Analyses of Hazardous Substances in Air, Volume 5. DFG, Deutsche Forschungsgemeinschaft

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Analyses of Hazardous Substances in Air

Volume 5

edited by Antonius Kettrup
Working Group Analytical Chemistry

Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area
(Chairman: Helmut Greim)

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Preface

In Germany the publication of methods for the analysis of chemical compounds in the air is divided between the Working Group "Analytical Chemistry" of the Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area of the Deutsche Forschungsgemeinschaft (analysis in air of hazardous substances with MAK values) and the Analytical Working Group of the Expert Committee "Chemistry" of the Berufsgenossenschaften (Employment Accident Insurance Institutions of Germany) (analysis in air of carcinogenic substances, so-called BGI 505 procedures). The German editions of both methods are published independently of one other.

The Organisational Committee "Analysis" is made up of representatives from both working groups and coordinates the activities of the various groups with the aim of preventing work being carried out twice. This committee decided in 1994 to include the BGI 505 methods in the English edition of the DFG collection of methods *Analyses of Hazardous Substances in Air*.

The Commission hopes that by publishing both sets of methods in one English volume, the ever-growing repertoire of methods will be put to effective use, e. g. within the European Union in the efforts to protect health at the workplace.

The speciality of this volume is the fact that mostly methods for carcinogenic compounds are included. Furthermore a method for the analysis of 2,3,7,8-substituted polychlorinated dibenzodioxins and dibenzofurans is described.

My special thanks go to members of the Organisational Committee "Analysis", in particular Th. Brock, M.R. Lahaniatis and A. Kettrup, for their successful work and great personal engagement.

H. Greim
Chairman of the Commission for the
Investigation of Health Hazards of Chemical
Compounds in the Work Area

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Foreword

The protection of workers against risks form chemical agents is particularly important because of many effects on the individual which may be caused by exposure to harmful chemical agents at the work place.

In 1995, the European Commission decided to set up a Scientific Committee to give advice on the setting of Occupational Exposure Limits (OEL) based on scientific and technical data. By applying a well defined guidance note on procedures to set limit values, recommendations for more than 80 OELs have been made to the commission.

An even longer tradition regarding occupational exposure limits exists in Germany under the responsibility of the Deutsche Forschungsgemeinschaft and its Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area". MAK values (maximum workplace concentration) are established on the basis of toxicological data.

If the aim of the limit values to protect workers health is to be realised, then it is essential that measurements of exposure should be reliable. Persons who carry out measurements must possess the necessary expertise and facilities. Furthermore, the measuring procedure used, including limit of detection, sensitivity, precision and accuracy, must be appropriate to the chemical compound to be measured, its limit value and the workplace atmosphere.

Research and development of such procedures suitable for routine use, are the objectives of the Working Group "Analytical Chemistry" of the Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area. In response to the worldwide demand for reliable chemical methods for air analysis, the Working Subgroup "Analyses of Hazardous Substances in Air of Work Area" has chosen methods for publication, whose analytical reliability and reproducibility have been tested and confirmed by at least one examiner. The description of each method includes an evaluation of the method, a brief listing of the reliability criteria and general information on the chemical compound to be tested, i. e. its industrial importance, toxicity and its limit value at the workplace as far as it is known. This is followed by a detailed description of the preparatory and analytical steps, discussion of the reliability and a reference list.

Volume 5 comprises 17 analytical methods for the determination of hazardous substances in the air of workplaces.

We would like to thank the members and guests of the Working Subgroup without whose voluntary services this collection of methods would not have been possible. We thank the Deutsche Forschungsgemeinschaft for financial and organisational help in the development of this project. Our thanks go also to our publisher Dr. Eva E. Wille of Wiley-VCH with whom we have enjoyed long-standing and efficient collaboration. We also wish to thank Mrs. Julia Handwerker-Sharman for translation.

J. Angerer
Chairman of the Working Group "Analytical Chemistry" of the Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area

A. Kettrup
Chairman of the Working Subgroup "Analyses of Hazardous Substances in Air of Work Areas"

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Contents

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Analytical Methods

Analyses of Hazardous Substances in Air, Volume 5. DFG, Deutsche Forschungsgemeinschaft

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Aldehydes (Formaldehyde, Acetaldehyde, Propionaldehyde, Butyraldehyde, Glutaraldehyde, Pentanal, Hexanal, Heptanal, Octanal, Nonanal)

Method number	2
Application	Ambient air analysis
Analytical principle	High performance liquid chromatography
Completed in	March 1995

Summary

To determine the airborne aldehydes in working areas a measured volume of ambient air is drawn with a sampling pump through silica gel cartridges impregnated with 2,4-dinitrophenylhydrazine. The airborne aldehydes and ketones are transformed into the corresponding hydrazones. After desorption with acetonitrile, qualitative and quantitative determination is carried out by using HPLC.
Calibration curves determined by analysis of standard solutions are used for the quantitative evaluation; the aldehyde concentrations of the calibration standards are plotted versus the peak areas.

Precision (formaldehyde):	Standard deviation (rel.)	s_w = 5.0, 1.7 and 3.9%
	Mean variation	u = 11.9, 4.3 and 9.9%
	at concentrations of 150, 600 and 1200 µg of formaldehyde per m^3 air and for n = 6 determinations	
Detection limits (for a sample volume of 6 L air):	Formaldehyde	11 µg/m^3
	Acetaldehyde	4 µg/m^3
	Propionaldehyde	3 µg/m^3
	Butyraldehyde	6 µg/m^3

	Pentanal	11 μg/m^3
	Hexanal	6 μg/m^3
	Heptanal	15 μg/m^3
	Octanal	11 μg/m^3
	Nonanal	11 μg/m^3
	Glutaraldehyde	28 μg/m^3 (for both peaks)
	Acetone	17 μg/m^3
Recovery:	η = 1.01 (101%)	
Sampling recommendation:	Sampling time:	1 h
	Sample volume:	6 L

Aldehydes

Aldehydes may cause irritation of the mucous membranes (see Method No. 1 "Aldehydes" in Volume 2). Longer chain aldehydes with chain lengths of C-5 and longer are increasingly being detected in indoor air. Sources for these are, for example, oil-based paints.

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Aldehydes (Formaldehyde, Acetaldehyde, Propionaldehyde, Butyraldehyde, Glutaraldehyde, Pentanal, Hexanal, Heptanal, Octanal, Nonanal)

Method number	2
Application	Ambient air analysis
Analytical principle	High performance liquid chromatography
Completed in	March 1995

Contents

1 General Principles

To determine the airborne aldehydes in working areas a measured volume of ambient air is drawn with a sampling pump through silica gel cartridges impregnated with 2,4-dinitrophenylhydrazine. The airborne aldehydes and ketones are transformed into the corresponding hydrazones [1, 2]. After desorption with acetonitrile, qualitative and quantitative determination is carried out by using HPLC.
Calibration curves determined by analysis of standard solutions are used for the quantitative evaluation; the aldehyde concentrations of the calibration standards are plotted versus the peak areas.

2 Equipment, chemicals and solutions

2.1 Equipment

High performance liquid chromatograph equipped with gradient control and injector, if necessary with autosampler
UV-detector able to measure at 365 nm and integrator
Steel column: length 25 cm, internal diameter 3.0 mm, stationary phase RP18, 5 µm
Flow-stabilized sampling pump, flow rate about 100 mL/min
Titrator with 50 mL burette (Schott Geräte GmbH) T 100 or disposable syringes
Laboratory balance, e.g. Mettler AT 200
5 mL and 100 mL volumetric flasks
2, 5, 10, 20 and 25 mL glass pipettes
Barometer
Thermometer
Cartridges for sampling: DNPH-SILICA CARTRIDGE (Millipore) WATERS SEP-PAK

2.2 Chemicals

Acetonitrile, analytical grade (e.g. Merck)
Triple-distilled water
Concentrated sulfuric acid 95–97%
Ethanol, analytical grade (e.g. Baker)
2,4-Dinitrophenylhydrazine (2,4-DNPH), analytical grade (e.g. Fluka)
Formaldehyde solution, analytical grade
Acetaldehyde, analytical grade (e.g. Merck)
Propionaldehyde, analytical grade (e.g. Merck)
Butyraldehyde, analytical grade (e.g. Merck)
Pentanal, analytical grade (e.g. Merck)
Hexanal, analytical grade (e.g. Merck)

Heptanal, analytical grade (e. g. Merck)
Octanal, analytical grade (e. g. Merck)
Nonanal, analytical grade (e. g. Merck)
Glutaraldehyde solution, 25 % in water (e. g. Fluka)

2.3 Calibration standards

If the calibration standards are not available commercially they have to be synthesized in the laboratory.

Preparation of 2,4-dinitrophenylhydrazones [3]
2 mL of concentrated sulfuric acid are added to 0.4 g of 2,4-dinitrophenylhydrazine. Afterwards 3 mL of water are added dropwise while stirring or shaking. 10 mL of 95 % ethanol are added to the warm solution. To prepare the 2,4-dinitrophenylhydrazone about 1 mL of a 10–20 % ethanolic solution of the carbonyl compound is added while shaking. Normally the hydrazone precipitates after 5–10 minutes (in a few cases the solution must be left over night). The precipitated 2,4-dinitrophenylhydrazone is sucked off, thoroughly washed with water and recrystallised twice from hot ethanol.
The individual stock solutions with defined concentrations of these derivatives are prepared. 10 mg of each of the derivatives are weighed, dissolved in acetonitrile and the solutions are diluted to 100 mL with acetonitrile. The resulting concentrations of the stock solutions are as follows:

Component	Weight of derivative mg/100 mL CH3CN	Factor (molecular weight of the component/ molecular weight of the derivative)	Weight of the component mg/100 mL CH3CN
Formaldehyde	10	0.143	1.43
Acetaldehyde	10	0.196	1.96
n-C3-Aldehyde	10	0.244	2.44
n-C4-Aldehyde	10	0.286	2.86
n-C5-Aldehyde	10	0.323	3.23
n-C6-Aldehyde	10	0.357	3.57
n-C7-Aldehyde	10	0.388	3.88
n-C8-Aldehyde	10	0.416	4.16
n-C9-Aldehyde	10	0.441	4.41
Acetone	10	0.244	2.44
Glutaraldehyde	10	0.357	3.57

Three calibration standards are prepared from these stock solutions. For this purpose aliquots of the stock solutions are transferred to 100 mL volumetric flasks and after filling up to the mark are diluted with acetonitrile in ratios of 1 : 5 and 1 : 20. The resulting concentrations (related to a 6 L ambient air sample) are as follows:

Component	Calibration standard 1		Aldehyde concentration in µg/m^3 for 6 L air (1013 hPa/20 °C)		
	Volume of the stock solution in mL/100 mL	Concentration in µg/5 mL eluate	Calibration standard 1 (undiluted)	Calibration standard 2 (dilution 1 : 5)	Calibration standard 3 (dilution 1 : 20)
Formaldehyde	25	17.875	2979	596	149
Acetaldehyde	10	9.800	1633	327	82
n-C3-Aldehyde	2	2.400	407	81	20
n-C4-Aldehyde	2	2.860	477	95	24
n-C5-Aldehyde	2	3.230	538	108	27
n-C6-Aldehyde	2	3.570	595	119	30
n-C7-Aldehyde	2	3.880	647	129	32
n-C8-Aldehyde	2	4.160	693	139	35
n-C9-Aldehyde	2	4.410	735	147	37
Acetone	5	6.100	1017	203	51
Glutaraldehyde	10	17.850	2975	595	149

3 Sample collection and preparation

With a flow-stabilized pump an air sample is drawn through the cartridge at a flow rate of 100 mL/min. The sampling volume normally is 6 L, but can differ if analyte-concentrations require it. After sampling, the filter holder is closed with suitable stoppers. Surrounding temperature and atmospheric pressure are registered.

Capacity and break through behavior of the cartridge have to be taken into account for correct sampling in order not to overload the adsorbent. The cartridge is eluted with acetonitrile into a 5 mL volumetric flask at an elution rate of about 1 mL/min.

As blank values are obtained with the cartridges used, two unloaded cartridges are analyzed to determine these values. The blank values are subtracted from the analytical result.

4 Operating conditions for high performance liquid chromatography

Column:	Material:	Steel
	Length:	25 cm
	Internal diameter:	3 mm
Detector:	UV-detector able to measure at 365 nm	
Stationary phase:	Kromasil 100 C18 5 µm	

Column temperature: Room temperature
Mobile phase: Eluent A: Triple-distilled water
Eluent B: Acetonitrile

Gradient program:

Step	Time (min)	Eluent B (%)	Gradient profile (see Fig. 2)
0	15	50	
1	2	50	
2	10	100	9.0
3	18	100	
4	3	50	1.0

Flow rate: 0.6 mL/min
Injection volume: 10 µL

Figure 1 shows a high performance liquid chromatogram of a calibration standard.

5 Analytical determination

10 µL of the sample solution prepared as described in Section 3 is injected and analyzed under the conditions stated.

6 Calibration

Volumes of 10 µL of each of the calibration standards (see Section 2.3) are injected and analyzed in the same way as the sample solutions. For each component the peak areas obtained are plotted against the corresponding weights.

7 Calculation of the analytical result

Using the peak areas calculated by an integrator the corresponding weight X in µg is read from the calibration curve. The concentration by weight ρ is calculated according to the following equation:

$$\rho = \frac{X}{(V_Z \cdot \eta)} \tag{1}$$

At 20 °C and 1013 hPa:

$$\rho_0 = \rho_X \frac{(273 + t)}{293} \cdot \frac{1013}{p_a}$$

where:

X	Weight of the analyte in the solution
Vz	Sample volume in L
η	Recovery rate
t	Temperature of the room air in °C
p_a	Atmospheric pressure in hPa
ρ	Airborne concentration of the analyte in mg/m^3
ρ_0	Airborne concentration of the analyte in mg/m^3 at 20 °C and 1013 hPa

8 Reliability of the method

8.1 Precision (formaldehyde)

Formaldehyde test gases were prepared using DYNACAL permeation tubes and air at three concentration levels was drawn through 6 silica gel cartridges in each case. Concentrations of 150, 600 and 1200 µg/m^3 for a 6 L sample volume and 5 mL of eluate were tested.

The sample volume was drawn through silica gel cartridges impregnated with DNPH then eluted and analyzed by comparison with external standards. The blank values were subtracted from the analytical results. This yielded relative standard deviations s_w of 5.0, 1.7 and 3.9%, and mean variations u of 11.9, 4.3 and 9.9% for the formaldehyde concentrations of 150, 600 and 1200 µg/m^3. According to DIN EN 482 the uncertainty associated with the analysis was 22.8% for 150 µg/m^3, 9.2% for 600 µg/m^3 and 8.6% for 1200 µg/m^3.

8.2 Detection limits

To determine the detection limit a just detectable concentration of a diluted calibration standard was analyzed six times. The following detection limits were obtained (for sample volumes of 6 L):

Formaldehyde	11 µg/m^3
Acetaldehyde	4 µg/m^3
Propionaldehyde	3 µg/m^3
Butyraldehyde	6 µg/m^3
Pentanal	11 µg/m^3
Hexanal	6 µg/m^3
Heptanal	15 µg/m^3

Octanal	11 µg/m^3
Nonanal	11 µg/m^3
Glutaraldehyde	28 µg/m^3 (for both peaks)
Acetone	17 µg/m^3

8.3 Recovery rate

At a flow rate of 100 mL/min the recovery rate for a 6 L air sample volume was 101% under the conditions described in Section 8.1.

8.4 Sources of error

Compounds such as acrolein, crotonaldehyde, benzaldehyde, and ketones (acetone, butanone-2, methyl isobutyl ketone etc.) are also derivatised with 2,4-DNPH. These derivatives must be separated from other derivatives in the chromatogram. If such simultaneously eluting peaks are present the gradient program must be optimized. Under the given chromatographic conditions in the range below 2 mg/m^3 interference from NO_2 as described in [4] could not be detected. The peaks which occurred eluted before the formaldehyde derivative.

9 Discussion

The method described permits the simultaneous determination of the named aldehydes and ketones taking into consideration the above mentioned sources of interference. If the collection conditions are suitable (e. g. 1.5 L/min, 60 L air sample volume, Desaga GS 312 pump) formaldehyde concentrations in the lower environmental concentration range can be detected.

Apparatus: High performance liquid chromatograph equipped with pump (LC-95), UV-detector (LC-95), autosampler (ISS 200), integrator (1020 LC Plus) from Perkin-Elmer, Überlingen, and steel column with Kromasil phase from MZ, Mainz.

10 References

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[2] *D. Wolf* and *J. U. Hahn*: Aldehyde. In: J. Angerer, A. Kettrup (Eds): Analytische Methoden zur Prüfung gesundheitsschädlicher Arbeitsstoffe. Band 1: Luftanalysen. VCH, Weinheim, 7th issue (1992)

[3] *Beyer, Walter*, Lehrbuch der organischen Chemie, 21.Auflage, Hirzel Verlag Stuttgart, 1988
[4] *U. Karst*, Interferences of nitrogen dioxide in the determination of aldehydes and ketones by sampling on 2,4-dinitrophenylhydrazine-coated solid sorbent. Fresenius J. Anal. Chem. 345, 48–52 (1993)

Authors: *P. Schmitz, M. Tschickardt*
Examiners: *W. Kleiböhmer, D. Pop*

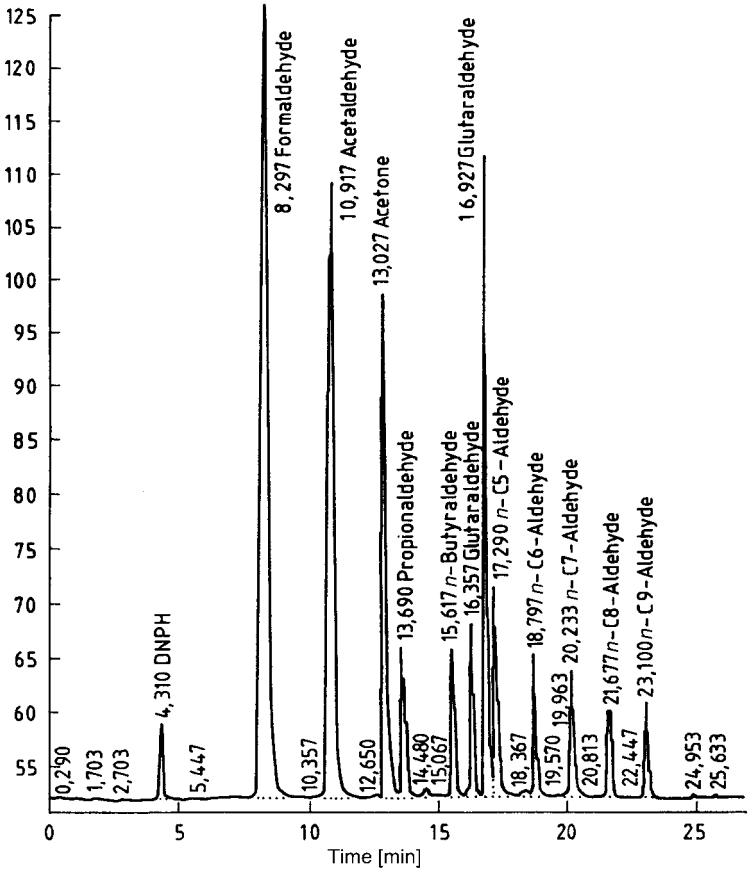

Fig. 1. High performance liquid chromatogram of a calibration standard.

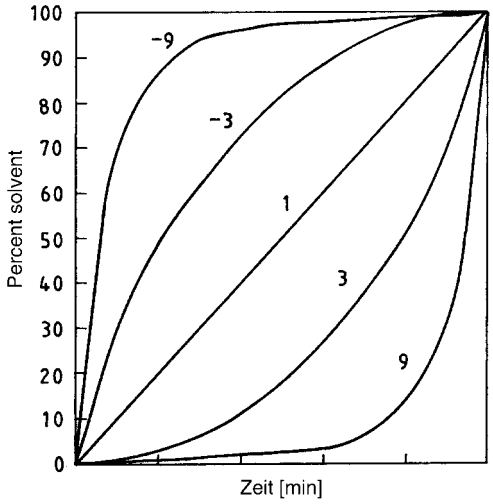

Fig. 2. Gradient profile of pump LC-250.

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Benzene

Method number 1

Application Air analysis

Analytical principle Gas chromatography

Completed in April 1995

Summary

To determine the benzene concentration in the air, measured air volumes are drawn with a pump through an adsorption tube containing activated carbon. The adsorbed benzene is eluted with carbon disulfide (CS_2) and separated from other hydrocarbons and air constituents by gas chromatography, and determined with a flame ionisation detector. Calibration standards are used for the quantitative evaluation. The peak areas of the calibration standards are plotted against the benzene concentrations.

Precision of the whole procedure:	Standard deviation (rel.)	s = 5.6%
	Mean variation	u = 12.5%
	for 10 activated carbon tubes each loaded with 14.2 µg of benzene	
Detection limit:	0.01 mL/m^3 of benzene in air (corresponding with 0.03 mg/m^3) for an air sample volume of 192 L	
Recovery:	η = 0.98	
Sampling recommendation:	Sampling time:	8 h
	Sample volume:	192 L

Benzene

Benzene is a colourless, inflammable liquid of low viscosity, with a characteristic smell.

In the past benzene was produced together with the so-called BTX aromatics (benzene, toluene and the three isomeric xylenes) by distillation from mineral coal and scrubbing of coke-oven gas. Increasing demand has led to the development of methods of production from crude oil. In the process of refining crude oil, during gasoline (petrol) re-

forming and cracking to produce olefins, fractions rich in aromatics are produced, which as reformate gasoline, pyrolysis gasoline and cracked gasoline are important sources for the production of benzene [1, 2].

Benzene is used as an additive in motor fuels (antiknock agent) and as a base material for the synthesis of many benzene derivatives, for example in the synthesis of aniline, nitrobenzene, styrene, synthetic rubber, plastics, phenol and pigments. Due to its carcinogenicity benzene is no longer used as a solvent [1].

Benzene is classified by the DFG Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area in Section III Category 1 for carcinogenic substances which may cause malignant tumours in man. The Committee for Hazardous Substances (AGS) has established a technical exposure limit (TRK value) of 1 and 2.5 mL/m^3 (1993) for benzene as a carcinogenic substance. Observance of the TRK value at the workplace is intended to reduce the risk of adverse effects on the health but it cannot be excluded completely.

Benzene has been proved to cause acute myeloid leukaemia. Increasingly other kinds of leukaemia, e. g. lymphatic leukaemia, are being considered to be the consequence of long-term exposure to benzene.

Benzene is carcinogenic, unlike its homologues, because in man it is oxidised at the aromatic nucleus during metabolism. The intermediate benzene epoxide is thought to be the ultimate carcinogenic agent because it can react covalently with DNA.

In the case of alkyl benzenes the aliphatic side-chain is oxidised and comparatively non-toxic aromatic carboxylic acids are formed. These compounds are excreted in the urine either as free carboxylic acid or bound to glycine.

Alkyl benzenes are oxidised at the aromatic nucleus to form alkyl phenols only to a small extent [3].

Further information on the toxicity and the metabolism of benzene and the other BTX aromatics can be found in recent monographs [3–10].

Benzene and its homologues are gaining in importance for environmental medicine because, as constituents of motor fuels, they are emitted during incomplete combustion with other exhaust gases [11]. Benzene and toluene have been detected in the atmosphere of urban areas [12–14]. At much used city crossroads benzene concentrations in the range of 30–165 $\mu g/m^3$ have been detected [15]. Other authors have arrived at similar results [16].

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Examiners: *E. Flammenkamp, A. Kettrup*

Benzene

Method number	1
Application	Air analysis
Analytical principle	Gas chromatography
Completed in	April 1995

Contents

1 General principles

To determine the benzene concentration in the air, measured air volumes are drawn with a pump through an adsorption tube containing activated carbon. The adsorbed benzene is eluted with carbon disulfide (CS_2) and separated from other hydrocarbons and air constituents by gas chromatography, and determined with a flame ionisation detector. Calibration standards are used for the quantitative evaluation. The peak areas of the calibration standards are plotted against the benzene concentrations (Fig. 1).

2 Equipment, chemicals and solutions

2.1 Equipment

Activated carbon tubes (e. g. Type B from Dräger)
Gas chromatograph equipped with flame ionisation detector
Flow meter or soap bubble meter (e. g. Supelco)
Barometer
Thermometer
20 mL Head-space vials with Teflon-coated butyl rubber caps
5 mL Syringe for gas chromatography (e. g. Hamilton)
10 mL Gastight syringe for transferring CS_2 onto the activated carbon (e. g. Hamilton)
Personal air sampler equipped with holder for adsorption tubes (e. g. battery-operated and with built-in counter, P 4000 from DuPont)
1 mL Flanged vials with Teflon-coated stoppers
Incubator, 110 °C

2.2 Chemicals

Carbon disulfide for the determination of volatile organic compounds (e. g. Baker)
Benzene, Uvasol Merck No. 1779

2.3 Solutions

Stock solution: To prepare the stock solution 50 µL of benzene is transferred to a 100 mL volumetric flask containing carbon disulfide and diluted to the mark with carbon disulfide. Before adding it to the stock solution the benzene is brought to 20 °C. The stock solution contains 440 mg of benzene per L of carbon disulfide.
From this stock solution calibration standards are prepared by diluting with carbon disulfide. They contain 0.22–44.0 mg/L of benzene.

Volume of the stock solution (mL)	Final volume of the calibration standard (mL)	Concentration of the calibration standard (mg/L)
0.05	100	0.22
0.1	100	0.44
0.2	100	0.88
0.4	100	1.76
1	100	4.40
2	100	8.80
4	100	17.6
10	100	44.0
20	100	88.0

3 Sample collection and preparation

For sampling at the workplace the adsorption tube is inserted into the holder of the personal air sampler. Then air from the room is drawn through the activated carbon for 8 hours at a flow rate of 0.4 L/min. After sampling the sample volume is noted. The temperatures and atmospheric pressures measured during sampling are noted. The closed tubes should be stored in a refrigerator until preparation.
For preparation the collection phase and the control phase are each transferred separately into a 20 mL flanged vial and closed immediately. With a gastight syringe 10 mL of carbon disulfide is injected through each of the butyl rubber stoppers. Then the vial contents are allowed to return to atmospheric pressure by letting air escape (e.g. using an injection needle). The flanged vials are allowed to stand for one hour with occasional shaking. About 500 µL of the CS_2 solution is then transferred to a 1 mL flanged vial and analysed by gas chromatography.
In each analysis series a reagent blank is prepared and analysed in the same way.

4 Operating conditions for gas chromatography

Column:	Material:	DB 5
	Length:	30 m
	Internal diameter:	0.32 mm
	Film thickness:	1.0 µm
Detector:	Flame ionisation detector	
Temperatures:	Column:	35 °C, 7 min, then 5 °C per minute to 110 °C, 10 min isothermal
	Injector block:	230 °C
	Detector:	300 °C
Carrier gas:	Purified nitrogen (column pressure 7 psi)	
Detector gas:	Compressed air (400 mL/min)	
	Hydrogen (30 mL/min)	
	Make-up gas	
Injected volume:	3 µL	
Split:	25 mL/min	

5 Analytical determination

With a 5 µL syringe 3 µL of the carbon disulfide solution is drawn from the organic phase and injected into the gas chromatograph under the operating conditions described above. After gas chromatographic separation of the benzene from the other components

collected on the activated carbon and eluted with carbon disulfide, the benzene is detected with the flame ionisation detector (Fig. 2).

