) \tag{4}$$

where:
X_A is the weight of the component to be determined in the activated carbon phase in µg
X_{is} is the given weight of the internal standard in µg
F_A is the size of the peak area for the component to be determined
F_{is} is the size of the peak area for the internal standard
R_A is the response factor for the component to be determined

When calibrating for the concentration of the components, the injection volume and the extraction volume must be taken into account when calculating the weight of the component.
The concentration by weight (ρ_{A}) for the component to be determined can then be calculated using the following equation

$$\rho_{\mathrm{A}} = X_{AS}/(V \times \eta) \tag{5}$$

At 20 °C and 1013 hPa:

$$\rho_0 = \rho_{\mathrm{A}} \times (273 + t_A)/293 \times (1013/p_A) \tag{6}$$

where:
X_{AS} is the sum of the weights of the component to be determined in the two activated carbon phases in µg
V is the air sample volume in L
η is the recovery
ρ_{A} is the concentration of the component to be determined in mg/m^3
ρ_0 is the concentration by weight in mg/m^3 at 20 °C and 1013 hPa
t_A is the temperature during sampling in °C
P_A is the atmospheric pressure during sampling in hPa

7 Reliability of the method

7.1 Precision

The precision is determined by measuring the concentrations at the workplace. Duplicate determinations (sampling and analysis) are carried out. A reference atmosphere with known concentrations of the lacquer particles and the solvents could not be produced.

To determine the precision of the determination of the lacquer particles, the standard deviation for 7 duplicate determinations was evaluated. The concentrations of the lacquer particles were in the range from 20 to 220 mg/m^3. The relative standard deviation for the duplicate determination of the lacquer particles was found to be 4.3%, the mean variation 10.1%.

To determine the precision for the determination of the solvents, the standard deviations of 4 duplicate determinations were evaluated, for example, for three typical lacquer solvents (Table 3).

Table 3. Standard deviation and mean variation for selected lacquer solvents.

Solvent	Concentration range mg/m^3	Standard deviation for duplicate determinations (rel.) s %	Mean variation u %
n-Butyl acetate	5–50	6.7	16.3
1,3,5-Trimethyl benzene	0.8–7	11.6	27.6
m-Xylene	2.5–26	4.5	10.7

7.2 Recovery

The recovery was determined by loading 0.1 times the MAK value, 0.5 times the MAK value and twice the MAK value of each solvent component onto an activated carbon tube, through which pure air was drawn at a flow rate of 0.333 L/min for 120 minutes and which was then analysed as described. The following recoveries were determined:

n-Butyl acetate	100%
1,3,5-Trimethyl benzene	91%
m-Xylene	90%

7.3 Limit of quantification

The limit of quantification for the lacquer particles collected as the inhalable fraction [1] was found to be 0.15 mg absolute. With sampling for 30 minutes and a flow rate of 3.5 L/min, this corresponds to a workplace concentration of 2.9 mg/m^3. For the individual solvents, the absolute limits of quantification are 40 µg on the collection phase. The resulting quantification limit for the workplace concentration is 0.4 mg/m^3 with sampling for 30 minutes.

7.4 Sources of error

Interference during sampling is possible. With high aerosol concentrations the sampling pumps may switch off if the filter becomes blocked by the collected particles. To avoid blocking of the filters, the sampling time should not exceed one hour.

With complex solvent mixtures, the use of the unspecific FID as the only GC detector may lead to false interpretations. To verify the assignment of the solvent peaks to the components, a mass spectrometer should be used as GC detector; alternatively, before sampling, the solvent components of the lacquers and thinners used can be analysed qualitatively by GC/MS (head-space analysis).

7.5 Results of comparative studies

To check the procedure, comparisons with the results obtained with two other sampling systems for simultaneous collection of the particles and solvents during lacquer spraying were carried out [3]. Two sampling systems were used simultaneously in duplicate.

The results of these comparisons are shown for particles and *n*-butyl acetate in "Lacquer aerosols, Method No. 1".

Apart from a few exceptions, the results for the relative analytical uncertainty [4] were consistently within a range of ± 30% around a common mean value. This was confirmed in further comparisons also for other solvents [3].