6 Calibration

3 µL from each of the calibration standards (see Section 2.3) is injected into the gas chromatograph and detected with the flame ionisation detector. To draw the calibration curve, the measured peak areas minus the peak areas of the reagent blanks are plotted against the benzene concentrations (mg/L) used.
To compensate for possible instabilities in the calibration curve, especially during routine analysis over longer periods, and to avoid repeat preparation of the calibration curve, in each analysis series a calibration solution with a concentration of 4.40 mg/L of benzene in carbon disulfide is analysed as an external standard. If the concentrations of the calibration standards determined in the analysis series differ from the target value, the measured values for the unknown air samples must be corrected. If there are significant differences, the calibration curve must be checked by at least one additional measuring point.

7 Calculation of the analytical result

The peak area of the reagent blank is subtracted from the measured peak area. This value is used to read from the calibration curve the corresponding benzene concentration in mg/L of solution. If the benzene concentration of the control phase exceeds 10 % of the total benzene concentration (collection phase and control phase), breakthrough occurred. In this case sampling has to be repeated under changed conditions (e. g. a lower sampling volume). The concentration by weight ρ (mg of benzene per m^3 of air) in the sample air is calculated according to the following equation:

$$\rho = \frac{a \cdot b}{V_Z \cdot \eta}$$

At 20 °C and 1013 hPa:

$$\rho_0 = \rho \cdot \frac{273 + t}{293} \cdot \frac{1013\ \text{hPa}}{p}$$

The corresponding concentration by volume – independent of the variables pressure and temperature – is:

$$\sigma = \rho_0 \cdot \frac{24.1\ \text{L} \cdot \text{mole}^{-1}}{78.12\ \text{g} \cdot \text{mole}^{-1}} = \rho \cdot \frac{273 + t}{293} \cdot \frac{1013\ \text{hPa}}{p} \cdot \frac{24.1\ \text{L} \cdot \text{mole}^{-1}}{78.12\ \text{g} \cdot \text{mole}^{-1}}$$

$$\sigma = \rho \cdot \frac{273 + t}{p} \cdot 1.07 \cdot \frac{\text{hPa} \cdot \text{mL}}{\text{mg}}$$

At $t = 20\,^{\circ}\text{C}$ and $p = 1013$ hPa:

$$\sigma = \rho \cdot 0.309\ \frac{\text{mL}}{\text{mg}}$$

Legend:
- a Benzene concentration in carbon disulfide in mg/L taken from the calibration curve
- b Carbon disulfide volume in L used to elute the adsorbed benzene
- V_Z Sample volume in m^3
- η Recovery rate
- t Temperature of the ambient air in °C
- p Atmospheric pressure of the ambient air in hPa
- ρ Benzene concentration in the ambient air in mg/m^3 at t and ρ_0
- ρ_0 Benzene concentration in the ambient air in mg/m^3 at 20 °C and 1013 hPa
- σ Benzene concentration in the ambient air in mL/m^3

8 Reliability of the method

8.1 Accuracy

The accuracy of the method was checked by participating in the collaborative study included in the BCR project "Workplace air sampling" at the VITO (November 19th–21st) in Mol (Belgium). The results were as follows:

Target value	Benzene concentration Value obtained ($n = 6$)	Accuracy
0.165 ppm	0.167 ppm	101.2%
0.453 ppm	0.440 ppm	97.1%
1.790 ppm	1.797 ppm	100.4%

8.2 Precision

To determine the precision 10 activated carbon tubes were each loaded with 14.2 µg of benzene and then prepared. The standard deviation (rel.) was $s = 5.6\%$ and the mean variation was $u = 12.5\%$

8.3 Recovery rate

The method was checked by loading activated carbon tubes with measured amounts of 20–100 µg of benzene. A mean recovery rate of $\eta = 0.98$ was obtained.

8.4 Detection limit

Under the given analytical conditions the detection limit of the method was 0.01 mL/m^3 (ppm corresponding to 0.03 mg/m^3) determined from three times the standard deviation of the reagent blank.

9 Discussion of the method

Compared to spot checks of the ambient air e. g. using gas collection tubes, the method described has the following advantages: by using an adsorption phase this method permits longer averaging times. Therefore average values covering longer observation times can be calculated from a smaller number of samples. In addition, very low benzene concentrations, e. g. as occur in the environment, can be reliably determined.
Due to the good separation properties of the gas chromatographic column, the method is sufficiently selective to be able to separate ubiquitous aliphatic hydrocarbons from benzene even in the environmental concentration range.
The carbon disulfide used as an elution agent must be free from benzene. Many firms do not offer carbon disulfide free from benzene. During the development of this method the best experience was with the carbon disulfide "for the determination of volatile organic compounds" from Baker.
Furthermore the head-space vials or flanged vials, and the Teflon-coated butyl rubber stoppers must be heated before use. The heating time should be three days at 110 °C in a drying cupboard. As a result of heating, the traces of benzene in the butyl rubber stoppers or on the glass walls are volatilised.
To check the accuracy of the method it is possible to participate in the collaborative studies regularly held by the Occupational Safety Institute (BIA). Soon reference material (CRM 562) will be offered in the EU.
Under laboratory conditions (fume cupboard) no damage to health is to be expected as a result of the use of carbon disulfide as an elution agent.

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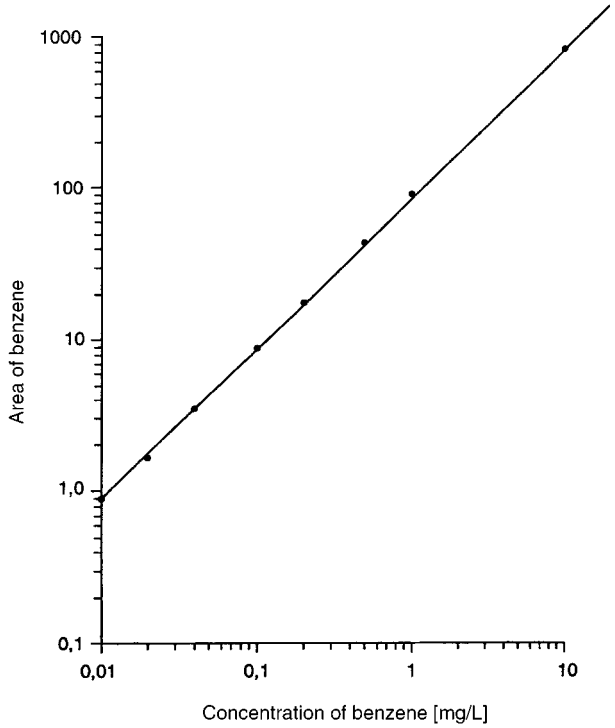

Fig. 1. Example of a calibration curve.

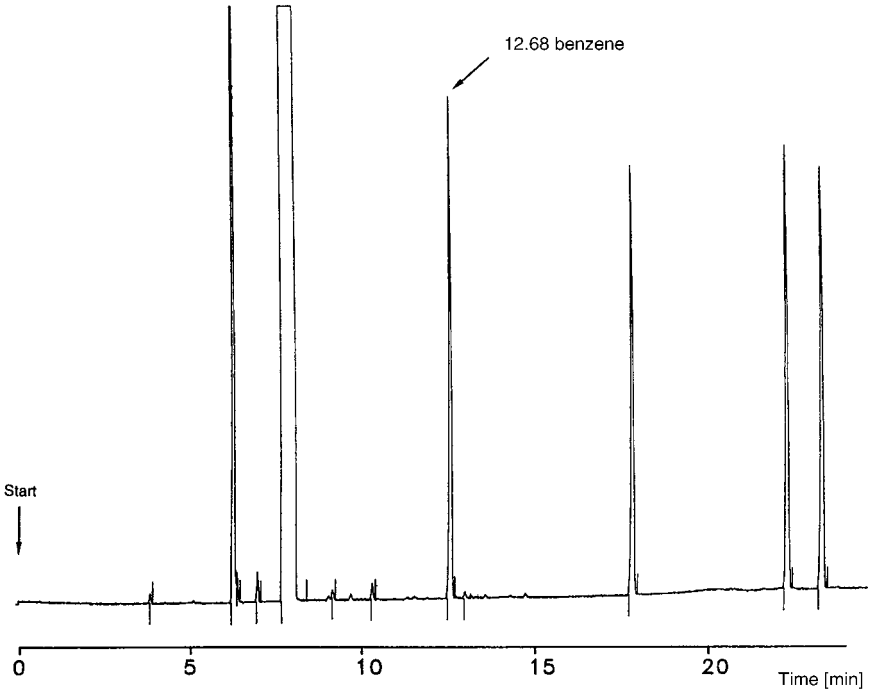

Fig. 2. Gas chromatogram of a benzene determination.

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Alte Heerstraße 111, 53757 Sankt Augustin
Expert Committee Chemistry

Carcinogenic substances Order number: BGI 505-6E
Established methods Issue: July 1997

Method for the determination of bis(chloromethyl)ether (BCME) (1,1′-dichlorodimethyl ether)

Method tested and recommended by the Berufsgenossenschaften for the determination of BCME in working areas after discontinuous sampling:

1 Sampling with a pump and adsorption on Porapak Q,
gas chromatography after desorption.
(Issue: December 1983, withdrawn July 1997)

2 Sampling with a pump, adsorption on Tenax-TA, thermal desorption,
gas chromatography and mass-selective detection.
"BCME-2-ATD-GC-ITD"
(Issue: July 1997)

This procedure replaces method No 1.

IUPAC name:
oxybis(chloromethane)
bis(chloromethyl)ether

CAS No:
542-88-1

Molecular weight:
M(BCME) = 115 g/mol

Molecular formula:
$C_2H_4OCl_2$

2 Sampling with a pump, adsorption on Tenax-TA, thermal desorption, gas chromatography and mass-selective detection

This method permits the determination of bis(chloromethyl)ether (BCME) concentrations in working areas averaged over the sampling time after personal or stationary sampling.

Principle: With a pump a measured air volume is drawn through a Tenax-TA adsorption tube spiked with methyl isobutyl ketone (MIBK) as internal standard. Adsorbed BCME is thermally desorbed together with the internal standard, separated with a gas chromatograph and the masses determined using an ion trap detector (ITD). Sampling and analytical determination are controlled by means of the internal standard, MIBK.

Technical data:

Quantification limit: absolute: 1 ng BCME per adsorption tube.
relative: 0.33 µg/m^3 BCME for 3 L air sample corresponding to 0.07 µL/m^3 (ppb).

Selectivity: The procedure is highly selective due to the combination of gas chromatographic separation and mass-selective detection. In practice the use of the given analytical column and the ion mass *m/z* 79 for detection of BCME has proved reliable [1, 3].

Advantages: Highly selective with a low quantification limit.

Disadvantages: Concentration peaks not recorded, sophisticated equipment needed.

Apparatus: Pump,
gas meter or flow meter,
adsorption tubes for automatic thermal desorption,
combined automatic thermal desorber (ATD),
gas chromatograph (GC) with capillary column and ion trap detector (ITD).

Comments: The sophisticated measuring technique used in this procedure requires a great deal of practical experience with methods of sampling and analysis. During calibration, it is necessary to handle BCME. Because of the high toxicity of BCME, appropriate safety precautions must be taken [2].

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling and preparation:

Membrane pump with adjustable flow rate in the range between 0.005 and 0.05 L/min (e. g. PP1 from Gilian (supplier in Germany: GSM GmbH, Neuss-Norf))

Gas meter or digital flow meter for the set pump range (e. g. from Analyt GmbH, Müllheim)

Adsorption tubes made of glass or steel, standardised for automatic thermal desorption (e. g. from Perkin Elmer, Ueberlingen)
- Length: 90 mm
- External diameter: 6.35 mm (1/4″)
- Filling: 100 mg adsorbent

Caps for transport and storage of the adsorption tubes

Sampling caps

Cap with a borehole of 2 mm diameter for injecting the calibration gas

Tenax adsorbent as filling for the adsorption tubes (e.g. Tenax-TA 60/80 mesh, from Chrompack, Frankfurt/Main)
5 mL and 20 mL Graduated gas-injection syringes
10 µL Microlitre syringe
1000 mL and 200 mL Gas pipettes made of glass, with two spindle stopcocks facing each other made of polytetrafluoroethylene (PTFE) or a device for sampling the gas via a sampling port sealed with a PTFE coated septum

For sample preparation and analysis:
Personal environment chamber made of glass or transparent plastic with good visibility and with sufficient exhaust air flow, equipped with flanged hand holes which allow work to be carried out with protective gloves to be attached with an airtight seal or while wearing protective gloves.
Combined automatic thermal desorber (ATD), gas chromatograph with ion trap detector (ITD) and control unit and data analysis device
25 mL Beaded rim glass with PTFE septum and aluminium crimp cap
Crimper and opening tongs
Analytical balance with 0.01 mg readability

1.2 Chemicals

Bis(chloromethyl)ether (BCME)
Methyl isobutyl ketone (MIBK), internal standard, purity >99.5%
Gas for producing the calibration gases: dry nitrogen, purity 99.996%
Gas for operating the analytical apparatus: helium, purity 99.9999%

1.3 Calibration gases

MIBK stock gas:
Gas mixture containing 4.75 µg/mL MIBK.
5 µL of MIBK, density 0.95 kg/L, corresponding to 4.75 mg of MIBK, is injected into a dry evacuated 1000 mL gas pipette which is then filled with dry nitrogen.

MIBK calibration gas:
Gas mixture containing 9.5 ng/mL MIBK (sampling standard, internal standard).
With a 5 mL gas syringe 2 mL of MIBK stock gas (for example) is diluted in a dry evacuated 1000 mL gas pipette as described above. The MIBK concentration in this gas pipette is then 9.5 ng/mL.
1 mL of this calibration gas – applied to an adsorption tube and then analysed – produces a signal corresponding to ten times the quantification limit of MIBK in air for an air sample volume of 3 L, i.e. a concentration of 3.2 $\mu g/m^3$ or 0.66 $\mu L/m^3$ (ppb) MIBK.

BCME stock gas:
Gas mixture containing 6.58 µg/mL BCME.

Taking the necessary precautions 5 µL of BCME, density 1.315 kg/L, corresponding to 6.58 mg BCME, are injected with a microlitre syringe into a dry evacuated 1000 mL gas pipette which is then filled with dry nitrogen.

BCME calibration gas:
Gas mixture containing 13.2 ng/mL; 1.3 ng/mL BCME.
With a 5 mL gas syringe 2 mL of BCME stock gas (for example) is diluted in a dry evacuated 1000 mL gas pipette as described above. The BCME concentration in this gas pipette is then 13.2 ng/mL. With a 20 mL gas syringe 20 mL (for example) of the BCME calibration gas produced is diluted in a dry evacuated 200 mL gas pipette as described above. The BCME concentration in this gas pipette is then 1.3 ng/mL. 1 mL of each of the calibration gases – applied to adsorption tubes and then analysed – produces signals corresponding to the quantification limit and ten times the quantification limit of BCME in air for an air sample volume of 3 L, i.e. the calibration concentration range covered is 4.3 µg/m^3 or 1 µL/m^3 (ppb) to 0.43 µg/m^3 or 0.1 µL/m^3 (ppb) BCME.

2 Sampling

2.1 Sample preparation

Pre-cleaning using thermal desorption:
An adsorption tube is heated in a thermal desorption unit not more than 24 hours before use so that under analytical conditions no evidence can be detected of contamination with impurities which interfere with the analysis of BCME. The tube is placed in a thermal desorber and heated for 10 minutes at 150 °C.
The adsorption tube is then closed with caps which have been freshly heated in a vacuum drying cabinet for 24 hours at 40 °C under vacuum (e.g. 0.01 bar).

Checking the blank value:
The blank value is checked taking into consideration any blank value from the blank value mass chromatogramme, obtained by treating the same adsorption tube – after thermal pre-cleaning and before adding the internal standard – like a sample for analytical determination (cf. Sect. 3.2).

Note: This procedure is necessary for significantly loaded adsorption tubes before these can be used again for sampling. For adsorption tubes freshly filled with Tenax-TA, the procedure may have to be repeated several times. For adsorption tubes that have been used before, use of the heating procedure described above after the analytical determination is generally sufficient to obtain an adsorption tube free of a blank value.

Applying the sampling standards:
The caps are removed from the adsorption tube in the laboratory immediately before sampling. The adsorption tube is then connected to a membrane pump set at a flow rate of about 0.05 L/min. The adsorption tube is then connected directly on the inlet side to an empty adsorption tube (pre-tube), which is closed with a cap with a borehole

of 2 mm in diameter. The pump is started. With an injection syringe 1 mL of MIBK calibration gas (cf. Sect. 1.3) is then slowly injected into the pre-tube through the cap – as far as the injection needle reaches – within about 15 to 30 seconds. The pump should be allowed to run for at least one minute more. The tubes are then separated and the filled adsorption tube closed again with the caps.

2.2 Implementation

The membrane pump is set using a flow meter to a flow rate of about 0.015 L/min. The adsorption tube is connected to the membrane pump after removing the caps and fixed in the breathing area of a person or placed stationary at the sampling site. After sampling, the adsorption tube is closed with the caps and immediately analysed.

3 Analytical determination

3.1 Sample preparation and analysis

The tube is placed in the automatic thermal desorber and then analysed.
Recovery (function test):
To check that recovery of the sampling standard MIBK is sufficient and that the condition of the analytical system meets the requirements of the method with regard to sensitivity and the blank value, three adsorption tubes per sampling series, prepared for sampling but without an air load, are subjected to analytical determination (cf. Sect. 3.2).

3.2 Operating conditions

The method was characterized under the following experimental conditions:

Apparatus:	Combined automatic thermal desorber ATD 400 from Perkin Elmer, gas chromatograph 3400 from Varian and ion trap detector ITD 800 from Finnigan, control device or computer with quantification programme for the ion trap detector

Operating conditions for the thermal desorber ATD 400:

Temperatures and times:		
Desorption oven:	Desorption temperature:	150 °C
	Desorption time:	15 min
Cold trap:	Low temperature:	–25 °C
	High temperature:	150 °C
	Heating mode:	trap fast heat (40 ° C/s)

Transfer line:	Temperature:	150 °C
Carrier gas:	Helium, 90 kPa	
Desorption flow:	10 mL/min	
Inlet split mode:	"off"	
Outlet split:	3 mL/min	

Operating conditions for gas chromatography:

Column:	Material:	Quartz capillary
	Stationary phase:	OV 1 (methyl silicon) e. g. from Macherey-Nagel
	Film thickness:	1.02 µm
	Length:	50 m
	Internal diameter:	0.32 mm
	Temperatures and times:	
Furnace temperature programme:		
	Initial temperature:	40 °C
	Hold time 1:	4 min
	Temperature programme:	10 °C/min
	Final temperature:	150 °C
	Hold time 2:	5 min

Operating conditions for the ion trap detector:

Recording mode:	full scan
Mass range:	40–200 amu
Scan duration:	1 s
Recorded ions:	*m/z* 79, *m/z* 81, *m/z* 49 for BCME *m/z* 43, *m/z* 58 for MIBK (sampling standard, internal standard)

4 Evaluation

4.1 Calibration

The ion mass *m/z* 79 is used for the quantitative determination of BCME [4, 5]. The accompanying ion mass *m/z* 81 serves as a control; because of the chlorine isotope ratio, it occurs at a third of the intensity of the ion mass *m/z* 79. If this is not the case, interfering components prevent the determination of BCME. If necessary the fragment yielding an ion mass *m/z* 49 can be used. The ion mass *m/z* 49, the intensity of which is like that of *m/z* 79, often has a better signal:noise ratio. The quantification limit does not change significantly when this alternative ion is used. The MIBK ion mass *m/z* 43 is evaluated as internal standard. The accompanying mass *m/z* 58 serves as a control; its intensity must be about 25% of that of the ion mass *m/z* 43. If this is not the case, interfering components prevent the determination of MIBK.

The calibration curve, determined using the most intensive ion masses in the mass spectrum, *m/z* 79 for BCME and *m/z* 43 for MIBK, corresponding to the quantification limit for BCME, ten times the quantification limit and one hundred times the quantification limit, is not linear. In practice, however, the concentration range to be checked is sufficiently linear between the calibration point at the quantification limit and the one at ten times the quantification limit.

For each of the selected calibration gas concentrations, six adsorption tubes are each loaded with 1 mL of BCME calibration gas and additionally with 1 mL of MIBK calibration gas (cf. Sect. 2.1), closed with caps and placed in the autosampler of the thermal desorber. These calibration tubes are analysed under the operating conditions given in Section 3. For each calibration gas concentration, the selected calibration ion masses for BCME and MIBK are recorded automatically and the peak areas calculated. To determine the calibration factors the mean values of the six individual determinations are used.

The calibration factor is determined using the peak areas calculated for BCME and the internal standard MIBK according to Equation (1):

$$f = \frac{F_{isc} \cdot w}{F_c \cdot w_{is}} \tag{1}$$

Legend:

f Calibration factor for BCME

F_c Peak area of the BCME ion mass *m/z* 79 in the mass chromatogramme of the calibration tube

F_{isc} Peak area of the MIBK ion mass *m/z* 43 in the mass chromatogramme of the calibration tube

w Weight of BCME contained in 1 mL of calibration gas

w_{is} Weight of MIBK contained in 1 mL of calibration gas

If the calibration factors for the two BCME calibration masses differ by less than 10 %, the mean value can be used. With a difference of > 10 % but < 30 % linear interpolation within the analytical range is permissible. Greater differences indicate faulty equipment and require that this be checked.

Recovery of the sampling standard MIBK:

The recovery rate is calculated using the standardised peak area of MIBK from the analysis of the control tube included in a sample series (cf. Sect. 3.1) and the standardised peak area of MIBK from the analysis of a sample tube according to Equation (2):

$$\eta = \frac{F_{is}}{F_{ctr}} \tag{2}$$

Legend:

η Recovery rate

F_{is} Peak area of the MIBK ion mass *m/z* 43 in the mass chromatogramme of the sample tube (cf. Sect. 4.2)

F_{ctr} Peak area of the MIBK ion mass *m/z* 43 in the mass chromatogramme of the control tube

Recovery rate of MIBK serves as a qualitative control of the sampling procedure. It should be at least 0.5. Low recovery rate indicates problems during sampling.

4.2 Calculation of the analytical result

The concentration by weight of BCME in $\mu g/m^3$ is calculated according to Equation (3):

$$c_w = \frac{F \cdot w_{is} \cdot \bar{f}}{F_{is} \cdot V} \tag{3}$$

The concentration by volume c_v in mL/m^3 for 20 °C and 1013 hPa is calculated according to Equation (4):

$$c_v = 0.21 \cdot c_w \tag{4}$$

Legend:

c_w Concentration by weight of BCME in the air sample in $\mu g/m^3$
c_v Concentration by volume of BCME in the air sample in $\mu L/m^3$ (ppb)
F Peak area of the BCME ion mass *m/z* 79 in the mass chromatogramme of the sample tube
F_{is} Peak area of the MIBK ion mass *m/z* 43 in the mass chromatogramme of the sample tube
$\bar{f}$ Mean calibration factor for BCME
w_{is} Weight of MIBK (sampling standard, internal standard) in the sample tube in ng
V Air sample volume in L

5 Reliability of the method

5.1 Accuracy and recovery

As described in Sect. 4.1 on the determination of the calibration factors, six adsorption tubes were each loaded with 1 mL of one of the selected concentrations of BCME calibration gas and additionally with 1 mL of the MIBK calibration gas. Then under sampling conditions 3 L of laboratory air were drawn through each of the adsorption tubes. The adsorption tubes were analysed under the conditions described in Sect. 3. The weights of adsorbed BCME corresponded with the quantification limit and ten times the quantification limit. Carrying out the described procedure six times yielded relative standard deviations of $< 15\%$ in each case. Under the conditions described in Sect. 3.2 the recovery rate was over 0.9 in each case.

5.2 Quantification limit

The absolute quantification limit under analytical conditions is 1 ng of BCME per adsorption tube. For a 3 L air sample this corresponds to a relative quantification limit of 0.33 µg/m^3 BCME or 0.07 µL/m^3 (ppb) BCME.

5.3 Selectivity

The combination of gas chromatographic separation and mass-selective detection makes the procedure very selective. The use of the recommended column and the ion mass *m/z* 79 to detect BCME have proved reliable [1, 3].

6 Discussion

To determine the maximum volume of sample air, experiments were carried out in which up to 10 L of laboratory air were drawn through adsorption tubes loaded with BCME and MIBK. With air samples up to 3 L no BCME losses were detected. For air sample volumes of 5 L recovery was over 0.85, but the number of tubes in which losses occurred increased markedly from air samples of 5 L and more. This is because the variation in the hardness and homogeneity of the Tenax-TA filling cannot be kept within very narrow limits. It is therefore recommended that adsorption tubes be tested and selected according to their BCME retention capacity.

7 Chromatogrammes and spectra

The three figures shown below are all from the same analytical run with a real sample. The concentration measured corresponds to twice the quantification limit for BCME.
The top figure contains the total ion current chromatogramme and the mass chromatogrammes of the ion masses *m/z* 43 and *m/z* 58 for the internal standard MIBK.
The figure in the middle contains the mass chromatogrammes of the ion masses *m/z* 79, *m/z* 81, and *m/z* 49 for BCME.
The figure at the bottom contains the mass spectrum registered at the maximum of the BCME peak after background subtraction.

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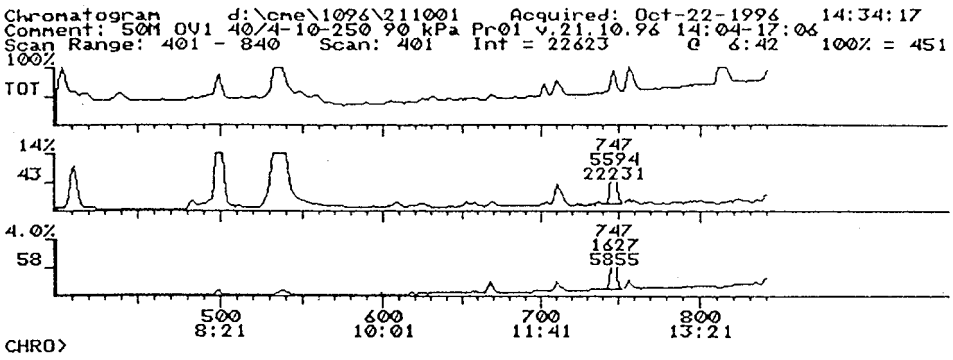
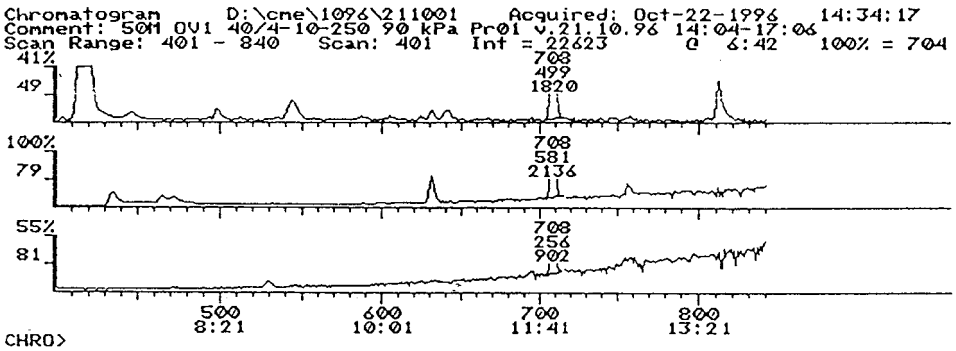
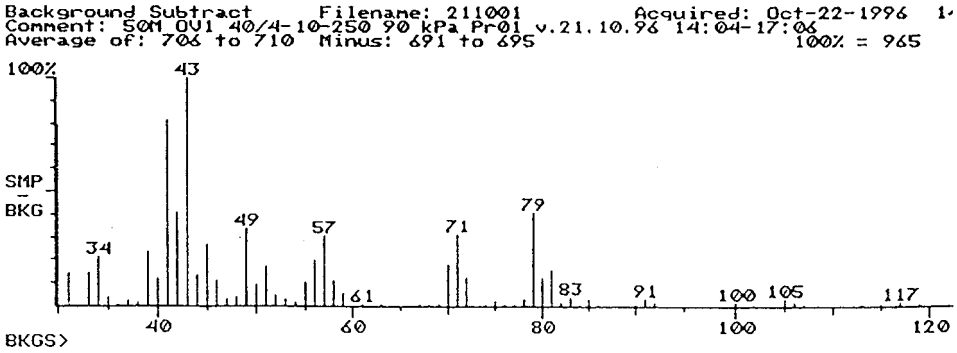
Appendix: Chromatograms and Spectra







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Carcinogenic substances Order number: BGI 505-59E
Established methods Issue: December 1996

Method for the determination of α-chlorotoluene

Method tested and recommended by the Berufsgenossenschaften for the determination of α-chlorotoluene (benzyl chloride) 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 adsorption on Tenax, gas chromatography after desorption.
"α-Chlorotoluene-1-GC"
(Issue: December 1996)

IUPAC name:	**CAS No:**
α-chlorotoluene	100-44-7

1 Sampling with a pump and adsorption on Tenax, gas chromatography after desorption

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

Principle: With a pump a measured air volume is drawn through a Tenax tube. The adsorbed α-chlorotoluene is then desorbed with *n*-hexane and determined by gas chromatography.

Technical data:

Quantification limit: absolute: 0.5 ng α-chlorotoluene,
relative: 0.01 mg/m^3 α-chlorotoluene for 48 L air sample, 1 mL desorption solution and 1 µL injection volume.

Selectivity: Interfering components may cause too high values. In general, interferences can be eliminated by selecting a column with different separating characteristics.

Advantages: Both personal and selective sampling are possible.

Disadvantages: No indication of concentration peaks.

Apparatus: Pump,
gas meter or flow meter,
Tenax tubes,
gas chromatograph (GC) with flame ionisation detector (FID).

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:

Pump, suitable for a flow rate of 100 mL/min (e.g. PP1 from Gilian, supplier in Germany: DEHA-Haan & Wittmer GmbH, 71288 Friolzheim)

Gas meter or flow meter

Adsorption tubes with Tenax, standardised, consisting of two Tenax fillings of about 50 mg and 100 mg separated with glass wool (e.g. Catalogue No 226-35-03 from SKC, supplier in Germany: MTC-GmbH, Müllheim)

Caps for the opened Tenax tubes

For sample preparation and analysis:

2 mL Beaded rim vials with polytetrafluoroethylene (PTFE)-coated septa and crimp caps

Crimper

Shaking machine

50 mL Volumetric flask

0.2, 0.5, 1, 2 and 5 mL Pipettes

10 and 50 µL Injection syringes

Gas chromatograph with FID
Data analysis device

1.2 Chemicals

n-Hexane, purity at least 99%, water-free
α-Chlorotoluene, purity at least 99%
Gases for operating the gas chromatograph: Helium, purity 99.995%
Hydrogen, purity 99.995%
Synthetic air, free from hydrocarbons

1.3 Solutions

α-Chlorotoluene stock solution:
Solution of 10 mg/mL α-chlorotoluene in *n*-hexane.
Approx. 500 mg of α-chlorotoluene is weighed into a 50 mL volumetric flask to the nearest 0.1 mg. The volumetric flask is filled to the mark with *n*-hexane.

Calibration solutions:
Solutions of 1.0 µg/mL, 4 µg/mL, 10 µg/mL, 40 µg/mL, 0.1 mg/mL, 0.4 mg/mL and 1 mg/mL of α-chlorotoluene in *n*-hexane.
5 µL, 20 µL, 50µL, 0.2 mL, 0.5 mL, 2 mL and 5 mL of the α-chlorotoluene stock solution are each transferred to 50 mL volumetric flasks already containing about 10 mL of *n*-hexane. The volumetric flasks are filled to the mark with *n*-hexane.
With these solutions and an air sample volume of 48 L and 1 mL of desorption solution a concentration range of 21 µg/m^3 to 21 mg/m^3 α-chlorotoluene in air is covered.

2 Sampling

The flow rate of the pump is set to a maximum of 100 mL/min. With sampling for 8 hours this corresponds to a maximum air sample volume of 48 L. A Tenax tube is opened and connected to the pump. During working hours the pump and tube are worn by a person or used in a stationary position. After sampling, the tube is closed with caps.

3 Analytical determination

3.1 Sample preparation and analysis

The contents of the loaded Tenax tube are transferred to a 2 mL beaded rim vial and 1 mL of *n*–hexane is added. The beaded rim vial is closed and shaken for 30 minutes. 1 µL of the supernatant solution (desorption solution) is injected into the gas chromatograph.
To ensure that the desorption solvent and the Tenax tube do not contain any impurities, the filling of an unloaded Tenax tube is treated with 1 mL of *n*-hexane (blank solution). 1 µL of the blank solution is injected into the gas chromatograph.

3.2 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Gas chromatograph, Hewlett-Packard 5890 with FID	
Column:	Material:	Quartz capillary
	Length:	50 m
	Internal diameter:	0.32 mm
	Stationary phase:	SE 54
	Film thickness:	0.5 µm
Temperatures:	Injector:	200 °C
	Detector:	300 °C
	Furnace temperature programme:	
	Starting temperature:	60 °C, 2 min isothermal
	Heating rate:	10 °C/min
	Final temperature:	280 °C
Injection mode:	Splitless, 0.5 min	
Carrier gas:	Helium, approx. 2.5 mL/min	
Detector gases:	Hydrogen, 35 mL/min	
	Air, 400 mL/min	
Make-up gas:	Helium, 15 mL/min	
Injection volume:	1 µL	

4 Evaluation

4.1 Calibration

1 mL of each of the calibration solutions described in Sect. 1.3 are added to the contents of an unloaded Tenax tube in beaded rim vials and analysed as described in Sect. 3.1.

The calibration curve is obtained by plotting the measured peak areas or peak heights against the α-chlorotoluene weights contained in the various calibration solutions. The calibration curve is linear in the given concentration range.

4.2 Calculation of the analytical result

Quantitative evaluation of the chromatogrammes is carried out according to the external standard method. The concentration by weight c_w in the air sample in mg/m^3 is calculated according to Equation (1):

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

The concentration by volume c_v in mL/m^3 calculated from c_w for 20 °C and 1013 hPa is:

$$c_v = 0.19 \cdot c_w \tag{2}$$

Legend:
c_w Concentration by weight of α-chlorotoluene in the air sample in mg/m^3
c_v Concentration by volume of α-chlorotoluene in the air sample in mL/m^3
w Weight of α-chlorotoluene in the desorption solution in µg
V Air sample volume in L
η Recovery rate

5 Reliability of the method

5.1 Accuracy and recovery

To determine the relative standard deviation of the method, different weights of α-chlorotoluene were each loaded onto six Tenax tubes by means of a syringe. Six tubes were prepared with 0.5 µL of the calibration solution with the highest concentration, 0.5 µL stock solution and 1 µL stock solution. Under the sampling conditions described in Sect. 2, 48 L of air were drawn through each of the tubes. The tubes were then analysed. This loading corresponded to air sample concentrations of 0.01, 0.1 and 0.2 mg/m^3 α-chlorotoluene.
Under the given conditions the 6 independent measurements yielded the relative standard deviations and recoveries listed in Table 1.

Table 1. Standard deviation (rel.) *s* and recovery rate.

Concentration mg/m^3	Standard deviation (rel.) *s* %	Recovery rate
0.01	6.9	0.91
0.1	2.3	0.85
0.2	7.5	0.87

5.2 Quantification limit

The absolute quantification limit is 0.5 ng of α-chlorotoluene. It was determined from the signal noise ratio of the chromatogrammes.
The relative quantification limit is 0.01 mg/m^3 α-chlorotoluene for a 48 L air sample, 1 mL desorption solution and a 1 µL injection volume.

5.3 Selectivity

The selectivity of the method depends on the type of column used. In practice the given column has proved reliable. In case of interfering components, a column with other separation characteristics should be used.

6 Discussion

As the quality of the Tenax tubes varies greatly, the blank value of each Tenax tube used should always be checked.
The loaded tubes can be stored at 5–7 °C for at least 7 days without any loss of adsorbed α–chlorotoluene.
The stock solution and calibration solutions must be freshly prepared each day due to the sensitivity of α-chlorotoluene to hydrolysis.

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Expert Committee Chemistry

Carcinogenic substances Order number: BGI 505-63E
Established methods Issue: December 1998

Method for the determination of 1,5-diaminonaphthalene

Method tested and recommended by the Berufsgenossenschaften for the determination of 1,5-diaminonaphthalene 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 adsorption on an impregnated filter,
high performance liquid chromatography (HPLC) after desorption.
"1,5-diaminonaphthalene-1-HPLC"
(Issue: December 1998)

IUPAC name:
1,5-diaminonaphthalene, 1,5-naphthalenediamine

CAS No:
2243-62-1

Molecular weight:
158.20 g/mol

Molecular formula:
$C_{10}H_{10}N_2$

1 Sampling with a pump and adsorption on a filter, HPLC after desorption

This method permits the determination of 1,5-diaminonaphthalene concentrations in working areas averaged over the sampling time after personal or stationary sampling.

Principle: With a pump a measured air volume is drawn through a glass fibre filter impregnated with hydrochloric acid as stipulated in the definition of inhalable dust fraction [1]. The adsorbed 1,5-diaminonaphthalene is desorbed with a mixture of acetonitrile and aqueous ammonia and analysed by means of high performance liquid chromatography (HPLC).

Technical data:

Quantification limit: absolute: 20 ng 1,5-diaminonaphthalene,
relative: 0.016 mg/m^3 1,5-diaminonaphthalene for 500 L air sample, 5 mL desorbate (dilution in the ratio 1 : 1 v/v) and 25 µL injection volume.

Selectivity: Interfering components may cause too high values. In general, interferences can be eliminated by selecting different chromatography conditions.

Advantages: Both personal and selective sampling are possible.

Disadvantages: No indication of concentration peaks.

Apparatus: Pump,
gas meter or flow meter,
glass fibre filter impregnated with hydrochloric acid,
filter holder,
HPLC apparatus equipped with UV/VIS-detector.

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:
Pump, suitable for a flow rate of 2 L/min (e.g. PP5 ex from Gilian, supplier in Germany: DEHA-Haan & Wittmer GmbH, 71288 Friolzheim)
Gas meter or flow meter
Filter holder (e.g. aerosol monitor, Catalogue No. M000 037 AO from Millipore, 65731 Eschborn)
Glass fibre filter, diameter 37 mm (e.g. No. 9 from Schleicher & Schüll, 37582 Dassel)

For sample preparation and analysis:
10, 25 and 50 mL Volumetric flasks
Adjustable pipettes, suitable for delivering 5 µL to 5 mL (e.g. Pipetman P from Abimed, 40736 Langenfeld)
20 mL Sample vials, amber
PTFE syringe prefilter (e.g. Millex FG13, 0.2 µm pore size from Millipore)
2 mL Disposable syringes

HPLC apparatus equipped with UV/VIS-detector
Data analysis device
Water-purification unit (e. g. Nanopure II from Barnsteadt, supplier in Germany: Wilhelm Werner GmbH, 51381 Leverkusen)
10 mL Glass vessels with snap-on caps, amber
Ultrasonic bath
Shaker (e. g. MTS 4 from IKA, 79219 Staufen)

1.2 Chemicals

1,5-Diaminonaphthalene, purity 97% (e. g. from Aldrich, 89552 Steinheim)
Aqueous ammonia, 25%, analytical grade (e. g. from Merck, 64271 Darmstadt)
Hydrochloric acid, 32%, analytical grade (e. g. from Merck, 64271 Darmstadt)

For HPLC:
Ultra pure water (e. g. prepared with the Nanopure II (UHQ water))
Acetonitrile, LiChrosolv (e. g. from Merck, 64271 Darmstadt)

1.3 Solutions

Desorption solution:
Mixture of 92 parts by volume of acetonitrile and 8 parts by volume of aqueous ammonia.

Solvent mixture 1:
Mixture of acetonitrile/water (1 : 1 v/v).

Solvent mixture 2:
Mixture of 96 parts by volume of solvent mixture 1 and 8 parts by volume of aqueous ammonia.

Stock solution:
Solution of about 1 mg of 1,5-diaminonaphthalene per millilitre solvent mixture 2.
About 25 mg of 1,5-diaminonaphthalene is weighed the nearest to 0.1 mg in a 25 mL volumetric flask. The flask is filled to the mark with the solvent mixture 2.

Calibration solutions:
Solutions of 0.5, 1.0, 5, 10, 15, 20 and 25 mg of 1,5-diaminonaphthalene per millilitre solvent mixture 1.
A few millilitres of solvent mixture 1 are added to each 10 mL volumetric flask. Then 5, 10, 50, 100, 150, 200 and 250 µL of the stock solution are each pipetted into one of the volumetric flasks and then the flasks are filled to the mark with solvent mixture 1. With these solutions and an air sample volume of 500 L a 1,5-diaminonaphthalene concentration range of 10 to 500 $\mu g/m^3$ is covered.
The stock solution and calibration solutions are not stable and must be freshly prepared before use.

1.4 Impregnation of the filter

The glass fibre filters are dipped into a mixture of 22 mL of UHQ water and 3 mL of 32% hydrochloric acid and dried in the air on a watch glass. The impregnated filters have a shelf life of at least four weeks.

2 Sampling

For sample collection a filter holder is equipped with two of the impregnated glass fibre filters and connected to the pump. The filter holder is wrapped in aluminium foil to exclude light. During working hours the pump and filter holder are carried by a person or used in a stationary position. The flow rate is set at 2 L/min in accordance with the definition of inhalable dust fraction [1]. With sampling for four hours this corresponds to an air sample volume of 480 L.

3 Analytical determination

3.1 Sample preparation and analysis

For sample preparation the filters are each placed in a glass vessel with a snap-on cap and 5 mL of desorption solution is added. After treatment in an ultrasonic bath and shaking (both for 15 minutes) solid parts are separated from the desorbate by filtering through a 0,2 µm PTFE syringe prefilter. An aliquot of these desorbates is then diluted with UHQ water in the ratio 1 : 1 v/v. This is imperative to avoid damaging the chromatography column.
To ensure that the water used for desorption and the glass fibre filter do not contain interfering substances, an unloaded impregnated filter is also prepared (blank solution).
25 µL is taken from each diluted desorbate, injected into the high performance liquid chromatograph and chromatogrammes are recorded as described in Sect. 3.2. After chromatographic separation 1,5-diaminonaphalene is detected at a wave length of 229 nm.

3.2 Operating conditions for high performance liquid chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Hewlett Packard 1090 equipped with diode array detector (DAD) and autosampler.	
Pre-column:	Length:	30 mm
	Internal diameter:	4 mm

	Stationary phase:	250/8/4 Nucleosil 100-5 C_{18} AB from Macherey & Nagel
Column:	Length:	250 mm
	Internal diameter:	4 mm
	Stationary phase:	250/8/4 Nucleosil 100-5 C_{18} AB from Macherey & Nagel
Elution:	Isocratic	
Eluent:	Acetonitrile/UHQ water (20/80 v/v)	
Flow rate:	0.7 mL/min	
Injection volume:	25 µL	
Detection wavelength:	229 nm	
Column temperature:	40 °C	

4 Evaluation

4.1 Calibration

25 µL of each of the calibration solutions described in Sect. 1.3 are injected into the high performance liquid chromatograph and chromatogrammes are recorded. The calibration curve is obtained by plotting the measured peak areas against the 1,5-diaminonaphthalene concentrations contained in the various calibration solutions. The calibration curve is linear in the given concentration range.

4.2 Calculation of the analytical result

The 1,5-diaminonaphthalene concentration in the air sample in mg/m^3 is calculated according to equation (1):

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

c_w Concentration by weight of 1,5-diaminonaphthalene in the air sample in mg/m^3
w Sum of the 1,5-diaminonaphthalene weights in the desorbate in µg determined from the calibration curve
V Air sample volume in L
η Recovery rate

If more than 10% of the weight of 1,5-diaminonaphthalene deposited on the first filter is found on the second filter, sampling must be repeated with a smaller volume of air.

5 Reliability of the method

5.1 Accuracy and recovery

To determine the relative standard deviation of the procedure and the recovery,

- 20 µL of a solution of 0.66 mg of 1,5-diaminonaphthalene per millilitre solvent mixture 2,
- 20 µL of a solution of 2.64 mg of 1,5-diaminonaphthalene per millilitre solvent mixture 2,
- 20 µL of a solution of 5.07 mg of 1,5-diaminonaphthalene per millilitre solvent mixture 2

were each transferred to two impregnated glass fibre filters placed one behind the other. After the solutions were added the filter holders were wrapped in aluminium foil to exclude light. Then 500 L of laboratory air was drawn through the filters as described in Sect. 2. The spiked weights of 1,5-diaminonaphthalene correspond for the 500 l air volumes to concentrations of 0.026, 0.11 and 0.20 mg/m^3. The filters were then analysed as described in Sect. 3.1. Six individual determinations were carried out for each concentration. The relative standard deviations and recovery rates found are listed in the Table 1:

Table 1. Standard deviation (rel.) *s* and recovery rate.

Concentration mg/m^3	Standard deviation (rel.) *s* %	Recovery rate
0.026	3.9	0.92
0.11	1.9	0.94
0.20	1.8	0.96

5.2 Quantification limit

The absolute quantification limit is 20 ng of 1,5-diaminonaphthalene. It was determined from the signal/noise ratio of the blank value chromatogrammes.
The relative quantification limit is 0.016 mg/m^3 1,5-diaminonaphthalene for a 500 L air sample, 5 mL desorbate, dilution of the desorbate in a ratio of 1 : 1 v/v and 25 µL injection volume.

5.3 Selectivity

Interfering components may cause too high values. In general, interferences can be eliminated by selecting different chromatography conditions. In practice the separation conditions described above have proved reliable.

6 Discussion

The loaded filters can be stored in the dark at room temperature for at least a week without any loss of adsorbed 1,5-diaminonaphthalene.
In addition to 1,5-diaminonaphthalene also 1,2-phenylenediamine and 1,3-phenylenediamine can be determined in the workplace air with the method described.

7 References

[1] *European Committee for Standardization (CEN)* (1993) DIN EN 481, Workplace atmospheres – Size fraction definitions for measurement of airborne particles. Brussels. Beuth Verlag, Berlin.

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Carcinogenic substances Order number: BGI 505-42E
Established methods Issue: December 1996

Method for the determination of α,α-dichlorotoluene (benzal chloride)

Method tested and recommended by the Berufsgenossenschaften for the determination of α,α-dichlorotoluene (benzal chloride) 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 adsorption on activated carbon, gas chromatography after desorption.
"α,α-Dichlorotoluene-1-GC"
(Issue: March 1989)

2 Sampling with a pump and adsorption on Tenax, gas chromatography after desorption.
"α,α-Dichlorotoluene-2-GC"
(Issue: December 1996)

IUPAC name: **CAS No:**
α,α-dichlorotoluene 98-87-3

1 Sampling with a pump and adsorption on activated carbon, gas chromatography after desorption

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

Principle: With a pump a measured air volume is drawn through a glass tube filled with activated carbon. The adsorbed α,α-dichlorotoluene is then desorbed with carbon disulfide and determined by gas chromatography.

Technical data:

Quantification limit: absolute: 0.2 ng α,α-dichlorotoluene.
relative: 0.01 mg/m^3 ≙ 0.0015 mL/m^3 (ppm) α,α-dichlorotoluene for 20 L air sample, 1 ml desorption solution and 1 µl injection volume

Selectivity: As a result of interfering components the values may be too high. In general, interference can be eliminated by selecting a different column.

Advantages: Both personal and selective sampling are possible.

Disadvantages: No indication of concentration peaks; time-consuming.

Apparatus: Pump,
gas meter or flow meter,
activated carbon tubes,
gas chromatograph with flame ionisation detector (FID).

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:
Pump with gas meter or flow meter
Adsorption tubes with activated carbon, (standardised, consisting of two activated carbon fillings of about 100 mg and 50 mg separated with porous polymeric material)

For analytical determination:
Gas chromatograph with flame ionisation detector
Recording and/or data analysis device: compensation recorder or computing integrator

1.2 Chemicals

α,α-Dichlorotoluene (benzal chloride), purity >99%,
Carbon disulfide, analytical grade
Gases for operating the gas chromatograph: Helium,
hydrogen,
synthetic air

1.3 Solutions

α,α-Dichlorotoluene stock solution I:
Solution of 10 mg/mL α,α-dichlorotoluene in carbon disulfide.
100 mg of α,α-dichlorotoluene is dissolved in carbon disulfide in a 10 mL volumetric flask and the flask is filled to the mark with carbon disulfide.

α,α-Dichlorotoluene stock solution II:
Solution of 0.05 mg/mL α,α-dichlorotoluene in carbon disulfide.
50 µL of α,α-dichlorotoluene stock solution I is pipetted into a 10 mL volumetric flask and the flask is filled to the mark with carbon disulfide.

α,α-Dichlorotoluene calibration solutions:
Solutions of 0.5, 1.0 and 1.5 µg/mL α,α-dichlorotoluene in carbon disulfide.
Volumes of 100, 200 and 300 µL of α,α-dichlorotoluene stock solution II are transferred to three different 10 mL volumetric flasks. The volumetric flasks are filled to the mark with carbon disulfide. With these solutions and an air sample volume of 20 L and 1 mL of sample solution a concentration range of 0.025–0.075 mg/m^3 α,α-dichlorotoluene in air is covered.

2 Sampling

An activated carbon tube is opened and connected to the pump. During working hours the pump and tube are worn by a person or used in a stationary position or placed at the sampling site. The flow rate is set to about 4 L/h.

3 Analytical determination

3.1 Sample preparation and analysis

The contents of the loaded activated carbon tube are transferred to a 2 mL sample vial and desorbed with 1 mL of carbon disulfide (desorption solution).
After desorption of the activated carbon with carbon disulfide, the solution must immediately be analysed by gas chromatography, as the solution is instable.
To ensure that the carbon disulfide and the activated carbon do not contain any impurities, the filling of an unloaded activated carbon tube is desorbed with 1 mL of carbon disulfide (blank solution).
1 µL of the desorption solution and of the blank solution are each injected into the gas chromatograph and a gas chromatogram is recorded as described in Sect. 3.2. Quantitative evaluation is carried out according to the external standard method using the area or height of the α,α-dichlorotoluene peak.

3.2 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Gas chromatograph, Hewlett-Packard 5890 A with on-column inlet and FID	
Column:	Material:	Quartz capillary
	Length:	50 m
	Internal diameter:	0.32 mm
	Stationary phase:	Chrompack CP-Sil 5 CB
	Film thickness:	1.2 µm
Temperatures:	Injector block:	not heated
	Detector:	300 °C
	Furnace temperature programme:	
	Starting temperature:	100 °C
	Heating rate:	15 °C/min
	Final temperature:	280 °C
Carrier gas:	Helium, column pressure 195 kPa ≙ approx. 3.3 mL/min	
Detector gases:	Hydrogen, approx. 30 mL/min	
	Synthetic air, approx. 300 mL/min	
Injection mode:	Cool on column	

4 Evaluation

4.1 Calibration

1 µL of each of the calibration solutions are injected into the gas chromatograph. The calibration curve is obtained by plotting the measured areas or heights of the α,α-dichlorotoluene peaks against the α,α-dichlorotoluene weights in µg contained in 1 mL of the various calibration solutions.

4.2 Calculation of the analytical result

The α,α-dichlorotoluene weight in µg contained in 1 mL of the desorption solution is read from the calibration curve via the peak area (height). The α,α-dichlorotoluene concentration in the air sample in mg/m^3 is calculated according to Equation (1):

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

The concentration by volume c_v in mL/m^3 calculated from c_w for 20 °C and 1013 hPa is:

$$c_v = 0.15 \cdot c_w \tag{2}$$

Legend:
c_w Concentration by weight of α,α-dichlorotoluene in the air sample in mg/m^3
c_v Concentration by volume of α,α-dichlorotoluene in the air sample in mL/m^3 (ppm)
w Weight of α,α-dichlorotoluene in the desorption solution in µg determined from the calibration curve
V Air sample volume in L

5 Reliability of the method

5.1 Accuracy

The relative standard deviation was determined by adding 1 µL α,α-dichlorotoluene calibration solution at a concentration of 1.35 µg/mL to the activated carbon filling of a sampling tube. It was determined from 9 individual measurements as being ±10 %. The range of scatter was ±8 % (P = 95 %).

5.2 Quantification limit

The absolute quantification limit is 0.2 ng of α,α-dichlorotoluene. This corresponds to 0.2 µg of α,α-dichlorotoluene per activated carbon tube or sample.
The relative quantification limit for the method used here is 0.01 mg/m^3 α,α-dichlorotoluene for 20 L air sample, 1 mL desorption solution and 1 µL injection volume.

5.3 Selectivity

The selectivity of the method depends above all on the type of column used. In practice the given column has proved reliable. Toluene, α-chlorotoluene (benzyl chloride) and α,α,α-trichlorotoluene (benzotrichloride) can be simultaneously determined using this method.
In case of interfering components, a column with a different stationary phase should be used.

5.4 Recovery

Recovery is dependent on both the relative humidity and the concentration.
Laboratory experiments yielded a recovery of 72 % at a concentration of 0.03 mg/m^3 and of 95 % at a concentration of 0.14 mg/m^3 (injection of 5 and 25 µL of a solution with a concentration of 114 µg/mL α,α-dichlorotoluene on the collection phase followed by drawing 20 L of air through the tube). The relative humidity in both cases was max. 65 %.

2 Sampling with a pump and adsorption on Tenax, gas chromatography after desorption

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

Principle: With a pump a measured air volume is drawn through a Tenax tube. The adsorbed α,α-dichlorotoluene is then desorbed with *n*-hexane and determined by gas chromatography.