8 Discussion of the method

The particle and solvent fractions of lacquer aerosols are collected simultaneously. By drawing clean air through the sampling system after the actual sampling, solvent vapour evaporating as the particles dry is also collected. For sampling, the flow rate for the workplace air at the inlet of the sampling device must be set to 1.25 m/s ± 10%. After the particles are deposited on the filter, the air is drawn through the collection phase (activated carbon) on which the solvent vapour is adsorbed.

The preparation and analysis of the collected particles and solvents are carried out separately, the former gravimetrically and the latter by desorption with a ternary solvent mixture and subsequent gas chromatographic determination.

Extensive comparisons with two other simultaneously collecting sampling systems yielded similar results for the determinations of lacquer particles and solvents as stipulated in EN 482 [4].

9 References

[1] *Europäisches Komitee für Normung* (CEN) (1993). DIN EN 481 – Arbeitsplatzatmosphäre – Festlegung der Teilchengrößenverteilung zur Messung luftgetragener Partikel. Brüssel. Beuth-Verlag, Berlin

[2] *Angerer J., Flammenkamp E., Hebisch R., Krämer W., Kuck M., Lichtenstein N., Risse U., Schröter U., Tschickardt M.* (2002) Solvent mixtures, Meth.-Nr. 1. In: Analyses of Hazardous Substances in Air, Vol. 6 (Greim H., Ed.). Wiley-VCH Verlag, Weinheim, 123–135

[3] *Lichtenstein N., Hennig M., Friedrich C., Auffart J., Hebisch R., Rentel K.H., Fricke, H.H., Möcklinghoff K., Dahmann D.* (1997). Messmethoden zur Bestimmung der Exposition gegenüber Lackaerosolen und Lösemitteldämpfen beim Spritzlackieren. Staub – Reinh. Luft 57: 39–45

[4] *Europäisches Komitee für Normung* (CEN) (1994). DIN EN 482 – Arbeitsplatzatmosphäre – Allgemeine Anforderungen an Verfahren für Messung von chemischen Arbeitsstoffen. Brüssel. Beuth-Verlag, Berlin

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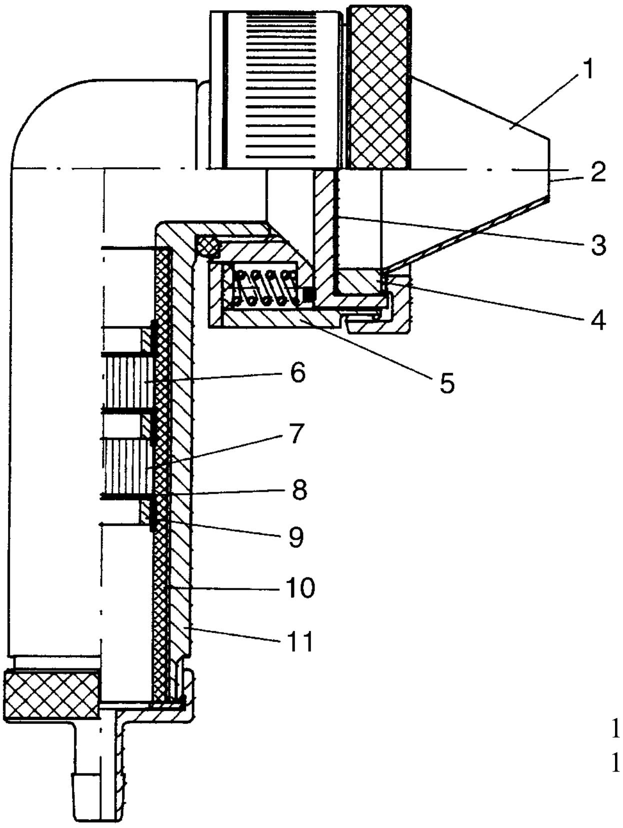

1	Inlet cone
2	Inlet
3	Glass fibre filter
4	Filter holder
5	Filter holder body
6	Collection Phase
7	Control phase
8	PTFE sieve
9	O ring
10	Glass cartridge
11	Cartridge holder

Fig. 1. System for the personal sampling of total inhalable dust and gas with glass cartridge for the activated carbon.