Technical data:

Quantification limit: absolute: 0.5 ng of α,α-dichlorotoluene.
relative: 0.01 mg/m^3 α,α-dichlorotoluene for 48 L air sample, 1 mL desorption solution and 1 µL injection volume.

Selectivity: Interfering components may cause too high values. In general, interference can be eliminated by selecting a column with different separating characteristics.

Advantages: Both personal and selective sampling are possible.

Disadvantages: No indication of concentration peaks.

Apparatus: Pump,
gas meter or flow meter,
Tenax tubes,
gas chromatograph with flame ionisation detector (FID).

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:
Pump, suitable for a flow rate of 100 mL/min (e.g. PP1 from Gilian, supplier in Germany: DEHA-Haan & Wittmer GmbH, 71288 Friolzheim)
Gas meter or flow meter
Adsorption tubes with Tenax, standardised, consisting of two Tenax fillings of about 50 mg and 100 mg separated with glass wool (e.g. Catalogue No. 226-35-03 from SKC, supplier in Germany: MTC GmbH, Müllheim)
Caps for the opened Tenax tubes

For sample preparation and analysis:
2 mL Beaded rim vials with polytetrafluoroethylene (PTFE) coated septa and crimp caps
Crimper
Shaking machine
50 mL Volumetric flask
0.2, 0.5, 1, 2 and 5 mL Pipettes
10 and 50 µL Injection syringes
Gas chromatograph with FID
Data analysis device

1.2 Chemicals

n-Hexane, purity at least 99%, water-free,
α,α-Dichlorotoluene, purity at least 99%
Gases for operating the gas chromatograph: Helium, purity 99.995%
Hydrogen, purity 99.995%
Synthetic air, free from hydrocarbons

1.3 Solutions

α,α-Dichlorotoluene stock solution:
Solution of 10 mg/mL α,α-dichlorotoluene in *n*-hexane.
Approx. 500 mg of α,α-dichlorotoluene is weighed into a 50 mL volumetric flask to the nearest 0.1 mg. The volumetric flask is filled to the mark with *n*-hexane.

Calibration solutions:
Solutions of 1.0 µg/mL, 4 µg/mL, 10 µg/mL, 40 µg/mL, 0.1 mg/mL, 0.4 mg/mL and 1 mg/mL α,α-dichlorotoluene in *n*-hexane.
5 µL, 20 µL, 50 µL, 0.2 mL, 0.5 mL, 2 mL and 5 mL of the α,α-dichlorotoluene stock solution are each transferred to 50 mL volumetric flasks already containing about 10 mL of *n*-hexane. The volumetric flasks are filled to the mark with *n*-hexane.
With these solutions and an air sample volume of 48 L and 1 mL of desorption solution a concentration range of 21 µg/m^3 to 21 mg/m^3 α,α-dichlorotoluene in air is covered.

2 Sampling

The flow rate of the pump is set to a maximum of 100 mL/min. With sampling for 8 hours this corresponds to a maximum air sample volume of 48 L. A Tenax tube is opened and connected to the pump. During working hours the pump and tube are worn by a person or used in a stationary position. After sampling, the tube is closed with caps.

3 Analytical determination

3.1 Sample preparation and analysis

The contents of the loaded Tenax tube are transferred to a 2 mL beaded rim vial and 1 mL of *n*-hexane is added. The beaded rim vial is closed and shaken for 30 minutes. 1 µL of the supernatant solution (desorption solution) is injected into the gas chromatograph.

To ensure that the desorption solvent and the Tenax tube do not contain any impurities, the filling of an unloaded Tenax tube is treated with 1 mL of *n*-hexane (blank solution). 1 µL of the blank solution is injected into the gas chromatograph.

3.2 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Gas chromatograph, Hewlett-Packard 5890 with FID	
Column:	Material:	Quartz capillary
	Length:	50 m
	Internal diameter:	0.32 mm
	Stationary phase:	SE-54
	Film thickness:	0.5 µm
Temperatures:	Injector block:	200 °C
	Detector:	300 °C
	Furnace temperature programme:	
	Starting temperature:	60 °C, 2 min isothermal
	Heating rate:	10 °C/min
	Final temperature:	280 °C
Injection mode:	Splitless, 0.5 min	
Carrier gas:	Helium, approx. 2.5 mL/min	
Detector gases:	Hydrogen, 35 mL/min	
	Air, 400 mL/min	
Make-up gas:	Helium, 15 mL/min	
Injection volume:	1 µL	

4 Evaluation

4.1 Calibration

1 mL of each of the calibration solutions described in Sect. 1.3 are added to the contents of an unloaded Tenax tube in beaded rim vials and analysed as described in Sect. 3.1.
The calibration curve is obtained by plotting the measured peak areas or peak heights against the α,α-dichlorotoluene weights contained in the various calibration solutions. The calibration curve is linear in the given concentration range.

4.2 Calculation of the analytical result

Quantitative evaluation of the chromatogrammes is carried out according to the external standard method. The concentration by weight c_w in the air sample in mg/m^3 is calculated according to equation (1):

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

The concentration by volume c_v in mL/m^3 calculated from c_w for 20 °C and 1013 hPa is:

$$c_w = 0.15 \cdot c_w \tag{2}$$

Legend:
c_w Concentration by weight of α,α-dichlorotoluene in the air sample in mg/m^3
c_v Concentration by volume of α,α-dichlorotoluene in the air sample in mL/m^3
w Weight of α,α-dichlorotoluene in the desorption solution in µg
V Air sample volume in L
η Recovery rate

5 Reliability of the method

5.1 Accuracy and recovery

To determine the relative standard deviation of the method, different weights of α,α-dichlorotoluene were each loaded onto six Tenax tubes by means of a syringe. Six tubes were prepared with 0.5 µL of the calibration solution with the highest concentration, 0.5 µL stock solution and 1 µL stock solution. Under the sampling conditions described in Sect. 2, 48 litres of air were drawn through each of the tubes. The tubes were then analysed. This loading corresponded to air sample concentrations of 0.01, 0.1 and 0.2 mg/m^3 α,α-dichlorotoluene.
Under the given conditions the 6 independent measurements yielded the relative standard deviations and recoveries listed in Table 1.

Table 1. Standard deviation (rel.) s and recovery rate.

Concentration mg/m^3	Standard deviation (rel.) s %	Recovery rate
0.01	6.6	0.95
0.1	4.3	0.85
0.2	9.5	0.97

5.2 Quantification limit

The absolute quantification limit is 0.5 ng of α,α-dichlorotoluene. It was determined from the signal noise ratio of the chromatogrammes.
The relative quantification limit is 0.01 mg/m^3 α,α-dichlorotoluene for a 48 L air sample, 1 mL of desorption solution and a 1 µL injection volume.

5.3 Selectivity

The selectivity of the method depends on the type of column used. In practice the given column has proved reliable. In case of interfering components, a column with other separation characteristics should be used.

6 Discussion

As the quality of the Tenax tubes varies greatly, the blank value of each Tenax tube used should always be checked.
The loaded tubes can be stored at 5–7 °C for at least 7 days without any loss of adsorbed α,α-dichlorotoluene.
The stock solution and calibration solutions must be freshly prepared each day due to the sensitivity of α,α-dichlorotoluene to hydrolysis.

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Centre for Accident Prevention and Occupational Medicine
Alte Heerstraße 111, 53757 Sankt Augustin
Expert Committee Chemistry

Carcinogenic substances Order number: BGI 505-18E
Established methods Issue: April 1997

Method for the determination of diethyl sulfate

Methods tested and recommended by the Berufsgenossenschaften for the determination of diethyl sulfate in working areas after discontinuous sampling.
For the assessment of working areas, both personal and stationary sampling are possible:

1 Sampling with a pump, adsorption on silica gel, desorption, derivatisation and thin-layer chromatography.
(Issue: December 1983)

2 Sampling with a pump, adsorption on silica gel, desorption, gas chromatography and sulfur-specific detection
(Issue: December 1983)

3 Sampling with a pump, adsorption on Tenax-TA, desorption gas chromatography and sulfur-specific detection
(Issue: January 1987)

Methods 1 to 3 are carried out in the same way as described for dimethyl sulfate (cf. BGI 505-7E). They are therefore not described in detail again here.

4 Sampling with a pump, adsorption on Tenax-TA, desorption, gas chromatography and mass-selective detection.
"Diethyl sulfate-4-GC"
(Issue: April 1997)

The methods are also suitable for determining other dialkyl sulfates.

IUPAC name:	**CAS No:**
diethyl sulfate	64-67-54

4 Sampling with a pump, adsorption on Tenax-TA, desorption, gas chromatography and mass-selective detection

This method permits the determination of diethyl sulfate (DES) concentrations in working areas averaged over the sampling time after personal or stationary sampling.

Principle: With a pump a measured air volume is drawn through a Tenax tube. The adsorbed diethyl sulfate is desorbed with toluene and analysed using a gas chromatograph with mass-selective detector.

Technical data:

Quantification limit: absolute: 0.4 ng diethyl sulfate
relative: 0.01 mg/m^3 diethyl sulfate for 20 L air sample, 1 mL desorption solution and 2 µL injection volume.

Selectivity: The method is selective as a result of the combination of gas chromatographic separation and mass-selective detection.

Advantages: Both personal and selective sampling are possible.

Disadvantages: Concentration peaks not recorded.

Apparatus: Pump,
gas meter or flow meter,
Tenax tubes,
gas chromatograph with mass-selective detector.

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:
Pump, suitable for a flow rate of 50 mL/min (e.g. PP1 from Gilian (supplier in Germany: GSM GmbH, Neuss-Norf))
Gas meter or flow meter
Sampling tubes: A glass tube which can be closed with plastic caps is filled with about 50 mg Tenax-TA. The Tenax-TA is held in place with small silanised glass wool plugs. The dimensions of the sampling tubes must match the dimensions of the sampling head of the pump. Sampling tubes of 50 mm in length, with a 6 mm external diameter and a 4 mm internal diameter have proved suitable. 50 mg Tenax-TA in a tube of this size fills 35 mm of the tube.
Caps for the opened Tenax tubes

For sample preparation and analysis:
50 mL Volumetric flasks
2 and 5 mL Sample vials with polytetrafluoroethylene (PTFE)-coated septa and aluminium crimp caps.
Crimper for closing the sample vials.
Shaking machine

0.5 mL and 1 mL Pipettes
10, 50 and 100 µL Microlitre syringes
Gas chromatograph with mass-selective detector
Evaluation unit

1.2 Chemicals

Diethyl sulfate, purity at least 99% (e. g. from Fluka, 89231 Neu-Ulm)
Toluene, dried over a molecular sieve (desorption solvent)
Gases for operating the gas chromatograph:
Helium, suitable for operating a mass spectrometric detector in selected ion monitoring mode

1.3 Solutions

DES stock solution:
Solution of 0.2 mg DES in 1 mL toluene.
A few millilitres of the desorption solvent toluene are placed in a 50 mL volumetric flask and 8.5 µL (10 mg) DES is added with a 10 µL syringe. The flask is then filled to the mark with toluene.

Calibration solutions:
Solutions of 0.2, 2 and 4 µg DES per mL toluene.
Volumes of 50 µL, 0.5 mL and 1 mL stock solution are each pipetted into a 50 mL volumetric flask containing a few millilitres of toluene. The flask is then filled to the mark with toluene. With these solutions a concentration range of 0.01 to 0.2 mg/m^3 is covered for an air sample volume of 20 L and 1 mL desorbate.

2 Sampling

A Tenax tube is opened and connected to the pump. The flow rate is set to approx. 3.3 L/h. With sampling for about 6 hours this corresponds to an air sample volume of approx. 20 L. During working hours the pump and tube are carried by a person or used in a stationary position. After sampling, the tubes are closed with caps. The method was tested up to an air sample volume of 40 L with a maximum flow rate of 4 L/h.

3 Analytical determination

3.1 Sample preparation and analysis

The contents of the loaded Tenax tube are transferred to a 5 mL sample vial. After the addition of 1 mL toluene the vial is closed, carefully shaken for 30 minutes and immediately analysed. To ensure that the toluene and Tenax-TA used do not contain any interfering substances, the filling of an unloaded tube is treated as described above (blank value solution).
2 µL desorbate and 2 µL blank value solution are each injected into the gas chromatograph. Quantitative evaluation of the chromatograms is carried out according to the external standard method.

3.2 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Gas chromatograph Hewlett-Packard 5890 with MSD HP 5970, split/splitless injector and autosampler HP 7673.	
Column:	Material:	Quartz capillary
	Length:	50 m
	Internal diameter:	0.20 mm
	Stationary phase:	95% methyl silicone + 5% methyl phenyl silicone (HP-5 from Hewlett-Packard)
	Film thickness:	0.33 µm
Temperatures:	Injector:	200 °C,
	Transfer line:	250 °C
	Furnace temperature programme:	
	Starting temperature:	50 °C, 2 min isothermal
	Heating rate 1:	10 °C/min to 220 °C
	Heating rate 2:	30 °C/min
	Final temperature:	250 °C, 15 min isothermal
Injection mode:	Splitless, 1 min	
Carrier gas:	Helium, column pressure 180 kPa	
Injection volume:	2 µL	
Ionisation mode:	Electron-impact ionisation (70 eV)	
Detection mode:	Selected ion monitoring (SIM mode)	
Recorded masses (m/z):	111, 125, 139	
Dwell time:	200 ms/recorded mass	

4 Evaluation

4.1 Calibration

2 µL of each of the calibration solutions described in Sect. 1.3 are injected into the gas chromatograph. The calibration curve is obtained by plotting the measured peak areas against the concentrations in µg/mL contained in the various calibration solutions.
The calibration curves are not linear for the whole concentration range tested. Within narrow concentration ranges, however, the calibration curves are sufficiently linear. The non-linear calibration curve can be drawn by joining the points with straight lines.

4.2 Calculation of the analytical result

The DES concentration by weight in the air sample in mg/m^3 is calculated according to the following Equation (1):

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

For the calculation of the concentration c_v in mL/m^3 from c_w at 20 °C and 1013 hPa:

$$c_v = 0.16 \cdot c_w \tag{2}$$

Legend:
c_w Diethyl sulfate concentration in the air sample in mg/m^3
c_v Diethyl sulfate concentration in the air sample in mL/m^3 (ppm)
w Weight of diethyl sulfate in the desorbate in µg determined from the corresponding calibration curve
V Air sample volume in L
η Recovery rate

5 Reliability of the method

5.1 Accuracy and recovery

5 sampling tubes were each loaded with 0.4, 4 and 8 µg diethyl sulfate (contained in 100 µL calibration solution of the concentration 4 µL/L, 20 µL or 40 µL stock solution; all in 15 tubes). Then laboratory air (15–25% relative humidity) was drawn through each tube for about 6 hours at a flow rate of 3.3 L/h. The spiked weights correspond to concentrations of 0.02 to 0.4 mg/m^3 for an air sample volume of 20 L. The obtained relative standard deviations are shown in Table 1:

Table 1. Standard deviation (rel.) *s*.

Concentration mg/m^3	Standard deviation (rel.) *s* %
0.02	2.4
0.2	1.5
0.4	2.8

The recovery rate was over 0.9 for an air volume of 20 L and a flow rate of about 3.3 L/h.

5.2 Quantification limit

The absolute quantification limit for DES is 0.4 ng. This corresponds to 0.2 µg per Tenax tube or sample.
The quantification limit was determined according to DIN 32645 as a multiple of the standard deviation of the method.
The relative quantification limit for DES is 0.01 mg/m^3 for a 20 L air sample, 1 mL desorbate, and a 2 µL injection volume.

5.3 Selectivity

The method is selective as a result of the combination of gas chromatographic separation and mass-selective detection.

6 Discussion

The shelf life (refrigerator) of diethyl sulfate in adsorbed state is at least 14 days. The calibration solutions and the stock solution must be freshly prepared after 48 hours at the latest, as residual water present in the toluene decomposes the diethyl sulfate.
Before each analytical series, the gas chromatographic system must be conditioned with diethyl sulfate. A volume of 2 µL of a solution containing approx. 0.2 mg diethyl sulfate in 1 mL toluene is injected into the gas chromatograph twice. Then, by injecting 2 µL toluene, it is checked that no memory effects occur. If necessary toluene must be injected into the system again.
It has proved advantageous to use the column only for dialkyl sulfate analyses.

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Expert Committee Chemistry

Carcinogenic substances Order number: BGI 505-7E
Established methods Issue: April 1997

Method for the determination of dimethyl sulfate (DMS)

Methods tested and recommended by the Berufsgenossenschaften for the determination of dimethyl sulfate in working areas after discontinuous sampling.
For the assessment of working areas, both personal and stationary sampling are possible:

1 Sampling with a pump, adsorption on silica gel, desorption, derivatisation and thin-layer chromatography.
(Issue: December 1983)

2 Sampling with a pump, adsorption on silica gel, desorption, gas chromatography and sulfur-specific detection.
(Issue: December 1983)

3 Sampling with a pump, adsorption on Tenax-TA, desorption, gas chromatography and sulfur-specific detection.
(Issue: January 1987)

4 Sampling with a pump, adsorption on Tenax-TA, desorption, gas chromatography and mass-selective detection. "Dimethyl sulfate-4-GC".
(Issue: April 1997)

The methods are also suitable for determining other dialkyl sulfates.

IUPAC name:	**CAS No:**
dimethyl sulfate	77-78-1

1 Sampling with a pump, adsorption on silica gel, desorption, derivatisation and thin-layer chromatography

Principle: With a pump a measured air volume is drawn through silica gel. After desorption with acetone and derivatisation with 4-nitrophenol sodium, the DMS is determined as 4-nitroanisole by thin-layer chromatography.

Technical data:

Quantification limit: absolute: 50 ng DMS when using silica gel 60 pre-coated TLC plates.
relative: 0.02 mL/m^3 (ppm) ≙ 0.1 mg/m^3 DMS for 100 L air sample.

Selectivity: Selectivity must be checked in each case.
Interference can result from substances which have a similar R_f value to 4-nitroanisole and yield derivatives with similar colouring.

Advantages: Selective analysis is possible, no complicated apparatus needed.

Disadvantages: To achieve the necessary sensitivity, the sampling time must be at least 60 minutes, therefore concentration peaks are not recognisable.
Because of the size of the sampling apparatus, personal sampling is not possible.

Apparatus: Sampling equipment, consisting of
adsorption tube,
pump,
gas meter or flow meter,
basic equipment for thin-layer chromatography,
silica gel 60 pre-coated TLC plates (without fluorescence indicator).

Detailed description of the method

Contents

1 Summary

This method (cf. Sect. 10) permits the determination of DMS concentrations in working areas averaged over the sampling time after stationary sampling.
With a pump a measured air volume is drawn through a sampling tube filled with silica gel. Then the adsorbed DMS is desorbed with acetone within three hours. After desorption, the desorbate is immediately reacted with 4-nitrophenol sodium to yield 4-nitroanisole. Analysis is then carried out using thin-layer chromatography.
The absolute quantification limit is 50 ng DMS.
The relative quantification limit is 0.02 mL/m^3 (ppm) = 0.1 mg/m^3 DMS for a 100 L air sample.
Detector tubes are not suitable for analyses carried out in working areas. Provided appropriate preliminary studies have been carried out, they can be used to check for leaks in closed systems and for range-finding. Sampling can also be carried out with an evacuated gas pipette. After addition of acetone the DMS contained in the gas pipette is absorbed by shaking. Analysis is then carried out as described above.

The method is also suitable for determining other dialkyl sulfates that can be analysed using thin-layer chromatography. It has been tested with diethyl sulfate.

2 Equipment, chemicals and solutions

2.1 Equipment

For sampling (cf. Fig. 1):

Sampling tube (S), consisting of a sealable glass tube. 10 g silica gel is placed in the tube which is plugged with a glass frit or a plug made of quartz wool. An example is shown in Figure 2.

Throttle valve (T), if necessary, for setting the flow rate

Pump (P), flow rate of at least 100 L/h under the pressure conditions occurring during sampling

Gas meter (G), calibrated, suitable for measuring 100 L within 60 minutes

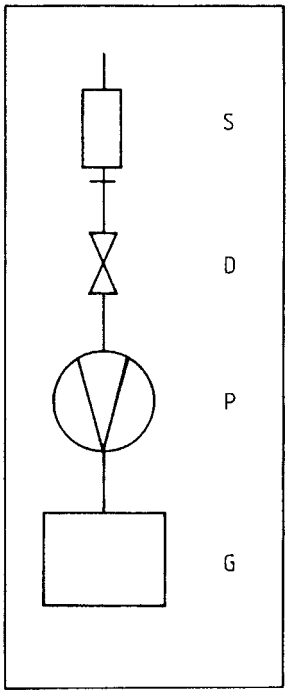

Fig. 1. Sampling apparatus.
S Sampling tube
T Throttle valve
P Pump
G Gas meter

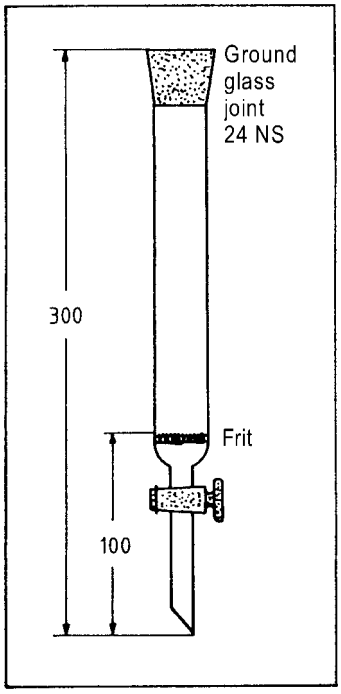

Fig. 2. Sampling tube.

For sample preparation and analysis:
250 mL Erlenmeyer flasks with ground glass joint, NS 29
Reflux condenser, NS 29
Buchner filter made of glass
Boiling stones
Rotary evaporator with the usual accessories (heating bath, pear-shaped distilling flask with ground glass joint, steam duct, receiving flask with spherical joint, water jet vacuum pump)
5 mL Separatory funnel
10 µL Syringe
25 mL Burette
100 mL Volumetric flasks
Basic equipment for thin-layer chromatography
Silica gel 60 pre-coated plates for thin-layer chromatography

2.2 Chemicals

Acetone, tested for adequate purity for thin-layer chromatography
Dimethyl sulfate, redistilled
Silica gel, particle size 0.063–0.20 mm, cf. Sect. 9
4-Nitrophenol, analytical grade
Sodium hydroxide, analytical grade
Ethanol, analytical grade, 96%
4-Nitrophenol sodium tested for adequate purity for thin-layer chromatography:
40 g sodium hydroxide is stirred into 500 mL ethanol and 25 mL water without cooling and the solution is then filtered using a glass Buchner funnel. The filtrate is added to a solution of 4-nitrophenol in hot ethanol. This solution is cooled while being stirred continuously, during which time 4-nitrophenol sodium crystals are formed. After filtration the product is washed twice with cold ethanol and cold acetone and dried at 50 °C in a drying cabinet.
4-Nitroanisole, tested for adequate purity for thin-layer chromatography
Toluene, analytical grade
Acetic acid methyl ester, analytical grade
Titanium(III) chloride solution, 0.2 N
Acetic acid, analytical grade, 100%
Pyridine, analytical grade
Sulphuric acid, analytical grade, concentrated
Ammonium chloride, analytical grade
Hydrochloric acid, analytical grade, concentrated
Sodium nitrite, analytical grade,
N-(1-Naphthyl)ethylenediamine dihydrochloride, analytical grade

2.3 Solutions

Spray solutions

Reducing solution:
40 mL titanium(III) chloride solution, 40 mL pyridine and 20 mL acetic acid are mixed together (mixture must be freshly prepared daily).

Coupling solution:
0.5 g *N*-(1-Naphthyl)ethylenediamine dihydrochloride is dissolved in 100 mL water containing two drops of concentrated hydrochloric acid.

4-Nitroanisole stock solution:
24.3 mg 4-nitroanisole (≙ 20.0 mg DMS) is placed in a 100 mL volumetric flask and the flask is filled to the mark with acetone. This solution contains 200 µg/mL DMS (as 4-nitroanisole).

Calibration solutions:
Volumes of 2.5, 4.0, 5.0, 10.0, 15.0 and 25.0 mL of the stock solution are run from a 25 mL burette into six 100 mL volumetric flasks. All flasks are filled to the mark with acetone.
These solutions contain 5, 8, 10, 20, 30 and 50 µg/mL DMS (as 4-nitroanisole).

3 Sampling

The sampling apparatus is set up as shown in Figure 1. After the gas meter has been read, the pump is switched on and the flow rate set to about 100 L/h, for example with a throttle valve (T). After the end of sampling (sampling duration about 1 hour), the gas meter is read again.
Because of various sources of interference, e.g. adsorption onto the walls, tubing should be avoided if possible in the sampling apparatus.
Water vapour present in the air sample is adsorbed by the silica gel during sampling. Because of this, or due to other interfering components that can be adsorbed, the shelf life of the samples is very limited (cf. Sect. 7.5). They can be stored only for a maximum of three hours. Within this period the sample must be processed further.

4 Sample preparation

For elution, about 100 mL acetone is poured onto the silica gel in the sampling tube and the eluate is collected in a 250 mL Erlenmeyer flask with a ground glass joint containing 100 mg 4-nitrophenol sodium.
The sample solution is then boiled for an hour under reflux (boiling stones).

The dimethyl sulfate reacts with the 4-nitrophenol sodium to form 4-nitroanisole. The reaction solution is then concentrated to about 1 mL using a rotary evaporator, transferred to a 5 mL separatory funnel with a little acetone and diluted with acetone to 2 mL.
The solution in acetone (sample solution) is analysed using thin-layer chromatography.

5 Analytical determination

5.1 Conditions for thin-layer chromatography

Layer:	Silica gel 60 pre-coated TLC plates
Solvent:	Toluene/acetic acid methyl ester, 95 : 5 v/v
Solvent front:	Ascending about 18 cm
Chromatography time:	about 60 minutes
Temperature:	about 20 °C
Volumes to be applied:	10 µL sample solution and 10 µL calibration solutions

5.2 Chromatographic determination

After chromatographic separation, the thin-layer chromatographic plate is dried with warm air and sprayed with the reducing solution (not until it becomes transparent). The plate is left exposed to air until it is completely colourless and then dried with warm air. Then it is placed in a tank containing hydrogen chloride (made from concentrated sulfuric acid and ammonium chloride). After about 5 minutes, the plate is exposed to nitrous gases (made from concentrated hydrochloric acid and sodium nitrite) in another tank for diazotisation. After removing the excess nitrous gases with a stream of air (fume hood!) at room temperature, the plate is sprayed with the coupling solution until it is transparent. During this reaction (coupling) blue-violet spots of azo dyes are formed.

5.3 Evaluation by comparison of the coloured spots

To evaluate the thin-layer chromatograms, the intensity of the coloured spots produced by the sample solution is compared with that from the calibration solutions. Intermediate values can be estimated.
The result is concentration X of the dimethyl sulfate sample solution in µg/mL.
An optical thin-layer chromatography analysis device with variable wave length can also be used. Particular care must be taken that the measurements are not falsified by contaminants in the air.

6 Calculation of the analytical result

The dimethyl sulfate concentration in the air sample c_w is calculated in mg/m^3 taking into account the mean recovery rate of 0.9 according to the Equation (1):

$$c_w = 0.02 \cdot X \tag{1}$$

For the volumes given in the method
Air sample: 100 L
Sample solution: 2 mL
Calibration solutions and sample solution applied to the thin-layer chromatographic plate: 10 µL of each

If the given volumes must be changed, the following equation applies:

$$c_w = \frac{X \cdot V_T \cdot V_1}{V \cdot V_2} \tag{2}$$

Legend:
c_w Dimethyl sulfate concentration in the sample air in mg/m^3
X Dimethyl sulfate concentration in the sample solution given in Section 5.3 in µg/mL
V_T Volume of the sample solution in mL
V Air sample volume in L
V_1 Volume of the applied calibration solution in µL
V_2 Volume of the applied sample solution in µL

7 Reliability of the method

7.1 Precision

The relative standard deviation for determination by comparison of spots after thin-layer chromatography is $\pm 25\%$.

7.2 Quantification limit

Absolute quantification limit for the whole procedure:
50 ng dimethyl sulfate for silica gel 60 pre-coated TLC plates.
Relative quantification limit for the whole procedure:
0.02 mL/m^3 (ppm) $\triangleq$ 0.1 mg/m^3 dimethyl sulfate for 100 L air sample, 2 mL sample solution, and 10 µL sample solution applied to the thin-layer chromatographic plate.

7.3 Selectivity

The selectivity must be checked in each case. Interferences can occur only from substances which also methylate 4-nitrophenol sodium to yield 4-nitroanisole, e. g. monochloromethane, and substances which have a similar R_f value to 4-nitroanisole and produce a similar colouring.

7.4 Recovery

To determine the recovery, the sampling apparatus shown in Figure 1 was used. A U-tube was connected to the sampling tube using ground glass joints. 0.025 mg dimethyl sulfate dissolved in acetone was placed in the U-tube and about 500 L air was drawn through the tube.
From 12 measurements a mean recovery of $90 \pm 10\,\%$ was calculated. Although this value is achieved with as little as 3 g silica gel in the tube, in this method, to be on the safe side, 10 g silica gel is used. The fluctuations in recovery are attributed mainly to differences in the humidity of the air drawn through the U-tube.
In range-finding studies it was further demonstrated that when 10 g silica gel is used, the whole amount of dimethyl sulfate is contained in the first 10 mL of the desorbate.

7.5 Shelf life

As a result of hydrolysis, dimethyl sulfate can only be stored for a limited period of time on silica gel and in the acetone solution, as the silica gel itself already contains water and, because of the humidity of the air, additional water is adsorbed by the silica gel during sampling. In the acetone desorbates up to 7 % water could be detected. The acetone solution should therefore be reacted with 4-nitrophenol sodium as soon as possible after desorption, certainly, however, after two hours.
Storage experiments with dimethyl sulfate on silica gel at room temperature revealed the following dimethyl sulfate losses:
after 22 hours about 40 %, after 44 hours about 58 % and after 104 hours about 83 %.
The sample tubes should therefore be desorbed immediately after sampling, if possible, and at the latest after three hours.

8 Notes on the procedure

The procedure described is designed for the determination of dimethyl sulfate concentrations between 0.02 and 0.2 mL/m^3 (ppm) $\triangleq$ 0.1 and 1 mg/m^3 (100 L air sample, 2 mL sample solution, which can contain between 0.01 and 0.1 mg dimethyl sulfate, 10 µL sample solution applied to the thin-layer chromatographic plate).

In practice most cases involve discontinuous exposure. The results obtained after sampling for about 1 hour are therefore suitable for evaluating work areas.

9 Manufacturers

Pump:
e. g. Edwards, Kniese & Co, Hochvakuum GmbH, Marburg,
trivac pump S2A (or ″4A), from Leybold-Heraeus GmbH & Co KG, Köln,
Du Pont Instruments,
Supplier in Germany: DEHA-Haan & Wittmer GmbH, Friolzheim

Silica gel:
e. g. E. Merck AG, Darmstadt 2 (Article No. 7734),
Chemie-Mineralien KG, Bremen (Silicagel 958)

Pre-coated thin-layer chromatographicplates:
e. g. Kieselgel-60-Fertigplatten,
E. Merck AG, Darmstadt 2 (Article No. 5721)

10 References

[1] *Keller J* (1974) Bestimmung von Dimethylsulfatspuren in der Luft. Z. Anal. Chem. 269: 206–208.

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

Principle: With a pump a measured air volume is drawn through silica gel. After desorption with acetone, the DMS is determined using gas chromatography with a sulfur-specific flame photometric detector (FPD).

Technical data:

Quantification limit: absolute: 3 ng DMS.
relative: 0.008 mL/m^3 (ppm) ≙ 0.04 mg/m^3 DMS for 100 L air sample.

Selectivity: The method is selective as a result of the combination of gas chromatographic separation and sulfur-specific detection.

Advantages: Selective for the determination of DMS.

Disadvantages: To achieve the necessary sensitivity, the sampling time must be at least 60 minutes, therefore concentration peaks are not detectable.
Because of the size of the sampling apparatus, personal sampling is not possible.

Apparatus: Sampling equipment, consisting of
adsorption tube,
pump,
gas meter or flow meter,
gas chromatograph with flame photometric detector (FPD).

Detailed description of the method

Contents

1 Summary

This method (cf. Sect. 12) permits the determination of DMS concentrations in working areas averaged over the sampling time after stationary sampling.
With a pump a measured air volume is drawn through a sampling tube filled with silica gel. Then the adsorbed DMS is desorbed with acetone within three hours. Gas chromatography is carried out immediately after desorption using a gas chromatograph equipped with a flame photometric detector.
The absolute quantification limit is 3 ng DMS.
The relative quantification limit is 0.008 mL/m^3 (ppm) ≙ 0.04 mg/m^3 DMS for a 100 L air sample.
Detector tubes are not suitable for analyses carried out in working areas. Provided appropriate preliminary studies have been carried out, they can be used to check for leaks in closed systems and for range-finding. Sampling can also be carried out with an evacuated gas pipette. After addition of acetone the DMS contained in the gas pipette is absorbed by shaking. Analysis is then carried out as described above.
The method is also suitable for determining other dialkyl sulfates that can be analysed using gas chromatography. It has been tested with diethyl sulfate.

2 Equipment, chemicals and solutions

2.1 Equipment

For sampling (cf. Fig. 1):

Sampling tube (S), consisting of a sealable glass tube. 10 g silica gel is placed in the tube which is plugged with a glass frit or a plug made of quartz wool. An example is shown in Figure 2.

Throttle valve (T), if necessary, for setting the flow rate

Pump (P), flow rate of at least 100 L/h under the pressure conditions occurring during sampling

Gas meter (G), calibrated, suitable for measuring 100 L within 60 minutes

25 mL Volumetric flask with ground-glass stopper

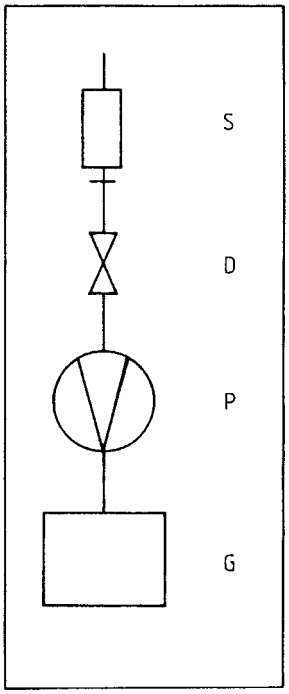

Fig. 1. Sampling apparatus.
S Sampling tube
T Throttle valve
P Pump
G Gas meter

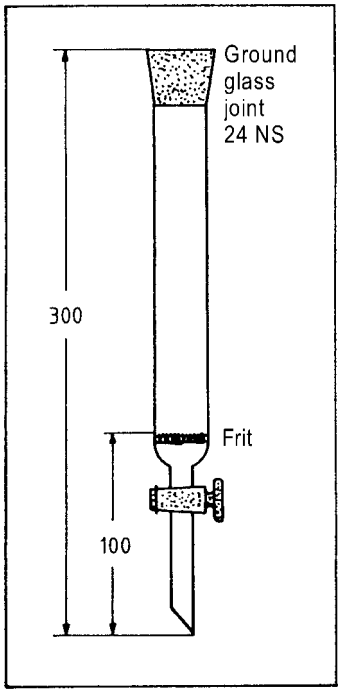

Fig. 2. Sampling tube.

For analysis:
Gas chromatograph with sulfur-specific flame photometric detector and packed analytical column. A three-way valve between the column and detector is useful for discharging the acetone so that it does not reach the detector.
Syringes: 1. Maximum dispensing volume 10 µL,
2. Maximum dispensing volume 25 µL or 50 µL
Evaluation unit: Integrator

2.2 Chemicals

Acetone, analytical grade
Tested to ensure that there are no interfering sulfur compounds present
Dimethyl sulfate, distilled
Silica gel, particle size 0.063–0.20 mm, cf. Sect. 12
Gases for operating the gas chromatograph:
Helium, synthetic air, oxygen or hydrogen

2.3 Solutions

Dimethyl sulfate stock solution:
7.5 µL ≙ 10 mg dimethyl sulfate is dissolved in 25 mL acetone using a syringe. This solution contains 400 µg/mL DMS.

Calibration solutions:
Solutions with dimethyl sulfate conconcentrations in the range of those of the sample solutions (desorbate) are produced from the stock solution by dilution, e.g. 2, 5, 10, 20 and 50 µg dimethyl sulfate each in 25 mL acetone. These calibration solutions must be freshly prepared each day.

3 Sampling and sample preparation

The sampling apparatus is set up as shown in Figure 1. After the gas meter has been read, the pump is switched on and the flow rate set to about 100 L/h, for example with a throttle valve (T). After the end of sampling (sampling duration about 1 hour), the gas meter is read again.
Because of various sources of interference, e.g. adsorption onto the walls, tubing should be avoided if possible in the sampling apparatus.
Water vapour present in the air sample is adsorbed by the silica gel during sampling. Because of this, or due to other interfering components that can be adsorbed, the shelf-life of the samples is very limited (cf. Sect. 8.5). They can be stored only for a maximum of three hours. Within this time period the sample must be processed further.

For desorption, about 20 mL acetone is poured onto the silica gel in the sampling tube and the desorbate is collected in a 25 mL volumetric flask. The flask is filled to the mark with acetone.
During desorption, water adsorbed by the silica gel is also desorbed and dissolved in the acetone. Dimethyl sulfate can therefore only be stored for a limited period of time in the desorbate (cf. Sect. 8.5). Gas chromatographic analysis should therefore take place immediately, at the latest, however, within two hours.

4 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Gas chromatograph Carlo Erba, model 2150, with flame photometric detector, model 250. Between the column and detector there was a three-way valve for discharging the acetone so that it did not reach the detector.	
Column:	Material:	Stainless steel
	Length:	120 cm
	Internal diameter:	3 mm
	Stationary phase:	10% OS 138 (polyphenyl ether) on Gaschrom Q W DMCS
	Particle size:	80–100 mesh
Temperatures:	Injector block:	200 °C
	Column:	160 °C, isothermal
	Detector:	200 °C
Flow rates:	Carrier gas	Helium, 150 mL/min
	Synthetic air	30 mL/min (pressure 250 kPa)
	Oxygen	30 mL/min (pressure 120 kPa)
	Hydrogen	85 mL/min (pressure 150 kPa)
Photomultiplier voltage:	710 V (cf. Sect. 11)	

5 Analytical determination

After the operating conditions have been set as described above (cf. Sect. 4), the gas chromatograph is left running until the base line is drift-free and interference-free (cf. Sect. 9).
For analysis 20 µL of the desorbate is injected into the gas chromatograph and the height or area of the dimethyl sulfate peak is determined. The retention time for dimethyl sulfate is about 1 minute under the conditions given in Section 4.

6 Calibration

Calibration is carried out according to the external standard method. 20 µL of each of the calibration solutions (cf. Sect. 2.2) are injected into the gas chromatograph.
A calibration curve is not drawn because of the possible fluctuations in sensitivity of the gas chromatographic system. For calibration the heights or areas of the dimethyl sulfate peaks of the calibration solutions are compared with height or area of the peak produced by the desorbate.
Analytical determination and calibration should be carried out with the same device settings and the same syringe.

7 Calculation of the analytical result

The dimethyl sulfate concentration in the air sample in mg/m^3 is calculated according to the equation:

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

For the calculation of the concentration c_v in mL/m^3 from c_w at 20 °C and 1013 hPa:

$$c_v = 0.19 \cdot c_w \tag{2}$$

Legend:
c_w Dimethyl sulfate concentration in the sample air in mg/m^3
c_v Dimethyl sulfate concentration in the sample air in mL/m^3 (ppm)
w Weight of dimethyl sulfate in the sample solution (desorbate) in µg corrected by the blank value
V Air sample volume in L

8 Reliability of the method

8.1 Precision

The relative standard deviation for the whole procedure (collaborative study) with dry test gas was $\pm$ 25 %.

8.2 Quantification limit

The absolute quantification limit is 3 ng dimethyl sulfate.
The relative quantification limit is 0.008 mL/m^3 (ppm) $\triangleq$ 0.04 mg/m^3 dimethyl sulfate for a 100 L air sample, 25 mL desorbate, and a 20 µL injection volume.

8.3 Selectivity

The method described is selective as a result of the combination of gas chromatographic separation and sulfur-specific detection.

8.4 Recovery

To determine the recovery, the sampling apparatus shown in Figure 1 was used. A U-tube was connected to the sampling tube using ground glass joints. 0.025 mg dimethyl sulfate dissolved in acetone was placed in the U-tube and about 500 L air was drawn through the tube. Quantitative determination of the dimethyl sulfate was carried out according to the external standard method.
From 12 measurements a mean recovery of 90 $\pm$ 10% was calculated. Although this value is achieved with as little as 3 g silica gel in the tube, in this method, to be on the safe side, 10 g silica gel is used. The fluctuations in recovery are attributed mainly to differences in the humidity of the air drawn through the U-tube. In range-finding studies it was further demonstrated that when 10 g silica gel is used, the whole amount of dimethyl sulfate is contained in the first 10 mL of the desorbate.

8.5 Shelf life

As a result of hydrolysis, dimethyl sulfate can only be stored for a limited period of time on silica gel and in the acetone solution as the silica gel itself already contains water and, because of the humidity of the air, additional water is adsorbed by the silica gel during sampling. In the acetone desorbates up to 7% water could be detected. The acetone solution should therefore be analysed using gas chromatography as soon as possible after desorption, certainly, however, after two hours.
Storage experiments with dimethyl sulfate on silica gel at room temperature revealed the following dimethyl sulfate losses:
after 22 hours about 40%, after 44 hours about 58% and after 104 hours about 83%.
The sample tubes should therefore be desorbed immediately after sampling, if possible, and at the latest after three hours.

9 Comments

Before each analytical series, the gas chromatographic system must be conditioned with dimethyl sulfate. A volume of 5 µL of a solution containing approx. 1 mg dimethyl sulfate in 25 mL acetone is injected into the gas chromatograph twice. Then, by injecting 20 µL acetone, it is checked that no memory effects occur. If necessary acetone must be injected into the system again. It has proved advantageous to use the column only for dialkyl sulfate analyses.

10 Notes on the procedure

In practice most cases are discontinuous exposure. The results obtained after sampling for about 1 hour are therefore suitable for evaluating work areas.

11 Manufacturers

Pump:
e.g. Edwards, Kniese & Co, Hochvakuum GmbH, Marburg,
trivac pump S2A (or ,4A), from Leybold-Heraeus GmbH & Co KG, Köln,
Du Pont Instruments,
Supplier in Germany: DEHA-Haan & Wittmer GmbH, Friolzheim

Silica gel:
e.g. E. Merck AG, Darmstadt 2 (Article No. 7734),
Chemie-Mineralien KG, Bremen (Silicagel 958)

Pre-coated thin-layer chromatographicplates:
e.g. Kieselgel-60-Fertigplatten,
E. Merck AG, Darmstadt 2 (Article No. 5721)

Gas chromatograph:
e.g. Carlo Erba,
Supplier in Germany: Erba Science, Hofheim/Ts.

12 References

[1] *Gilland JC, Bright AP* (1980) Determination of dimethyl and diethyl sulfate in air by gas chromatography. Am. Ind. Hyg. Assoc. J. 41: 459–461.
[2] *Keller J* (1974) Bestimmung von Dimethylsulfatspuren in der Luft. Z. Anal. Chem. 269: 206–208.

3 Sampling with a pump, adsorption on Tenax-TA, desorption and gas chromatography

Principle: With a pump a measured air volume is drawn through Tenax-TA. After desorption with methyl acetate, the DMS is determined using gas chromatography with a sulfur-specific flame-photometric detector (FPD).

Technical data:

Quantification limit: absolute: 3 ng DMS,
relative: 0.003 mL/m^3 (ppm) ≙ 0.015 mg/m^3 DMS for 10 L air sample.

Selectivity: The method is selective as a result of the combination of gas chromatographic separation and sulfur-specific detection.

Advantages: Selective for the determination of DMS,
low sensitivity to humidity and ammonia,
longer shelf life of the loaded tubes and desorbate,
determination of short-term exposures possible.

Disadvantages: Concentration peaks during sampling time not indicated,
time-consuming.

Apparatus: Pump with gas meter or flow meter,
adsorption tubes with Tenax-TA,
gas chromatograph with FPD.

Detailed description of the method

Contents

1 Summary

This method permits the determination of DMS concentrations in working areas averaged over the sampling time after personal and stationary sampling.
With a pump, which is carried by a person or fixed in a stationary position, a measured air volume is drawn through a glass tube filled with Tenax-TA. The DMS is adsorbed on Tenax-TA and then desorbed with methyl acetate. Analysis is carried out using a chromatograph equipped with an FPD.
The absolute quantification limit is 3 ng DMS.
The relative quantification limit is 0.003 mL/m^3 (ppm) $\triangleq$ 0.015 mg/m^3 DMS for a 10 L sample.
The method has been tested for dimethyl sulfate and diethyl sulfate.

2 Equipment, chemicals and solutions

2.1 Equipment

For sampling and sample preparation:
Pump with gas meter or flow meter
Sampling tube: A glass tube which can be closed with plastic caps is filled with about 50 mg Tenax-TA. The Tenax-TA is held in place with small plugs of silanised glass wool. The dimensions of the sampling tubes must match the dimensions of the sampling head of the pump. Sampling tubes of 50 mm in length, with a 6 mm external diameter and a 4 mm internal diameter have proved suitable. 50 mg Tenax-TA in a tube of this size fills 35 mm of the tube.
Sample vial, 2 mL volume, with polytetrafluoroethylene (PTFE)-coated septa and aluminium crimp caps
Crimper for closing the sample vials

For analysis:
Gas chromatograph with flame-photometric detector, packed analytical column and three-way valve
Recording evaluation unit analysis device: Compensation recorder or computing integrator

2.2 Chemicals

Methyl acetate, analytical grade
Tested to ensure that there are no interfering sulfur compounds present.
Dimethyl sulfate, distilled
Tenax-TA, 60–80 mesh
Gases for operating the gas chromatograph:
Helium, synthetic air, oxygen and hydrogen

2.3 Solutions

Dimethyl sulfate stock solution:
Solution of 200 µg DMS in 1 mL methyl acetate.
With a syringe 7.5 µL ≙ 10 mg dimethyl sulfate is dissolved in 50 mL methyl acetate.

Calibration solutions:
Solutions of e.g. 2, 5, 10, 20 and 50 µg dimethyl sulfate each in 50 mL methyl acetate are prepared from the stock solution by dilution.

3 Sampling and sample preparation

A glass tube filled with Tenax-TA is opened and connected to the pump. During working hours the pump and tube are carried by a person or used in a stationary position. The flow rate is set to about 4 L/h.
After sampling, the contents of the tube are transferred to a sample vial (cf. Sect. 2.1). After the addition of 1 mL methyl acetate the sample vial is closed with septum and cap and shaken for 1 minute. After settling of Tenax-TA the supernatant solution (desorbate) is used for gas chromatographic analysis.

4 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Gas chromatograph Carlo Erba, model 2150, with flame photometric detector, model 250 Between the column and detector there was a three-way valve. This is necessary for discharging the methyl acetate, which can cause considerable interference.	
Column:	Material:	Stainless steel
	Length:	120 cm
	Internal diameter:	3 mm
	Stationary phase:	10% OS 138 (polyphenyl ether) on Gaschrom Q
	Particle size:	80–100 mesh
Temperatures:	Injector block:	200 °C
	Column:	160 °C, isothermal
	Detector:	200 °C
Carrier gas:	Helium, flow rate 150 mL/min	
Detector gases:	Synthetic air, flow rate 30 mL/min Oxygen, flow rate 30 mL/min Hydrogen, flow rate 85 mL/min	
Photomultiplier voltage:	710 V	

5 Analytical determination

After conditioning the gas chromatographic system (cf. Sect. 9), 20 µL of the desorbate is injected into the gas chromatograph for analytical determination and the height or area of the dimethyl sulfate peak is determined. The retention time for dimethyl sulfate is about 1 minute under the conditions given in Section 4.

6 Calibration

A calibration curve is not drawn because fluctuations in sensitivity of the gas chromatographic system are possible.
Calibration is carried out according to the external standard method. 20 µL of each of the calibration solutions (cf. Sect. 2.2) are injected into the gas chromatograph.
After gas chromatographic analysis of the sample solution (desorbate, cf. Sect. 5), the calibration solutions whose peak height or area for DMS are nearest in size to the DMS peak of the sample solution are used to calculate the analytical results.
Analytical determination and calibration should be carried out with the same device settings and the same syringe.
To ensure that the Tenax-TA and methyl acetate do not contain any interfering impurities, 1 mL methyl acetate is added to about 50 mg of the Tenax-TA used and analysed.

7 Calculation of the analytical result

The dimethyl sulfate concentration in the air sample is calculated in mg/m^3 according to Equation (1):

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

For the calculation of the concentration c_v in mL/m^3 from c_w at 20 °C and 1013 hPa:

$$c_v = 0.19 \cdot c_w \tag{2}$$

Legend:
c_w Dimethyl sulfate concentration in the air sample in mg/m^3
c_v Dimethyl sulfate concentration in the air sample in mL/m^3 (ppm)
w Weight of dimethyl sulfate in the sample solution (desorbate) in µg
V Air sample volume in L

8 Reliability of the method

8.1 Precision

The relative standard deviation for the whole procedure was ± 12% (n = 10, P = 95%).

8.2 Quantification limit

The absolute quantification limit was 3 ng DMS.
The relative quantification limit was 0.003 mL/m^3 (ppm) ≙ 0.015 mg/m^3 DMS for a 10 L air sample, 1 mL desorbate, and a 20 µL injection volume.

8.3 Selectivity

As a result of the combination of gas chromatographic separation and sulfur-specific detection, the method described is selective.

8.4 Recovery

To determine the recovery, 50 µL toluene in which 1 µg DMS was dissolved was injected into the sampling tube and then 16 L air was drawn through the tube with a flow rate of 2 L/h. 19 determinations yielded a recovery of >93%.

8.5 Shelf life

Loaded sampling tubes and calibration solutions can be stored at room temperature for at least 10 days without losses.

9 Notes on the procedure

Before each analytical series, the gas chromatographic system must be conditioned with dimethyl sulfate. A volume of 5 µL of a solution containing about 1 mg dimethyl sulfate in 50 mL methyl acetate is injected into the gas chromatograph twice. Then, by injecting 20 µL methyl acetate, it is checked that no memory effects occur. If necessary methyl acetate must be injected again.
It has proved advantageous to use the column only for dimethyl sulfate analyses.

10 Manufacturers

Pump:
e. g. Model 4903, Compur Electronic, Munich

Tenax-TA:
e. g. Chrompak Deutschland, Müllhein/Baden,
Macherey-Nagel GmbH & Co KG, Düren

Gas chromatograph:
e. g. Carlo Erba,
Supplier in Germany: Erba Science, Hofheim/Ts.,
Siemens AG, Karlsruhe

4 Sampling with a pump adsorption on Tenax-TA, desorption, gas chromatography and mass-selective detection

This method permits the determination of dimethyl sulfate (DMS) concentrations in working areas averaged over the sampling time after personal or stationary sampling.

Principle: With a pump a measured air volume is drawn through a Tenax tube. The adsorbed dimethyl sulfate is desorbed with toluene and analysed using a gas chromatograph with mass selective detector

Technical data:

Quantification limit: absolute: 0.4 ng dimethyl sulfate,
relative: 0.01 mg/m^3 dimethyl sulfate for 20 L air sample, 1 mL of desorption solution and 2 µL injection volume.

Selectivity: The method is selective as a result of the combination of gas chromatographic separation and mass-selective detection.

Advantages: Both personal and selective sampling are possible.

Disadvantages: Concentration peaks not recorded.

Apparatus: Pump,
Gas meter or flow meter,
Tenax tubes,
Gas chromatograph with mass selective detection

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:

Pump, suitable for a flow rate of 50 mL/min (e.g. PP1 from Gilian (supplier in Germany: GSM GmbH, Neuss-Nerf))

Gas meter or flow meter

A glass tube which can be closed with plastic caps is filled with about 50 mg Tenax-TA. The Tenax-TA is held in place with small silanised glass wool plugs. The dimensions of the sampling tubes must match the dimensions of the sampling head of the pump. Sampling tubes of 50 mm in length, with a 6 mm external diameter and a 4 mm internal diameter have proved suitable. 50 mg Tenax-TA in a tube of this size fills 35 mm of the tube.

Caps for the opened Tenax tubes

For sample preparation and analysis:

50 mL Volumetric flasks

2 and 5 mL Sample vials with polytetrafluoroethylene (PTFE)-coated septa and aluminium crimp caps

Crimper for closing the sample vials

Shaking machine

0.5 mL and 1 mL Pipettes
10, 50 and 100 µL Microlitre syringes
Gas chromatograph with mass-selective detector
Evaluation unit

1.2 Chemicals

Dimethyl sulfate, purity at least 99% (e.g. from Fluka, 89231 Neu-Ulm)
Toluene, dried over a molecular sieve (desorption solvent)
Gases for operating the gas chromatograph:
Helium, suitable for operating a mass-selective detector in selected ion monitoring mode (SIM mode)

1.3 Solutions

DMS stock solution:
Solution of 0.2 mg DMS in 1 mL toluene.
A few millilitres of the desorption solvent toluene are placed in a 50 mL volumetric flask and 7.5 µL (10 mg) DMS is added with a 10 µL syringe. The flask is then filled to the mark with toluene.

Calibration solutions:
Solutions of 0.2, 2 and 4 µg DMS per mL toluene.
Volumes of 50 µL, 0.5 mL and 1 mL stock solution are each pipetted into a 50 mL volumetric. flask containing a few millilitres of toluene. The flask is then filled to the mark with toluene. With these solutions a concentration range of 0.01 to 0.2 mg/m^3 is covered for an air sample volume of 20 L and 1 mL desorbate.

2 Sampling

A Tenax tube is opened and connected to the pump. The flow rate is set to approx. 3.3 L/h. With sampling for about 6 hours this corresponds to an air sample volume of approx. 20 L. During working hours the pump and tube are carried by a person or used in a stationary position. After sampling, the tubes are closed with caps. The method was tested up to an air sample volume of 40 L with a maximum flow rate of 4 L/h.

3 Analytical determination

3.1 Sample preparation and analysis

The contents of the loaded Tenax tube are transferred to a 5 mL sample vial. After the addition of 1 mL toluene the vial is closed, carefully shaken for 30 minutes and immediately analysed. To ensure that the toluene and Tenax-TA used do not contain any interfering substances, the filling of an unloaded tube is treated as described above (blank value solution).
2 µL desorbate and 2 µL blank value solution are injected into the gas chromatograph. Quantitative evaluation of the chromatograms is carried out according to the external standard method.

3.2 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Gas chromatograph Hewlett-Packard 5890 with MSD HP 5970, split/splitless injector and autosampler HP 7673.	
Column:	Material:	Quartz capillary
	Length:	50 m
	Internal diameter:	0.20 mm
	Stationary phase:	95% methyl silicone + 5% methyl phenyl silicone (HP-5 from Hewlett-Packard)
	Film thickness:	0.33 µm
Temperatures:	Injector:	200 °C,
	Transfer line:	250 °C
	Furnace temperature programme:	
	Starting temperature:	50 °C, 2 min isothermal
	Heating rate 1:	10 °C/min to 220 °C
	Heating rate 2:	30 °C/min
	Final temperature:	250 °C, 15 min isothermal
Injection mode:	Splitless, 1 min	
Carrier gas:	Helium, column pressure 180 kPa	
Injection volume:	2 µL	
Ionisation mode:	Electron-impact ionisation (70 eV)	
Detection mode:	Selected ion monitoring (SIM mode)	
Recorded masses (m/z):	66, 95, 96	
Dwell time:	200 ms/recorded mass	

4 Evaluation

4.1 Calibration

2 µL of each of the calibration solutions described in Section 1.2 are injected into the gas chromatograph. The calibration curve is obtained by plotting the measured peak areas against the concentrations in µg/mL contained in the various calibration solutions. The calibration curves are not linear for the whole concentration range tested. Within narrow concentration ranges, however, the calibration curves are sufficiently linear. The non-linear calibration curve can be drawn by joining the points with straight lines.

4.2 Calculation of the analytical result

The DMS concentration by weight in the air sample in mg/m^3 is calculated according to Equation (1):

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

For the calculation of the concentration c_v in mL/m^3 from c_w at 20 °C and 1013 hPa:

$$c_v = 0.19 \cdot c_w \tag{2}$$

Legend:
c_w Dimethyl sulfate concentration in the air sample in mg/m^3
c_v Dimethyl sulfate concentration in the air sample in mL/m^3 (ppm)
w Weight of dimethyl sulfate in the desorbate in µg determined from the corresponding calibration curve
V Air sample volume in L
η Recovery rate

5 Reliability of the method

5.1 Accuracy and recovery

5 sampling tubes were each loaded 0.4, 4 or 8 µg dimethyl sulfate (contained in 100 µL calibration solution of the concentration 4 µg/mL, 20 µL or 40 µL stock solution, in all 15 tubes). Then laboratory air (15–25% relative humidity) was drawn through each tube for about 6 hours at a flow rate of 3.3 L/h. The spiked weights correspond to concentrations of 0.02 to 0.4 mg/m^3 for an air sample volume of 20 L. The obtained relative standard deviations are shown in Table 1:

Table 1. Standard deviation (rel.) *s*.

Concentration mg/m^3	Standard deviation (rel.) *s* %
0.02	4.1
0.2	1.6
0.4	3.2

The recovery rate was about 0.8 for an air volume of 20 L and a flow rate of about 3.3 L/h.

5.2 Quantification limit

The absolute quantification limit is 0.4 ng. This corresponds to 0.2 µg per Tenax tube or sample.
The quantification limit was determined according to DIN 32 645 as a multiple of the standard deviation of the method.
The relative quantification limit for DMS is 0.01 mg/m^3 for a 20 L air sample, 1 mL desorbate and a 2 µL injection volume.

5.3 Selectivity

The method is selective as a result of the combination of gas chromatographic separation and mass-selective detection

6 Discussion

The shelf life (refrigerator) of dimethyl sulfate in adsorbed state is at least 14 days. The calibration solutions and the stock solution must be freshly prepared after 48 hours at the latest, as residual water present in the toluene decomposes the dimethyl sulfate.
Before each analytical series, the gas chromatographic system must be conditioned with dimethyl sulfate. A volume of 2 µL of a solution containing approx. 0.2 mg dimethyl sulfate in 1 mL toluene is injected into the gas chromatograph twice. Then, by injecting 2 µL toluene, it is checked that no memory effects occur. If necessary toluene must be injected into the system again.
It has proved advantageous to use the column only for dialkyl sulfate analyses.

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Federation of the Employment Accidents Insurance Institutions of Germany
(Hauptverband der Berufsgenossenschaften)
Centre for Accident Prevention and Occupational Medicine
Alte Heerstraße 111, 53757 Sankt Augustin
Expert Committee Chemistry

Carcinogenic substances Order number: BGI 505-60E
Established methods Issue: February 1996

Method for the determination of dinitrotoluenes

Method tested and recommended by the Berufsgenossenschaften for the determination of dinitrotoluenes 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 adsorption on Tenax,
gas chromatography after desorption.
"Dinitrotoluenes-1-GC"
(Issue: February 1996)

IUPAC name:	**CAS No:**
1-methyl-2,3-dinitrobenzene	602-01-7
1-methyl-2,4-dinitrobenzene	121-14-2
1-methyl-2,6-dinitrobenzene	606-20-2
1-methyl-3,4-dinitrobenzene	610-39-9
1-methyl-3,5-dinitrobenzene	618-85-9

1 Sampling with a pump and adsorption on Tenax, gas chromatography after desorption

This method permits the determination of isomeric dinitrotoluenes (DNT) concentrations in working areas averaged over the sampling time after personal or stationary sampling.

Principle: With a pump a measured air volume is drawn through a Tenax tube. The dinitrotoluenes are solids at room temperature. For this reason the definition of inhalable dust fraction [1] must be taken into account during sampling. The adsorbed dinitrotoluenes are desorbed with acetone and determined by gas chromatography.

Technical data:

Quantification limit: absolute: 12 pg for each DNT isomer,
relative: 1 μg/m^3 of each DNT isomer for 60 L air sample, 5 mL desorption solution and 1 μL injection volume.

Selectivity: Interfering components may cause too high values. In general, interferences can be eliminated by selecting a different column.

Advantages: Both personal and selective sampling are possible.

Disadvantages: No indication of concentration peaks.

Apparatus: Pump with gas meter or flow meter,
Tenax tubes,
gas chromatograph with electron capture detector (ECD).

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:

Pump, suitable for a flow rate of 1 mL/min (e. g. S 2500 from DuPont Instruments, supplier in Germany: DEHA-Haan & Wittmer GmbH, Friolzheim)

Gas meter or flow meter

Adsorption tubes with Tenax, standardised, consisting of two Tenax fillings of about 50 and 100 mg separated with glass wool (e. g. Catalogue No 226-35-03 from SKC, supplier in Germany: MTC-GmbH, Müllheim)

Caps for the opened Tenax tubes

For sample preparation and analysis:

2 and 5 mL Vials, amber, with aluminium crimp caps with polytetrafluoroethylene (PTFE)-coated septa

Crimper

Shaking machine

5 and 10 mL Volumetric flask

5, 10, 25, 50 and 100 µL syringes

Gas chromatograph with electron capture detector (ECD)
Data analysis device

1.2 Chemicals

1-Methyl-2,3-dinitrobenzene (2,3-DNT), purity at least 99% (e. g. Riedel-de-Haen AG, Seelze)
1-Methyl-2,4-dinitrobenzene (2,4-DNT), purity at least 99% (e. g. Merck KGaA, Darmstadt)
1-Methyl-2,6-dinitrobenzene (2,6-DNT), purity at least 99% (e. g. Riedel-de-Haen AG, Seelze)
1-Methyl-3,4-dinitrobenzene (3,4-DNT), purity at least 99% (e. g. Aldrich-Chemie, Stuttgart)
1-Methyl-3,5-dinitrobenzene (3,5-DNT), purity at least 99% (e. g. Promochem GmbH, Wesel)
1,2-Dinitrobenzene, purity at least 99% (internal standard) (e. g. Riedel-de-Haen AG, Seelze)

Gases for operating the gas chromatograph:
Helium, purity suitable for operating an ECD
Nitrogen, purity suitable for operating an ECD

1.3 Solutions

Desorption solution:
Acetone.

DNT stock solution I:
Solution of 50 mg of each of the DNT isomers in 10 mL acetone.
Approx. 50 mg of each of the DNT isomers is weighed into a 10 mL volumetric flask to the nearest 0.01 mg. The volumetric flask is then filled to the mark with acetone.

DNT stock solution II:
Solution of 1,25 mg of each of the DNT isomers in 10 mL acetone.
250 µL of stock solution I is transferred to a 10 mL volumetric flask already containing acetone. The volumetric flask is then filled to the mark with acetone.

Internal standard solution I:
Solution of 200 mg 1,2-dinitrobenzene in 10 mL acetone.
Approx. 200 mg 1,2-dinitrobenzene is weighed into a 10 mL volumetric flask to the nearest 0.01 mg. The volumetric flask is then filled to the mark with acetone.

Internal standard solution II:
Solution of 2 mg 1,2-dinitrobenzene in 10 mL acetone.
100 µL of internal standard solution I is pipetted into a 10 mL volumetric flask already containing a few millilitres of acetone. The volumetric flask is then filled to the mark with acetone.

DNT calibration solutions:
Solutions of 0.25, 0.63, 1.25, 2.5, 5.0 and 7.5 µg of each of the DNT isomers and 1 µg 1,2-dinitrobenzene in 5 mL acetone.
2, 5, 10, 20, 40 and 60 µL of DNT stock solution II are each pipetted into 5 ml volumetric flasks already containing a few millilitres of acetone. Then 5 µL internal standard solution II is added to each and the volumetric flasks are filled to the mark. With these solutions and an air sample volume of 60 L a concentration range of 4 to 125 µg/m^3 of each of the DNT isomers in air is covered.

2 Sampling

The melting points of the dinitrotoluenes are in the range from 50 to 70 °C. They can occur in the work area to be investigated in particle form. Therefore, the definition of inhalable dust fraction [1] must be taken into account during sampling. A Tenax tube is opened and connected to the pump. During working hours the pump and tube are worn by a person or used in a stationary position. After sampling, the tube is closed with caps. The method was tested with an air sample volume of 60 L and a flow rate of 0.5 L/min.

3 Analytical determination

3.1 Sample preparation and analysis

The contents of the loaded Tenax tube are transferred to a 5 mL vial. 5 mL acetone and 5 µL of internal standard solution II are added and the vial is closed and carefully shaken for 1 hour. Then the supernatant solution (desorbate) is transferred to a 2 mL vial and this is also closed. To ensure that the acetone and the Tenax do not contain any impurities, the filling of an unloaded tube is treated as described above (blank solution).
1 µL of the desorbate and of the blank solution are injected into the gas chromatograph and a gas chromatogram is recorded as described in Sect. 3.2.
Quantitative determination is carried out according to the internal standard method.

3.2 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Gas chromatograph, Hewlett-Packard 5890 with ECD, split/splitless injector and autosampler HP 7673

Column:	Material:	Quartz capillary
	Length:	50 m
	Internal diameter:	0.25 mm
	Stationary phase:	Rtx-200 from Restek
	Film thickness:	0.25 µm
Temperatures:	Injector:	250 °C
	Detector:	300 °C.
	Furnace temperature programme:	
	Starting temperature:	80 °C, 2 min isothermal
	Heating rate 1:	3 °C/min
	Intermediate temperature:	120 °C, 10 min isothermal
	Heating rate 2:	3 °C/min
	Final temperature:	260 °C, 5 min isothermal
Injection mode:	Split	
Split:	20 mL/min	
Carrier gas:	Helium, 2 mL/min	
Make-up gas:	Nitrogen, 60 mL/min	
Injection volume:	1 µL	

4 Evaluation

4.1 Calibration

1 µL of each of the calibration solutions is injected into the gas chromatograph. The calibration curve is obtained by plotting the measured peak area ratios against the ratios of the individual weights of the DNT isomers to the weight of 1,2-dinitrobenzene in 5 mL of the respective calibration solution.

4.2 Calculation of the analytical result

The calibration curve is not linear over the whole concentration range tested. Within narrow concentration ranges the calibration curves are, however, sufficiently linear. The non-linear calibration curve can therefore be constructed by drawing straight lines between the plotted points.
The concentration by weight of the individual DNT isomers in the air sample in mg/m^3 is calculated according to Equation (1):

$$c_w = \frac{r \cdot w_{is}}{V \cdot \eta} \tag{1}$$

The concentration by volume c_v in mL/m^3 is calculated from c_w for 20 °C and 1013 hPa according to Equation (2):

$$c_v = 0.13 \cdot c_w \quad (2)$$

Legend:
c_w Concentration by weight of the DNT isomers in the air sample in mg/m^3
c_v Concentration by volume of the individual DNT isomers in the air sample in mL/m^3 (ppm)
w_{is} Weight of 1,2-dinitrobenzene (internal standard) in the desorbate in µg
r Ratio calculated from the calibration curve of the weight of the individual DNT isomer to 1,2-dinitrobenzene (internal standard) in the desorbate
V Air sample volume in L
η Recovery rate

5 Reliability of the method

5.1 Accuracy and recovery

Six separate sampling tubes were loaded with 0.25, 2.5 and 7.5 µg of each DNT isomer (injection with calibration solutions). Laboratory air (30–40% relative humidity) was then drawn through each tube at a flow rate of 0.5 L/min for 2 hours. The given dinitrotoluene weights correspond to concentrations of 4.2 to 125 µg/m^3 with a 60 L air sample volume. Implementation of the described sample preparation and analysis yielded the relative standard deviations listed in Table 1.

Table 1. Standard deviation (rel.) *s*.

Concentration µg/m^3	Standard deviation (rel.) *s* %				
	2,3-DNT	2,4-DNT	2,6-DNT	3,4-DNT	3,5-DNT
4.2	8.4	7.8	7.7	8.0	7.8
42	2.3	3.0	2.4	2.6	2.5
125	2.1	1.5	3.2	2.8	3.3

Under the conditions described, the recovery rate was over 0.9 for an air sample volume of 60 L and a flow rate of 0.5 L/min.

5.2 Quantification limit

The absolute quantification limit is 12 pg of DNT isomer. This corresponds to 0.06 µg DNT isomer/Tenax tube or sample.
The relative quantification limit is 1 µg/m^3 for a 60 L air sample, 5 mL desorbate and 1 µL injection volume.

5.3 Selectivity

Under the given GC conditions all DNT isomers are separated. In case of interfering components a column with other separation characteristics should be used.

6 Discussion

The shelf life of the loaded tubes in the dark and at room temperature is at least 14 days without losses.

7 References

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Metal-working fluid aerosols and vapours

Method number 1

Application Air analysis

Analytical principle Infrared spectrometry

Completed in November 1994

Summary

Metal-working fluid aerosols and vapour can be sampled with the combined inhalable aerosol vapour sampler (GGP) [1]. The aerosols are collected on a glass fibre filter and the vapour on a cartridge filled with XAD-2 adsorber resin.
Elution is carried out with tetrachloroethylene or with 1,1,2-trichlorotrifluoroethane. After filtration the analysis solutions are analysed by measuring the integral extinction in the infrared wave number range 3000–2800 cm^{-1}.

Precision:	Standard deviation (rel.)	s = 2.8–3.6%
	Mean variation	u = 6.4–8.3% for n = 11 determinations with a concentration range of 2.4–24 mg/m^3
Quantification limit:	0.5 mg/m^3 for a sample volume of 420 L	
Recovery rate:	$\eta \geq 0.95$ (95%)	
Operating range:	0.5–300 mg/m^3	
Sampling recommendation:	Sampling time:	2 h
	Sample volume:	420 L

Metal-working fluids

In metal working, metal-working fluids are used for moulding (e. g. casting), forming (e. g. rolling), changing of material properties (e. g. hardening) and cutting (e. g. machining) [2]. Generally, the composition of the metal-working fluids is different for all these processes. The properties required are achieved by a combination of various individual components. A list of the components (additives) of metal-working fluids is up-

dated and published regularly by the Commission of the Deutsche Forschungsgemeinschaft [3].
When metal-working fluids are being used, vapour and aerosols may be given off at the workplace. As the metal-working fluids represent complex multi-component mixtures, investigations of the toxic effects on the organism after inhalation of aerosols and vapour have been not successful. It must be assumed that the irritating and allergising effects are mainly caused by the additives [3]. Nevertheless, exposure should be limited to improve occupational hygiene and to reduce the effects on employees exposed to metal-working fluids. On the basis of this analytical procedure a threshold limit value should be evaluated which takes into account technical feasibility and the experience gained in occupational health and toxicology [4].

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Metal-working fluid aerosols and vapours

Method number	1
Application	Air analysis
Analytical principle	Infrared spectrometry
Completed in	November 1994

Contents

1 General principles

Metal-working fluid aerosols and vapour can be sampled with the combined inhalable aerosol vapour sampler (GGP) [1]. The aerosols are collected on a glass fibre filter and the vapour on a cartridge filled with XAD-2 adsorber resin.
Elution is carried out with tetrachloroethylene or with 1,1,2-trichlorotrifluoroethane. After filtration the analysis solutions are analysed by measuring the integral extinction in the infrared wave number range 3000–2800 cm^{-1}.

2 Equipment, chemicals and adsorbents

2.1 Equipment

Pump, flow rate 210 L/h
Gas meter
Total dust gas sampler to collect the respirable fraction according to DIN-EN-481 [5]
Fourier transformation infrared spectrometer
1000 mL Soxhlet apparatus
30 mL Vials equipped with screw caps and PTFE-coated septa
Disposable PTFE filters
10 mL Glass syringe with Luer lock
10 mm Quartz glass cuvettes for infrared spectroscopy
Laboratory sieve, 0.5 mm mesh

2.2 Chemicals

Tetrachloroethylene for spectroscopic use or 1,1,2-Trichlorotrifluoroethane for spectroscopic use
Tetrachloroethylene, high grade or 1,1,2-Trichlorotrifluoroethane, high-grade (With the solvent used, the reagent blanks in the range of 3000–2800 cm^{-1} must be as low as possible. The same batches of solvents should be used during measurement and calibration if possible.)

2.3 Adsorbents and filter material

Glass fibre filters, binder-free
(The blank value of the filter material must always be checked.)
XAD-2 adsorber resin
With fresh XAD-2 adsorber resin (grain-size range 0.2–0.9 mm) the fine grains have to be removed before use. For this purpose the XAD-2 is first dried overnight at 50 °C in

a drying cabinet. Then the fine grains < 0.5 mm are separated by sieving in a laboratory sieve. The XAD-2 obtained has a grain-size range of 0.5–0.9 mm. Before use, fresh and also used XAD-2 must be purified to ensure a constantly low blank value. The XAD-2 is extracted twice for 16 hours with fresh pure tetrachloroethylene (1,1,2-trichlorotrifluoroethane), in a Soxhlet apparatus. The purified XAD-2 is then left in a fume cupboard overnight and then dried in a drying cabinet for 24 hours at 50 °C. Before use the blank value must be checked. In a 10 mL standard solution it must not exceed a concentration of 0.01 mg/mL.

3 Calibration

As a great number of metal-working fluids of different composition are used calibration must be carried out with the metal-working fluid used at the workplace.
Problems do not occur with metal-working fluids which are not miscible with water. Normally they dissolve completely in tetrachloroethylene or 1,1,2-trichlorotrifluoroethane.
In the case of water-miscible metal-working fluids, the metal-working fluid concentrate should be used as a calibration standard. As the metal-working fluid concentrates are often not completely soluble only the part which dissolves in tetrachloroethylene (1,1,2-trichloro-trifluoroethane) is used. If a water-miscible metal-working fluid is found to form two phases, the mixture is treated ultrasonically for 15 minutes and then centrifuged. The organic phase is used for further calibration.
Occasionally there are aqueous metal-working fluids which are completely insoluble in tetrachloroethylene (1,1,2-trichlorotrifluoroethane). Such mixtures cannot be analysed using the method described. If metal-working fluid residues are even then detected in the measured samples from the workplace air it must be investigated whether metal-working fluids are also used in the adjacent working areas. In such cases the calibration has to be carried out with the metal-working fluid used there.
A solution of 50 mg of metal-working fluid in 50 mL of solvent (tetrachloroethylene, 1,1,2-trichlorotrifluoroethane for spectroscopic use) serves as stock solution. By appropriate dilution, calibration solutions are prepared with the concentrations 0.1 mg/mL, 0.3 mg/mL, 0.5 mg/mL, 0.7 mg/mL and 1.0 mg/mL.
10 mL of the calibration solutions are each transferred to 3 g of the XAD-2 adsorber resin and left overnight. The analysis is carried out as described in Section 5.
The calibration curves for four different metal-working fluids are shown in Fig. 1.
The calibration solutions can be used for the calibration of the glass fibre filters because the blank value of the glass fibre filter does not influence the analytical result.

4 Sampling

4.1 Preparation of the sample collector

The glass fibre filter is placed into the filter cassette and closed with the appropriate caps. 3 g of the purified XAD-2 is filled into glass or plastic cartridges and closed with special sieves. The flow resistance must be checked. It must not exceed 10 hPa. The XAD-2 cartridges are closed with polyethylene caps and stored together with the filter capsules until sample collection.
The sample collectors prepared in this way will remain stable for at least 1 month if they are stored appropriately.

4.2 Sample collection

The filter cassette and the glass cartridge are opened, placed in the sample collector GGP and connected with a flow-stabilised pump. For personal air sampling the sample collector must be fixed in the breathing area of the person. During sampling the flow rate is 210 L/h for a sampling time of 2 h.
After sample collection the filter cassette and the glass cartridge are removed from the sample holder, closed with appropriate caps and analysed.
The loaded sample collectors should be analysed immediately if possible, but within 10 days at most.

5 Sample preparation

The filter and the XAD-2 adsorber resin are transferred separately to 30 mL glass vessels with screw caps and are each covered with 10 mL of tetrachloroethylene (1,1,2-trichloro-trifluoroethane) for spectroscopic use. Then the vessels are closed. After 16 hours the vessels are carefully shaken and the contents filtered through a disposable filter. The filtrate is transferred to the infrared cuvette.
The blank values of every batch of XAD-2 and solvent must be checked.

6 Operating conditions for infrared spectrometry

Infrared instrument:	FT-IR spectrometer
Cuvette:	10 mm quartz glass cuvette
Resolution:	2 cm^{-1} or 4 cm^{-1}
Measuring range:	3000–2800 cm^{-1}

7 Calculation of the analytical result

In the infrared spectrometric determination of metal-working fluid vapour and aerosol concentrations in the air at workplaces the blanks of the solvent and the adsorbent must be subtracted from the integral extinction of the sample solution.

$$\Delta E = E - E_{b1} - E_{b2}$$

As the binder-free glass fibre filters yield no blank values the calculation formula is reduced to:

$$\Delta E = E - E_{b1}$$

If computer-controlled FT-IR spectrometers are used, the subtraction of the integral extinction is carried out by subtracting the solvent spectra and the XAD-2 sample spectra. The concentration by weight ρ is calculated according to the metal-working fluid-related calibration function (see Section 3):

$$\rho = \frac{(\Delta E - b)}{k_i \cdot V_z} \cdot V$$

where:

ΔE Measured extinction reduced by the blank values of the solvent and the XAD-2
E_{b1} Blank value of the solvent
E_{b2} Blank value of the XAD-2
ρ Concentration by weight of the metal-working fluid in the ambient air in mg/m^3
b Ordinate section of the calibration function
k_i Specific, metal-working fluid-dependent response factor in mL/mg
V Solvent volume in mL
V_z Air sample volume in m^3

8 Reliability of the method

The characteristic data given in the following section were determined with a metal-working fluid soluble in tetrachloroethylene under the conditions described in Section 6.

8.1 Precision

To determine the precision of the method, measured amounts of the metal-working fluid were added to the XAD-2, covered with a solvent and prepared according to Section 5. The corresponding concentrations in the air relate to a sampling time of 2 hours

and a sample volume of 0.420 m^3. The relative standard deviations and the mean variations were determined from 11 individual measurements.

Number of measurements	Concentration in the solvent mg/mL	Corresponding concentration in air mg/m^3	Standard deviation %	Mean variation %
11	0.1	2.4	3.58	8.3
11	0.5	12.0	2.80	6.4
11	1.0	24.0	3.36	7.7

8.2 Recovery rate

To check the recovery rate, measured amounts of metal-working fluids were transferred to the XAD-2 and 0.420 m^3 of air was drawn through the adsorption phase. Preparation was carried out according to Section 5.
The recovery rate was constantly >95% in the range of 0.5–300 mg/m^3.

8.3 Quantification limit

Under the given conditions the quantification limit is 0.02 mg/mL. For a solution volume of 10 mL and a sample volume of 0.42 m^3 this corresponds with a concentration of 0.5 mg/m^3.

8.4 Specificity

The infrared spectrometric determination method is not specific for metal-working fluids (see Section 9).

8.5 Sample stability

The sample stability was checked for a concentration of 12 mg/m^3. The sample collectors should be analysed within 10 days.

9 Discussion of the method

The infrared spectrometric determination method is based on the measurement of the C-H stretching vibration in the IR range of 2800–3000 cm^{-1}. With this method all compounds are detected which also have infrared absorption in the indicated range. It

must be checked whether sources of emission other than metal-working fluids are present in the working area. Especially highly volatile substances such as hydrocarbons from petrol or solvents can lead to falsification of the results. The measurement must not be influenced by external sources. Even other metal-working fluids used in the factory area may strongly influence the measurement.
The measurement should preferably be carried out in working areas where the technical processes produce higher concentrations.
For the analytical determination the blank values of the solvent used and the XAD-2 should be as low as possible. The blank values of all solvents and the batches of adsorbents must be checked.

10 References

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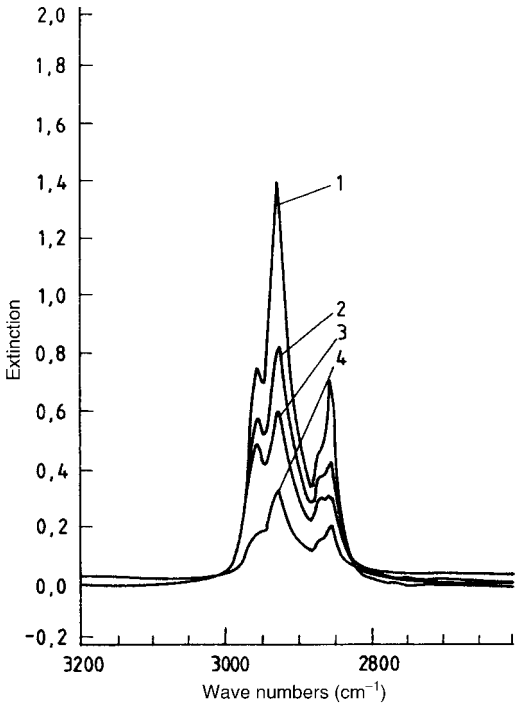

Fig. 1. Spectra of four metal-working fluids.
1 Metal-working fluid not miscible with water
2–4 Metal-working fluid miscible with water

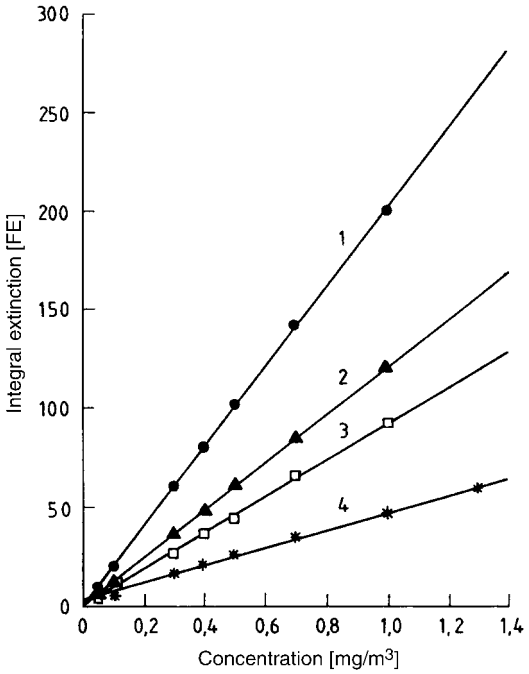

Fig. 2. Calibration curves of four metal-working fluids.
1 Metal-working fluid not miscible with water
2–4 Metal-working fluid miscible with water

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Alte Heerstraße 111, 53757 Sankt Augustin
Expert Committee Chemistry

Carcinogenic substances Order number: BGI 505-62E
Established methods Issue: December 1996

Method for the determination of *N*-nitrosomethylphenylamine (NMPA) and *N*-nitrosoethylphenylamine (NEPA)

Method tested and recommended by the Berufsgenossenschaften for the determination of *N*-nitrosomethylphenylamine (NMPA) and *N*-nitrosoethylphenylamine (NEPA) in working areas after discontinuous sampling.
For the assessment of working areas, only stationary sampling is possible:

1 Sampling with a pump and adsorption of gaseous nitrosamines in an annular denuder, gas chromatography after extraction and concentration of the extract.
"NMPA-NEPA-1-GC"
(Issue: December 1996)

IUPAC name:	**CAS No:**
N-nitrosomethylphenylamine	614-00-6
N-nitrosoethylphenylamine	612-64-6

1 Sampling with a pump and adsorption in an annular denuder, gas chromatography after extraction and concentration of the extract

This method permits the determination of *N*-nitrosomethylphenylamine (NMPA) and *N*-nitrosoethylphenylamine (NEPA) concentrations in working areas averaged over the sampling time after stationary sampling. A diffusion-based gas phase extractor (denuder) is used for sampling NMPA and NEPA. The named nitrosamines are selectively trapped. The secondary amines (methylphenylamine and ethylphenylamine) always present in the work areas in question pass through the sampling system without being trapped.

Principle: With a pump a measured air volume is drawn through the denuder at a flow rate of 8 L/min for 30 minutes.
Gaseous NMPA and NEPA are absorbed on the specially coated inside walls of the denuder. The absorbed nitrosamines are desorbed together with the coating (sink) with a mixture of 0.05 M sodium hydroxide solution and a toluene/dichloromethane mixture. Clean-up is carried out by liquid/liquid extraction. After further concentration of the sample the absorbed nitrosamines are analysed using a gas chromatograph equipped with a thermal energy analyser (TEA) detector.

Technical data:

Quantification limit: absolute: 0.1 ng NMPA or NEPA,
relative: 0.5 µg/m^3 NMPA or NEPA for 240 L air sample, 250 µL sample solution and 2 µL injection volume.

Selectivity: In the sampling system the named nitrosamines are separated from the corresponding amines, which are not collected. Semi volatile nitrosamines (e. g. N-nitrosomorpholine, N-nitrosopyrrolidine or N-nitrosodibutylamine) are incompletely deposited in the denuder system under the conditions described here. The TEA detector system is selective in combination with gas chromatographic separation. Because of the selectivity of the sampling system, interference from other organic nitrogen compounds is not to be expected.

Advantages: Selective and artefact-free determination from the gaseous phase.

Disadvantages: The sampling time is limited. Increased relative humidity (relative humidity >50%) leads to analytical values which are too low. Personal sampling is not possible.

Apparatus: Pump,
gas meter or flow meter,

annular denuder,
shaking machine,
centrifuge,
apparatus for concentrating solutions with an inert gas,
gas chromatograph with chemiluminescence detector (TEA detector).

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:

Pump, suitable for a flow rate of 8 L/min (e.g. MF 70 from BW Meßtechnik GmbH, 52074 Aachen; GSA 50-1 from GSA Meßgerätebau GmbH, 41469 Neuss; gas sampler VR 03 from Desaga, 69168 Wiesloch; MCS-30 from SKC, supplier in Germany: MTC, 79379 Müllheim)

Gas meter or flow meter (e.g. rotameter, measuring range from 1–10 L/min, gas meter,

Soap bubble flow meter, e.g. Gilibrator from Gilian, supplier in Germany: GSM GmbH, Neuss-Nerf)

Denuder, four-fold annular denuder with plane ground joints and end caps coated with polytetrafluoroethylene (PTFE) and adapter for regulating the flow (supplier in Germany: Laborgroßhandlung G. Felser, 44229 Dortmund), preparation of the denuder, cf. Sect. 1.4; sketch, cf. Appendix, Sect. 8

For sample preparation and analysis:

3, 10, 100 and 1000 mL Volumetric flasks

3 and 5 mL Sample vials with PTFE-coated septa and crimp caps
15 mL Graduated centrifuge tubes
Graduated evaporating tubes with conical base for concentration to small volumes of 0.5–1 mL
1 mL Autosampler vials with PTFE-coated caps and appropriate 150 µL conical inserts
5, 10, 25, 100, 500 µL and 5 mL Syringes
5 mL Dispensette
Flat-bed shaker (e.g. IKA, 79217 Staufen)
Laboratory centrifuge
Apparatus for concentration of solutions with an inert gas (e.g. Restek-Amchro, 65812 Bad Soden)
Gas chromatograph with split/splitless injector and TEA detector (Thermedics, supplier in Germany: Isconlab, 69123 Heidelberg)
Evaluation unit

1.2 Chemicals

Toluene, analytical grade
Dichloromethane, analytical grade
Ethanol, analytical grade
Methanol, analytical grade
Sodium hydroxide
Sodium chloride
Triethanolamine
Tetraethylene glycol
N-Nitrosomethylphenylamine (NMPA)
N-Nitrosoethylphenylamine (NEPA)
N-Nitroso-*n*-butyl-*n*-propylamine (NBPA, internal standard)

Gases for operating the gas chromatograph and for sample preparation:
Helium, purity at least 99.999%
Oxygen, medical grade
Nitrogen, purity at least 99.996%
Synthetic air free of hydrocarbons

1.3 Solutions

NMPA stock solution:
Solution of 100 µg/mL NMPA in dichloromethane.
100 mL dichloromethane are added to 1 g of the nitrosamine, which is supplied in a special safety bottle (e.g. ISO-PACK, Sigma, 82041 Deisenhofen). 100 µL of the concentrated solution of NMPA is transferred to a 10 ml volumetric flask and diluted to the mark with dichloromethane.

NEPA stock solution:
Solution of 300 µg/mL NEPA in dichloromethane (e. g. Promochem, 46485 Wesel).

Stock solution for preparing dilutions:
Solution of 10 µg/mL NMPE and 10 µg/mL NEPA in dichloromethane.
300 µL NMPA stock solution and 100 µL NEPA stock solution are transferred to a 3 ml volumetric flask and diluted to the mark with dichloromethane.

NBPA stock solution 1:
Solution of 1.3 mg/mL NBPA in ethanol.
In a 100 mL volumetric flask 129.5 mg of the nitrosamine, which are supplied in a special safety bottle (e. g. ISO-PACK, Sigma, 82041 Deisenhofen) is diluted to the mark with ethanol.

NBPA stock solution 2:
Solution of 26 µg/mL NBPA in ethanol.
60 µL of NBPA stock solution 1 is transferred to a 3 ml volumetric flask and diluted to the mark with ethanol.

Calibration solutions:
Solutions of 0.02, 0.04, 0.08, 0.10, 0.20 and 0.50 µg/mL NMPA and NEPA with internal standard.
1 mL toluene is added to each of 6 sample vials. Then 2, 4, 8, 10, 20 and 50 µL toluene are removed and replaced by the same volumes of the stock solution for preparing dilutions. Moreover 1 µL NBPA stock solution 2 is added to each and shaken. With these solutions a concentration range of 0.04–1 µg/m^3 NMPA and NEPA is covered for a 240 L air sample and 250 µL sample solution.

Elution agent mixture 1:
In an 1 L volumetric flask approx. 2 g sodium hydroxide and 30 g sodium chloride are diluted to the mark with deionised water and shaken.

Elution agent mixture 2:
Mixture of dichloromethane/toluene with internal standard.
5 mL toluene is placed in a 100 mL volumetric flask. 5 µL NBPA stock solution 2 is added. The flask is filled to the mark with dichloromethane and shaken.

Coating solution:
In a 50 mL volumetric flask10 g triethanolamine and 10 g tetraethylene glycol are diluted to the mark with methanol and shaken. This solution can be kept for several weeks.

1.4 Preparation of the denuder

Before sampling, the annular denuder is rinsed with distilled water, then again with methanol and dried in a stream of air. For coating, the denuder is completely filled with the coating solution. Then the denuder is emptied and dried in a gentle stream of nitrogen (max. 7 L/min). Prepared in this way and closed with PTFE caps the denuder has a shelf life of 2–3 weeks.

2 Sampling

For sampling, the coated denuder is fitted vertically in the sampling system with the suction opening at the bottom. An adapter is placed before the denuder to ensure a laminar air flow. The way the system is constructed is sketched in Figure 1.

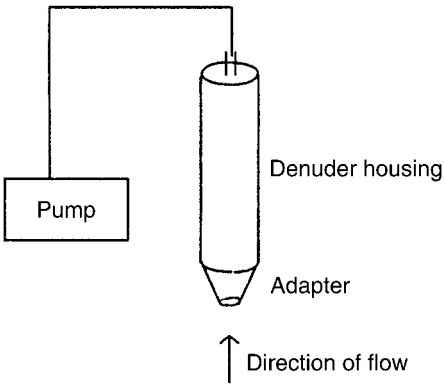


Fig. 1. Sketch of sampling system (cf. also Sect. 8, Appendix).

The flow rate is set to 8 L/min. The sampling period should not exceed 30 min. Sampling in this way for 30 minutes corresponds to an air sample volume of 240 L. After sampling, the denuder is closed with PTFE caps. The sample should be prepared and analysed immediately, if possible. After more than 7 days noticeable nitrosamine losses are observed.

3 Analytical determination

3.1 Sample preparation and analysis

5 mL of elution agent 1 and 5 mL of elution agent 2 are placed in the denuder. For an even wetting of the inner surface of the denuder and to mix the solutions well, the denuder is shaken on a flat-bed shaker for 20 min. The denuder must be placed on the shaker with its longitudinal axis in the direction of the shaking axis. To completely wet all the inner surfaces, the denuder must be rotated about the longitudinal axis after ten minutes.

The eluate is transferred to a graduated centrifuge tube and for better phase separation centrifuged for 20 min at 3000 rpm. Approximately 4 mL of the organic phase (bottom layer) is transferred with a 5 mL syringe to a graduated evaporation tube and in a gentle stream of nitrogen (rate of evaporation not greater than 1 mL/15 min) concentrated

to 150–300 µL (sample solution). Care must be taken that the sample is not warmed and that the nitrogen flow is so set that the surface of the sample is only slightly domed. The walls of the evaporation tube are rinsed with the sample solution and the concentrate transferred to an autosampler vial with conical insert. Analysis of the sample solution is carried out using GC/TEA.

To ensure that the solutions used do not contain any interfering substances, a coated, unloaded denuder is prepared and analysed (blank value).

To check the whole procedure a spiked denuder is prepared and analysed (control sample). The control analysis should yield a recovery of at least 70 %.

To spike the denuder, a short glass tube (evaporation tube) containing a defined volume of the stock solution for preparing dilutions (e. g. 5 µL) is attached to the front of the denuder. With a pump air is drawn through the denuder for 30 min at a flow rate of 8 L/min. For this purpose, the denuder should be placed horizontally as shown in Fig. 2.

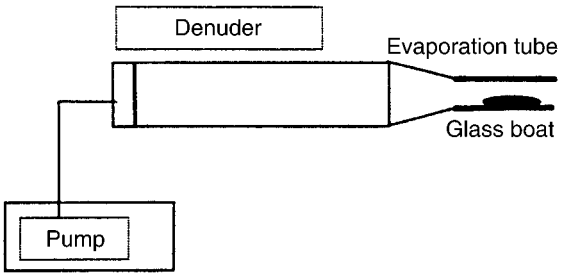


Fig. 2. Apparatus for spiking the denuder to test the preparation step.

3.2 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Gas chromatograph Sichromat 1–4 (Siemens, Karlsruhe) equipped with TEA detector 543 (Thermedics Inc., supplier in Germany: Isconlab, 69123 Heidelberg), split/splitless injector and autosampler (Siemens, Karlsruhe)	
Pre-column:	Material:	Quartz capillary, not coated, deactivated (from Chrompack, Frankfurt)
	Length:	1 m
	Internal diameter:	0.53 mm
		The pre-column prevents early contamination of the GC column and when high loads are analysed should be regularly exchanged to protect the analytical column.

Column:	Material:	Quartz capillary
	Length:	60 m
	Internal diameter:	0.53 mm
	Stationary phase:	polyethylene glycol (CP-WAX 52 CB from Chrompack, Frankfurt)
	Film thickness:	1.0 µm
Temperatures:	Injector:	130 °C
	Furnace temperature programme:	
	Starting temperature:	90 °C, 2 min isothermal
	Heating rate:	6 °C/min
	Final temperature:	140 °C, 30 min isothermal
Detector:	Interface:	210 °C
	Pyrolysis furnace:	500 °C
Injection mode:	Splitless	
Split:	25 mL/min, after 3 min	
Carrier gas:	Helium, 6.2 mL/min	
Detector:	Oxygen for operating the ozone generator, 3.6 mL/min	
Molecular sieve filter:	CTR™-Gas-Stream-Filter (Thermo Electron Corporation, supplier in Germany: Isconlab, 69123 Heidelberg)	
Injection volume:	2 µL	

4 Evaluation

4.1 Calibration

Volumes of 2 µL of the calibration solutions are injected into the gas chromatograph with the autosampler. Quantification is carried out with the aid of NBPA as internal standard. The calibration function is linear in the range from 20 to 500 ng/mL.
The calibration factor f is calculated according to Equation (1) using the peak areas for NMPA and NEPA and the internal standard NBPA obtained from the calibration solutions:

$$f = \frac{F_{is} \cdot w_c}{F \cdot w_{is}} \quad (1)$$

Legend:
f Calibration factor for NMPA or NEPA
F_{is} Peak area for the internal standard
F Peak area for the nitrosamine
w_{is} Weight of the internal standard in 1 mL of the particular calibration solution in µg
w_c Weight of the nitrosamine in 1 mL of the particular calibration solution in µg

The calibration factor is more or less the same for all calibration solutions. The mean calibration factor $\bar{f}$ can be used for calculating the analytical result.

4.2 Calculation of the analytical result

The concentration of NMPA or NEPA in the air sample in µg/m^3 is calculated according to the Equations (2) and (3):
The weight of the nitrosamine is calculated according to the following equation:

$$w = \frac{F \cdot w_{\text{ise}} \cdot \bar{f}}{F_{\text{is}}} \tag{2}$$

$$c_{\text{w}} = \frac{w \cdot 1000}{V \cdot \eta} \tag{3}$$

Legend:
w Weight of the nitrosamine in the elution solution in µg
w_{ise} Weight of the internal standard in the sample solution (enriched elution solution) in µg
F Peak area for the nitrosamine
$\bar{f}$ Mean calibration factor
F_{is} Peak area for the internal standard
c_{w} Nitrosamine concentration in the sample air in µg/m^3
V Air sample volume in L
η Recovery rate

5 Reliability of the method

5.1 Accuracy and recovery

To determine the relative standard deviation of the method 2, 5 and 10 µL of the stock solution for preparing dilutions and 10 µL of the NMPA stock solution were pipetted into the glass boat of the evaporation tube (cf. Fig. 2, Sect. 3.1). These volumes correspond to nitrosamine weights of 20 ng, 50 ng, 100 ng and 1 µg.
After the tube was attached to the denuder, ambient air was drawn through the apparatus at a flow rate of 8 L/min for 30 min. The NMPA or NEPA weights in the tube correspond to concentrations of 0.08–4.2 µg/m^3 for a 240 L air sample. The denuder was then closed and prepared and analysed as described in Sect. 3. The organic phase was concentrated to 200 µL. The procedure described was carried out six times and yielded the relative standard deviations and recoveries shown in the Table 1.

Table 1. Standard deviation (rel.) *s* and recovery.

Concentration µg/m³	Standard deviation (rel.) *s* %		Recovery rate	
	NEPA	NMPA	NEPA	NMPA
0.08	16	14	0.98	0.94
0.21	27	15	0.88	0.79
0.42	17	14	0.92	0.95
4.2	–	5	–	0.80

5.2 Quantification limit

The absolute quantification limit for NMPA or NEPA is 0.1 ng. It was determined according to DIN 32645 [1] (calibration curve method). The relative quantification limit is 0.05 µg/m³ NMPA or NEPA for a 240 L air sample, 250 µL sample solution and a 2 µL injection volume.

5.3 Selectivity

In the sampling system the named nitrosamines are selectively separated from the corresponding amines, which are not collected. Semi volatile nitrosamines (e. g. *N*-nitrosomorpholine, *N*-nitrosopyrrolidine or *N*-nitrosodibutylamine) are incompletely deposited in the denuder system under the conditions described here. The TEA detector system is selective in combination with gas chromatographic separation. As a result of the selectivity of the sampling system interference from other organic nitrogen compounds is not to be expected.

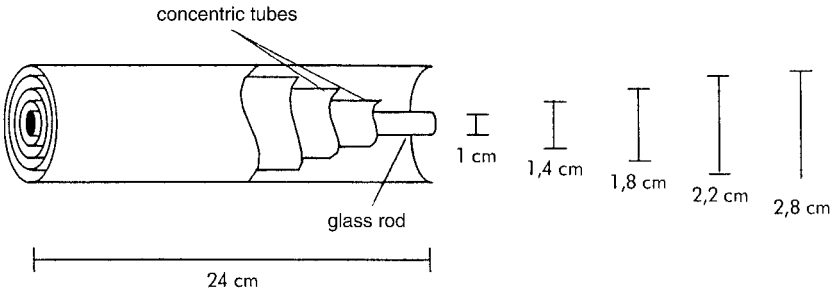
6 Discussion

The sampling of gaseous, aromatic nitrosamines in the annular denuder is restricted to a flow rate of 8 L/min and sampling for 30 minutes. Sampling is only possible at relative humidities below 50 %. At higher humidities recovery is reduced.
Under the sampling conditions described here, the corresponding amines are not deposited; therefore there is no artefactual formation of nitrosamines. Extensive laboratory experiments and investigations in practice have confirmed this [2, 3].
In addition to the two aromatic N-nitrosamines this procedure can also be used to determine semi volatile N-nitrosamines. For these compounds recovery is lower. Under the gas chromatographic conditions described, all components are completely separated.
With expected nitrosamine concentrations of >2.5 µg/m³ elution is possible without subsequent concentration of the solution.

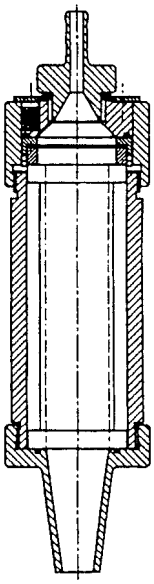
7 References

[1] DIN 32 645 (1994) Chemische Analytik – Nachweis-, Erfassungs- und Bestimmungsgrenze, Ermittlung unter Wiederholbedingungen. Beuth Verlag, Berlin.
[2] *Häger B, Nießner R* (1996) Determination of N-Nitrosomethylaniline and Methylaniline in the Gas Phase. Mikrochimica Acta 122:. 35–44.
[3] *Häger B, Breuer D* Ein neues Denuder-System zur Bestimmung von N-Nitrosomethylphenylamin und N-Nitrosoethylphenylamin in der Luft in Arbeitsbereichen. Gefahrstoffe-Reinhalt. Luft, in press.

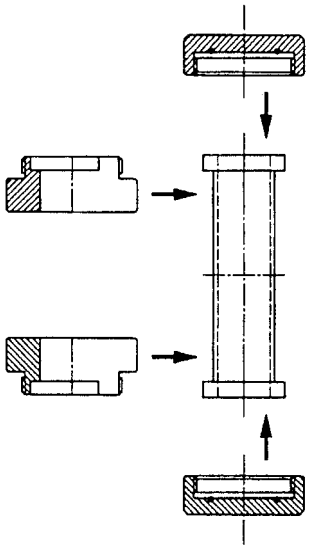
8 Appendix



Sketch: annular denuder



Sketch: denuder housing



Sketch: denuder with caps

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Federation of the Employment Accidents Insurance Institutions of Germany
(Hauptverband der Berufsgenossenschaften)
Centre for Accident Prevention and Occupational Medicine
Alte Heerstraße 111, 53757 Sankt Augustin
Expert Committee Chemistry

Carcinogenic substances Order number: BGI 505-64E
Established methods Issue: December 1998

Method for the determination of 1,2-phenylenediamine and 1,3-phenylenediamine

Method tested and recommended by the Berufsgenossenschaften for the determination of 1,2-phenylenediamine and 1,3-phenylenediamine 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 adsorption on an impregnated filter,
high performance liquid chromatography (HPLC) after desorption.
"1,2-phenylenediamine and 1,3-phenylenediamine-1-HPLC"
(Issue: December 1998).

IUPAC name:	**CAS No:**
1,2-phenylenediamine, 1,2-diaminobenzene	95-54-5
1,3-phenylenediamine, 1,3-diaminobenzene	108-45-2
Molecular weight:	**Molecular formula:**
108.14 g/mol	$C_6H_8N_2$

1 Sampling with a pump and adsorption on a filter, HPLC after desorption

This method permits the determination of 1,2-phenylenediamine and 1,3-phenylenediamine concentrations in working areas averaged over the sampling time after personal or stationary sampling.

Principle: With a pump a measured air volume is drawn through a glass fibre filter impregnated with hydrochloric acid as stipulated in the definition of inhalable dust fraction [1]. The adsorbed 1,2-phenylenediamine and 1,3-phenylenediamine is desorbed with a mixture of acetonitrile and aqueous ammonia and analysed by high performance liquid chromatography (HPLC).

Technical data:

Quantification limit: absolute: 7.3 ng 1,2-phenylenediamine and 5.5 ng 1,3-phenylenediamine,
relative: 0.006 mg/m^3 1,2-phenylenediamine and for 0.004 mg/m^3 1,3-phenylenediamine 500 L air sample, 5 mL desorbate (dilution in the ratio 1 : 1 v/v) and 25 µL injection volume.

Selectivity: Interfering components may cause too high values. In general, interferences can be eliminated by selecting different chromatography conditions.

Advantages: Both personal and selective sampling are possible.

Disadvantages: No indication of concentration peaks.

Apparatus: Pump,
gas meter or flow meter,
glass fibre filter impregnated with hydrochloric acid,
filter holder,
HPLC apparatus equipped with UV/VIS-detector.

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:
Pump, suitable for a flow rate of 2 L/min (e.g. PP5 ex from Gilian, supplier in Germany: DEHA-Haan & Wittmer GmbH, 71288 Friolzheim)
Gas meter or flow meter
Filter holder (e.g. aerosol monitor, Catalogue No. M000 037 AO from Millipore, 65731 Eschborn)
Glass fibre filter, diameter 37 mm (e.g. No. 9 from Schleicher & Schüll, 37582 Dassel)

For sample preparation and analysis:
10, 25 and 50 mL Volumetric flasks
Adjustable pipettes, suitable for delivering 5 µL to 5 mL (e.g. Pipetman P from Abimed, 40736 Langenfeld)
20 mL Sample vials, amber
PTFE syringe filter (e.g. Millex FG13, 0.2 µm pore size from Millipore)
2 mL Disposable syringes

HPLC apparatus equipped with UV/VIS-detector
Data analysis device
Water-purification unit (e. g. Nanopure II from Barnsteadt, supplier in Germany: Wilhelm Werner GmbH, 51381 Leverkusen)
10 mL Glass vessels with snap-on caps, amber
Ultrasonic bath
Shaker (e. g. MTS 4 from IKA, 79219 Staufen)

1.2 Chemicals

1,2-Phenylenediamine, purity >99% (e. g. from Aldrich, 89552 Steinheim)
1,3-Phenylenediamine, purity >99% (e. g. from Aldrich, 89552 Steinheim)
Aqueous ammonia, 25%, analytical grade (e. g. from Merck, 64271 Darmstadt)
Hydrochloric acid, 32%, analytical grade (e. g. from Merck, 64271 Darmstadt)

For HPLC:
Ultra pure water (e. g. prepared with the Nanopure II (UHQ water))
Acetonitrile, LiChrosolv (e. g. from Merck, 64271 Darmstadt)

1.3 Solutions

Desorption solution:
Mixture of 92 parts by volume of acetonitrile and 8 parts by volume of aqueous ammonia.

Solvent mixture 1:
Mixture of acetonitrile/water (1 : 1 v/v).

Solvent mixture 2:
Mixture of 96 parts by volume of solvent mixture 1 and 8 parts by volume of aqueous ammonia.

Stock solution:
Solution of about 1 mg of each of 1,2-phenylenediamine and 1,3-phenylenediamine per millilitre solvent mixture 2.
About 25 mg of each of 1,2-phenylenediamine and 1,3-phenylenediamine are weighed to the nearest 0.1 mg in a 25 mL volumetric flask. The flask is filled to the mark with the solvent mixture 2.

Calibration solutions:
Solutions of 0.5, 1.0, 5, 10, 15, 20 and 25 mg 1,2-phenylenediamine and 1,3-phenylenediamine per millilitre solvent mixture 1.
A few millilitres of solvent mixture 1 are added to each 10 mL volumetric flask. Then 5, 10, 50, 100, 150, 200 and 250 µL of the stock solution are each pipetted into one of the volumetric flasks and then the flasks are filled to the mark with solvent mixture 1.

With these solutions and an air sample volume of 500 L a concentration range of 10 to 500 µg/m^3 is covered for 1,2-phenylenediamine and 1,3-phenylenediamine.
The stock solution and calibration solutions are not stable and must be freshly prepared before use.

1.4 Impregnation of the filter

The glass fibre filters are dipped into a mixture of 22 mL UHQ water and 3 mL 32% hydrochloric acid and dried in the air on a watch glass. The impregnated filters have a shelf life of at least four weeks.

2 Sampling

For sample collection a filter holder is equipped with two of the impregnated glass fibre filters and connected to the pump. The filter holder is wrapped in aluminium foil to exclude light. During working hours the pump and filter holder are carried by a person or used in a stationary position. The flow rate is set at 2 L/min in accordance with the definition of inhalable dust fraction [1]. With sampling for four hours this corresponds to an air sample volume of 480 L.

3 Analytical determination

3.1 Sample preparation and analysis

For preparation the filters are each placed in a glass vessel with a snap-on cap and 5 mL desorption solution is added. After treatment in an ultrasonic bath and shaking (both for 15 minutes) solid parts are separated from the desorbates by filtering through a 0.2 µm PTFE syringe prefilter. An aliquot of these desorbates is then diluted with UHQ water in the ratio 1 : 1 v/v. This is imperative to avoid damaging the chromatography column.
To ensure that the water used for desorption and the glass fibre filter do not contain interfering substances, an unloaded impregnated filter is also prepared (blank solution).
25 µL is taken from each diluted desorbate, injected into the high performance liquid chromatograph and chromatograms are recorded as described in Sect. 3.2. After chromatographic separation 1,2-phenylenediamine and 1,3-phenylenediamine are detected at a wave length of 210 nm.

3.2 Operating conditions for high performance liquid chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Hewlett Packard 1090 equipped with diode array detector (DAD) and autosampler	
Pre-column:	Length:	30 mm
	Internal diameter:	4 mm
	Stationary phase:	250/8/4 Nucleosil 100-5 C_{18} AB from Macherey & Nagel
Column:	Length:	250 mm
	Internal diameter:	4 mm
	Stationary phase:	250/8/4 Nucleosil 100-5 C_{18} AB from Macherey & Nagel
Elution:	Isocratic	
Eluent:	Acetonitrile/UHQ water (20/80 v/v)	
Flow rate:	0.7 mL/min	
Injection volume:	25 µL	
Detection wavelength:	210 nm	
Column temperature:	40 °C	

4 Evaluation

4.1 Calibration

25 µL of each of the calibration solutions described in Sect. 1.3 are injected into the high performance liquid chromatograph and chromatograms are recorded. The calibration curves are obtained by plotting the measured peak areas against the 1,2-phenylenediamine and 1,3-phenylenediamine concentrations contained in the various calibration solutions. The calibration curves are linear in the given concentration range.

4.2 Calculation of the analytical result

The 1,2-phenylenediamine and 1,3-phenylenediamine concentrations in the air sample in mg/m^3 are calculated according to Equation (1):

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

Legend:

c_w Concentration by weight of 1,2-phenylenediamine or 1,3-phenylenediamine in the air sample in mg/m^3

w 1,2-phenylenediamine and 1,3-phenylenediamine weights in the desorbate in µg determined from the calibration curve
V Air sample volume in L
η Recovery rate

If more than 10% of the weight of 1,2-phenylenediamine or 1,3-phenylenediamine deposited on the first filter is found on the second filter, sampling must be repeated with a smaller volume of air.

5 Reliability of the method

5.1 Accuracy and recovery

To determine the relative standard deviation of the procedure and the recovery,

- 20 µL of a solution of 0.86 mg 1,2-phenylenediamine and 0.38 mg 1,3-phenylenediamine per millilitre solvent mixture 2,
- 17 µL of a solution of 2.96 mg of each of 1,2-phenylenediamine and 1,3-phenylenediamine per millilitre solvent mixture 2,
- 17 µL of a solution of 5.83 mg of each of 1,2-phenylenediamine and 1,3-phenylenediamine per millilitre solvent mixture 2

were each transferred to two impregnated glass fibre filters placed one behind the other. After the solutions were added the filter holders were wrapped in aluminium foil to exclude light. Then 500 L of laboratory air was drawn through the filters as described in Sect. 2. The spiked weights of 1,2-phenylenediamine and 1,3-phenylenediamine correspond for the 500 L air volumes to concentrations of 0.034, 0.1 and 0.2 mg/m^3 for 1,2-phenylenediamine (1,2-PDA) and 0.015, 0.1 and 0.2 mg/m^3 for 1,3-phenylenediamine (1,3-PDA). The filters were then analysed as described in Sect. 3.1. Six individual determinations were carried out for each concentration. The relative standard deviations and recovery rates found are listed in Table 1.

Table 1. Standard deviation (rel.) s and recovery rate.

Concentration mg/m^3	Standard deviation (rel.) s %		Recovery rate	
	1,2-PDA	1,3-PDA	1,2-PDA	1,3-PDA
0.015		5.8		0.94
0.034	3.6		0.90	
0.1	1.4	1.6	0.92	0.98
0.2	3.2	1.7	0.92	0.98

5.2 Quantification limit

The absolute quantification limit is 7.3 ng 1,2-phenylenediamine and 5.5 ng 1,3-phenylenediamine. It was determined from the signal/noise ratio of the blank value chromatograms.
The relative quantification limit is 0.006 mg/m^3 1,2-phenylenediamine and 0.004 mg/m^3 1,3-phenylenediamine for a 500 L air sample, 5 mL desorbate, dilution of the desorbate in a ratio of 1 : 1 v/v and 25 µL injection volume.

5.3 Selectivity

Interfering components may cause too high values. In general, interferences can be eliminated by selecting different chromatography conditions. In practice the separation conditions described above have proved reliable.

6 Discussion

The loaded filters can be stored in the dark at room temperature for at least a week without any loss of adsorbed 1,2-phenylenediamine and 1,3-phenylenediamine.
In addition to 1,2-phenylenediamine and 1,3-phenylenediamine also 1,5-diaminonaphthalene can be determined in the workplace air with the method described.

7 References

[1] *European Committee for Standardization (CEN)* (1993). s DIN EN 481-Workplace atmospheres-Size fraction definitions for measurement of airborne particles. Brussels. Beuth Verlag, Berlin.

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Phosphine

Method number 1

Application Air analysis

Analytical principle Photometry

Completed in April 1993

Summary

The method described by NIOSH [1] was modified so that determination of phosphine (PH_3) is possible in the range between 0.1 and 10 times the MAK value. During sampling, air containing phosphine is drawn through silica gel adsorption tubes impregnated with mercury cyanide.
Elution is carried out with potassium permanganate solution by oxidation of the resulting mercury-phosphane complex to form the phosphate. Preparation is carried out by adding various solutions and by extraction with isobutanol/toluene. A blue heteropolymolybdate colouring is formed which is measured photometrically.

Precision:	Standard deviation (rel.)	$s = 5.1\%$
	Mean variation	$u = 11.4\%$
	for $n = 10$ determinations and at a concentration of $c = 0.15$ mg/m^3	
Quantification limit:	0.5 µg PH_3 absolute ≅ 0.0125 mg/m^3	
Sampling recommendation:	Sampling time:	2 h
Sample volume:	100 L (for concentrations up to 10 times the MAK value)	

Phosphine (PH_3) [CAS No. 7803-12-2]

Phosphine (PH_3) is a colourless, unpleasant-smelling, highly toxic gas (molecular weight 34.0; melting point –133 °C; boiling point –87.0 °C; relative gas density 1.146, reference parameter air).
Phosphine is used as a pesticide (e. g. against granary weevils and flour moths). In addition, phosphine is formed during the processing of grey iron.

The currently valid MAK value (1993) is 0.14 mg/m^3 (0.1 ppm). Phosphine is classified in Peak limitation category I.

Author: *D. Breuer*
Examiners: *K. Goßler, H. Fischer*

Phosphine

Method number	1
Application	Air analysis
Analytical principle	Photometry
Completed in	April 1993

Contents

1 General principles

The method described by NIOSH [1] was modified so that determination of phosphine (PH_3) is possible in the range between 0.1 and 10 times the MAK value. During sam-

pling, air containing phosphine is drawn through silica gel adsorption tubes impregnated with mercury cyanide.
Elution is carried out with potassium permanganate solution by oxidation of the resulting mercury-phosphane complex to form the phosphate. Preparation is carried out by adding various solutions and by extraction with isobutanol/toluene. A blue heteropolymolybdate colouring is formed which is measured photometrically.

2 Equipment, chemicals, adsorption agents and solutions

2.1 Equipment

Sampling pump, flow rate 50 L/h
Gas meter
Photometer able to measure wave lengths in the 625 nm range with 5 cm or 2 cm cuvettes
Thermostatted water bath for incubating in the range of 65–70 °C
Adsorption tubes, made of Duran glass (internal diameter = 0.8 cm) filled with 2.0 g impregnated silica gel. Closed at both ends with glass wool.
100 mL Erlenmeyer flasks with ground glass joint NS 29/32
2 mL, 10 mL, 25 mL Pipettes
150 mL Separating funnel
25 mL, 1000 mL Volumetric flasks
Cuvettes, 2 or 5 cm optical path length (glass)
10 µL and 100 µL Syringes (gastight)
Silicon tubing, internal diameter = 0.9 cm

To remove traces of phosphate from the glass vessels pre-treatment with e.g. hot diluted hydrochloric acid (10%) and then with diluted sodium hydroxide solution (10%) is recommended, before they are rinsed with deionised water.

2.2 Chemicals

Mercury(II) cyanide [$Hg(CN)_2$], analytical grade
Potassium permanganate $KMnO_4$, analytical grade
Ammonium iron(II) sulfate $Fe(NH_4)_2(SO_4)_2 \cdot 6\ H_2O$, analytical grade
Ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$, analytical grade
Tin(II) chloride $SnCl_2 \cdot 2\ H_2O$, analytical grade
Methanol, analytical grade
Toluene, analytical grade
Isobutanol, analytical grade
Glycerol, analytical grade
Concentrated sulphuric acid

Dipotassium hydrogen phosphate K_2HPO_4 analytical grade, or for calibration with phosphine: PH_3 gas, 99.999% with special safety valve

2.3 Adsorption agents

Silical gel 0.5–1 mm/18–35 mesh (Macherey, Nagel u. Co., Düren) serves as adsorption agent. 100 g silica gel is made into a paste with 150 mL 2% mercury cyanide solution and left for 2 hours (and is occasionally carefully shaken). The silica gel is filtered off and dried overnight in a desiccator. 2 g of impregnated silica gel can bind up to 500 µg phosphine.

2.4 Solutions

Molybdate solution: 49.4 g of $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$ is dissolved in 112 mL of concentrated sulfuric acid and water and the flask is filled to the 1 L mark.

Toluene and isobutanol are mixed in the ratio 1 : 1.

Methanolic sulfuric acid: 5 mL of concentrated sulfuric acid (d = 1.84 g/mL) is dissolved while cooling in 95 mL of methanol. The methanolic sulfuric acid must always be freshly prepared.

Iron solution: 7.9 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6\ H_2O$ is dissolved in 100 mL of 1% sulfuric acid.

Potassium permanganate solution: 0.316 g of $KMnO_4$ is dissolved in water, 6 mL of concentrated sulfuric acid is added and the flask is filled to the 1 L mark with water.

Tin(II) chloride solution: 0.4 g of $SnCl_2$ is dissolved while heating in 50 mL of glycerol.

3 Calibration

As phosphine is highly toxic and readily inflammable extensive safety precautions must be taken when working with the gas. In addition to following the guidelines in the safety notes “Gefährliche Arbeitsstoffe“ (sheet No. F16) [3] care must be taken that silicon and polyethylene tubing is used instead of rubber tubing.
Due to the risk of explosion, phosphine residues must not be destroyed chemically, but should be removed by an efficient fume hood system.
It has been demonstrated that calibration with dipotassium hydrogen phosphate solutions leads to the same results as with phosphine. For reasons of practicability and safety it is recommended that calibration be carried out with dipotassium hydrogen phosphate solutions (see Section 3.1).

3.1 Calibration with dipotassium hydrogen phosphate

K_2HPO_4 calibration solutions are prepared in the concentration range 1 to 8 mg/L.
Preparation is carried out as described in Section 5. First of all 50 mL of the calibration solution is transferred to the separating funnel and then the molybdate solution is added.
Calculation of PH_3 from K_2HPO_4 is carried out using the following equation:

1 g PH_3 = 5.124 g K_2HPO_4.

This is graphically represented in Fig. 1.

3.2 Calibration with phosphine

For calibration, 10, 30, 50, 80 and 100 µL of phosphine gas are taken from a silicon tube with PH_3 gas flowing through it with a gastight 100 µL syringe and injected directly into the glass tube filled with impregnated silica gel.
Preparation is carried out as described in Section 5 with the following difference:
The volumes necessary to set the desired concentration of PH_3* (e.g. 1, 3, 5, 8, 10 mL) are taken from the extracted organic phase. It is thus possible to vary the concentration within a wide range.

Volume of PH_3 µL	Concentration (abs.) of PH_3 in 25 mL of toluene/isobutanol µg	Concentration (abs.) after removal from the organic phase µg				
		1 mL	3 mL	5 mL	8 mL	10 mL
10	14.14	0.57	1.70	2.83	4.52	5.66
30	42.42	1.70	5.09	8.48	13.57	16.97
50	70.70	2.83	8.48	14.14	22.62	28.28
80	113.10	4.52	13.57	22.62	36.19	45.25
100	114.40	5.66	16.97	28.28	45.25	56.56

0.57 µg $PH_3 \cong$ 0.014 mg PH_3/m^3 air sample
56.56 µg $PH_3 \cong$ 1.414 mg PH_3/m^3 air sample
(MAK value = 0.14 mg/m^3; air sample volume of 100 L)

From the measured extinction the calibration function $\Delta M = f_e(X^*)$ with $M = E$ was calculated by linear regression (graphic representation see Fig. 2). The course of the calibration is linear in the range $X^* = 0.5$ µg to $X^* = 20$ µg and follows the Lambert–Beer law.

* The absolute amount is always given as PH_3 although at this point oxidation to the phosphate has already taken place.

The calibration factor – for an optical path length of 5 cm – at a measuring wave length of 625 nm is k = 11.40 µg, the reciprocal calibration factor k' = 0.08775 μg^{-1}. The correlation coefficient of the calibration function is r = 0.9958. The blank value must be determined.

4 Sample collection

Using a flow-stabilised sampling pump for personal sampling or a pump together with a gas meter, air is drawn through a glass tube (internal diameter = 0.8 cm, length 10 cm) filled with 2.0 g silica gel (impregnated with $Hg(CN)_2$) with a flow rate of 50 L/h. If very high concentrations are expected, the flow rate should be reduced to 20 L/h.
The loaded tubes are closed with plastic caps *(PE or similar, do not use rubber caps)*, labelled and the sampling data noted in the sampling protocol. The tubes can be stored at room temperature without losses for up to six weeks.

5 Sample preparation and analytical determination

The contents of the tubes are transferred to 100 mL Erlenmeyer flasks and covered with 20 mL of potassium permanganate solution. The flasks are sealed and left to stand for 90 minutes in a water bath at 65–70 °C (and are occasionally shaken carefully).
After the solution has cooled to room temperature, two millilitres of iron solution are added to reduce the excess permanganate. The solution is tranferred into a 150 mL separating funnel with distilled water, 7.5 mL of molybdate solution and 25 mL of isobutanol/toluene (1 : 1) are added and the solution is shaken vigorously for one minute.
The aqueous phase is separated from the organic phase and the volume of the organic phase is determined. 10 mL of solution are taken with a pipette from the remaining organic phase in the separating funnel and transferred to a 25 mL volumetric flask. 10 mL of methanolic sulfuric acid are added. After adding 10 drops (about 200 µL) of tin(II) solution, the flask is filled to 25 mL with methanolic sulfuric acid.
The extinction of the solution is immediately measured using a 5 cm cuvette. The preparation steps after extraction must be carried out within one minute. To determine the blank value the complete preparation procedure should be carried out with impregnated silica gel which has not been loaded.

6 Calculation of the analytical result

The phosphine concentration in the workplace air is calculated according to the following equations:

$$\rho = \frac{E \cdot k'}{a \cdot V_Z \cdot \eta} \cdot \frac{273 + t}{273 + t} \text{ mg/m}^3$$

At 20 °C and 1013 hPa:

$$\rho_0 = \rho \frac{273 + t}{293} \cdot \frac{1013 \text{ hPa}}{p} \text{ mg/m}^3$$

The volume concentration σ – independent of the state parameters pressure and temperature – is:

$$\sigma = \rho_0 \cdot \frac{24.05 \text{ L/mole}}{34.0 \text{ g/mole}} = \rho_0 \cdot \frac{273 + t}{p} \cdot \frac{1013 \text{ hPa}}{293} \cdot \frac{24.05 \text{ L/mole}}{34.0 \text{ g/mole}}$$

$$\sigma = \rho \cdot \frac{273 + t}{p} \cdot 2.446 \cdot \frac{\text{hPa} \cdot \text{mL}}{\text{mg}}$$

For t_a = 20 °C and p_a = 1013 hPa:

$$\sigma = \rho \cdot 0.707 \frac{\text{mL}}{\text{mg}}$$

where:

$\Delta E = E - E_b$	Measured extinction, reduced by the mean blank value from reagent solutions and silica gel
k'	Reciprocal calibration factor in mg
a	Aliquot of the extraction liquid removed taking into consideration the volume contraction
V_z	Air sample volume read off in m^3
η	Recovery rate under the sampling conditions
t_a	Temperature of the ambient air in °C
t_g	Temperature in the gas meter in °C
p_a	Atmospheric pressure in the ambient air in hPa
ρ	Concentration of PH_3 in the air in mg/m^3 at temperature t_a and pressure p_a
ρ_0	Concentration of PH_3 in the air in mg/m^3 at 20 °C and 1013 hPa
σ	Concentration of PH_3 in the air in mL/m^3

7 Reliability of the method

7.1 Precision

To determine the precision, defined amounts of phosphine were injected into a dynamic test gas section with a gastight syringe (see Fig. 3). Concentrations of 0.025 mg/m^3, 0.15 mg/m^3 and 0.25 mg/m^3 were generated and 10 determinations carried out for each concentration.

Concentration µg/m^3	Relative standard deviation %
0.025	6.7
0.150	5.1
0.250	6.2

7.2 Quantification limit

Under the given conditions the detection limit is 0.5 µg PH_3 (absolute). This corresponds for an air sample volume of 100 L with a concentration of 0.0125 mg/m^3.

7.3 Specificity

There is interference from orthophosphates in the air. In addition, compounds which also form molybdate complexes and are soluble in isobutanol/toluene cause interference.

7.4 Recovery rate

The recovery rate is not concentration-dependent in the given range and is given as 96% (= 0.96).

7.5 Sample stability

The sample sstability was checked for a concentration of 0.15 mg/m^3 (MAK value). After six weeks storage (at room temperature) no influence could be found on the analytical result. Recovery after one, two, three, four and six weeks was on average 96%.

7.6 Influence of humidity on sampling

The results were obtained at room temperature and 40–50 % relative humidity. To check the influence of humidity, levels of humidity of more than 90 % were set in a dynamic test gas section and sampling was carried out. The recovery of PH_3 under these conditions was 90 %.

8 References

[1] *National Institute for Occupational Safety and Health* (NIOSH), Manual of Analytical Methods, No. S332 "Phosphine" Vol. 5 (Ed. D. C. Taylor) 1980
[2] *L. C. Thomas, G. J. Chamberlin*: Colorimetric Chemical Analysis Methods. Tintometer Ltd., Salisbury, England
[3] Merkblätter: Gefährliche Arbeitsstoffe Sheet No. F16. ecomed Verlagsgesellschaft, Landsberg

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Examiners: *K. Goßler, H. Fischer*

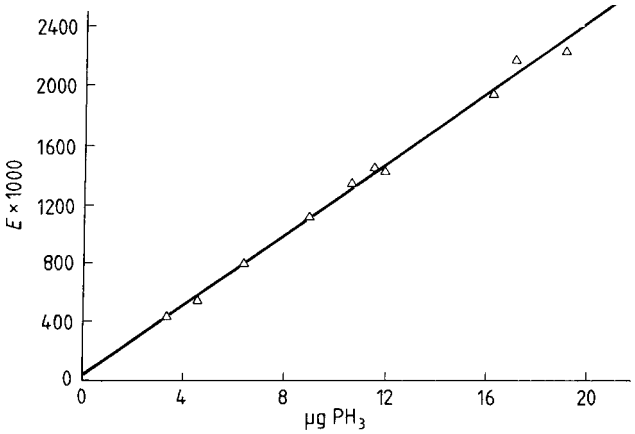

Fig. 1. Calibration curve with dipotassium hydrogen phosphate.

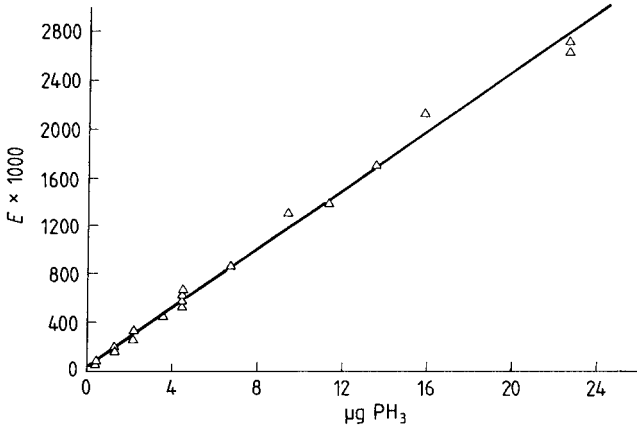

Fig. 2. Calibration curve with phosphine.

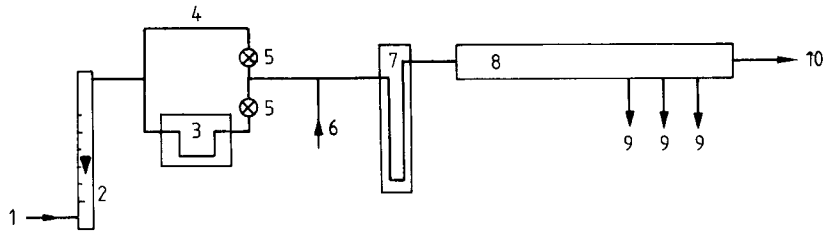

Fig. 3. Sampling apparatus for phosphine.
1 – Inlet, dried air (adjustable)
2 – Gas meter
3 – Thermostat, saturation of part of the gas stream with water
4 – Desiccator, part of the gas stream
5 – Setting of the partial flow rates for dry and moist air
6 – Injection of phosphine
7 – Gas mixing
8 – Sampling chamber
9 – Sampling points
10 – Gas outlet – fume hood

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Expert Committee Chemistry

Carcinogenic substances Order number: BGI 505-47E
Established methods Issue: July 1997

Method for the determination of 2,3,7,8-substituted polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs)

Methods tested and recommended by the Berufsgenossenschaften for the determination of PCDDs and PCDFs in working areas after discontinuous sampling.
Stationary sampling of the inhalable dust fraction according to EN 481 for the assessment of working areas.

1 Sampling with a pump, collection on a filter and adsorption on polyether urethan foam,
gas chromatography after desorption by extraction and purification of the extract,
detection by high-resolution mass spectrometry.
"PCDD/PCDF-1 GC-HRMS"
(Issue: July 1997)

This method replaces yellow print ZH 1/120.47 issued January 1991.

1 Sampling with a pump, collection on a filter and adsorption on polyether urethan foam, gas chromatography after desorption by extraction and purification of the extract, detection by high-resolution mass spectrometry

This method permits the determination of 2,3,7,8-substituted polychlorinated dibenzodioxin and dibenzofuran (PCDD/PCDF) concentrations in working areas averaged over the sampling time.

Principle: With a pump a measured air volume is drawn through an integrated collection system consisting of sampling inlet and glass-fibre deep bed filter followed by a section of toluene diisocyanate (TDI)-based polyether urethan foam (PUR foam). The inhalable fraction of particulate or particle-bound PCDDs/PCDFs is drawn in and collected on the filter or the fraction which passes the filter is adsorbed by the foam. Extraction is carried out with toluene in a Soxhlet extractor. The extracted PCDDs/PCDFs are separated from interfering components by a combination of preparation steps and then concentrated. The components of the purified extracts are separated by gas chromatography and the PCDDs/PCDFs are selectively determined using high-resolution mass spectrometry (HRMS). Sampling, sample preparation and analytical determination are checked by means of isotope-labelled PCDD/PCDF standards (isotope-dilution method). Quantitative evaluation is carried out using these internal standards. The analytical results are expressed in toxicity equivalents (TEs) taking into account toxicity equivalent factors (TEFs).

Technical data:

Quantification limits (per congener):

Absolute: 0.3 pg TCDD/TCDF, PeCDDs/PeCDFs, HxCDDs/HxCDFs,
1 pg HpCDDs/HpCDFs and
3 pg OCDD/OCDF

Relative: 0.15 pg/m^3 TCDD/TCDF, PeCDDs/PeCDFs, HxCDDs/HxCDFs,
0.5 pg/m^3 HpCDDs/HpCDFs and
1.5 pg/m^3 OCDD/OCDF for an air sample volume of 20 m^3, 30 µL sample solution and 3 µL injection volume.

Selectivity: The selectivity of the procedure depends above all on the mass spectrometric resolution, the type of column used and the matrix contaminants. In practice the GC columns named have proved reliable.

Advantages: Highly selective with a low quantification limit.

Disadvantages: Personal sampling is not possible, concentration peaks are not recorded; high sophisticated sampling and analytical procedure.

Apparatus: Sampling device consisting of sampling head with sampling inlet, filter holder and adsorption tube,
pump equipped with gas meter or flow meter,
combined GC/HRMS apparatus consisting of gas chromatograph with capillary column directly coupled with a high-resolution mass spectrometer.

Detailed description of the method

Contents

1 Preliminary remarks

Due to the importance of the subject and complexity of the procedure described here for determining PCDDs/PCDFs a great deal of practical experience is required in the techniques of sampling and sample preparation in ultra-trace analysis and the analysis of hazardous substances. Laboratories which carry out such analyses must regularly perform quality control. This is done, for example, internally by analysing certified standards and externally by participating in the collaborative studies organised by recognised institutions.
This method was elaborated and validated by six independent laboratories in a comparative study [1]. The laboratories all used the same sampling system, but different variants of the method for sample preparation and analysis. The methods used in the comparative study are listed as alternatives in Sect. 7.

2 Sampling

Collection of the particulate or particle-bound PCDDs/PCDFs is carried out according to the definition of inhalable dust fraction given in DIN/EN 481 [2] on a binder-free glass-fibre deep bed filter. The fractions of PCDDs/PCDFs which pass the filter are then adsorbed on PUR foam.
To differentiate between the PCDDs/PCDFs collected on the filter and those fractions that pass through the filter, the filter and PUR foam can be analysed separately.
The characteristics of the method were determined with the sampling system described below. It is suitable for stationary sampling and can, if necessary, be moved about within the work area as it can run without a mains power supply.

2.1 Equipment

The components of the sampling system are:

Sampling head PM4-G-D
Suction pump PM4
Tripod and connecting tube between pump and sampling head
Glass-fibre filter in a filter holder with lids

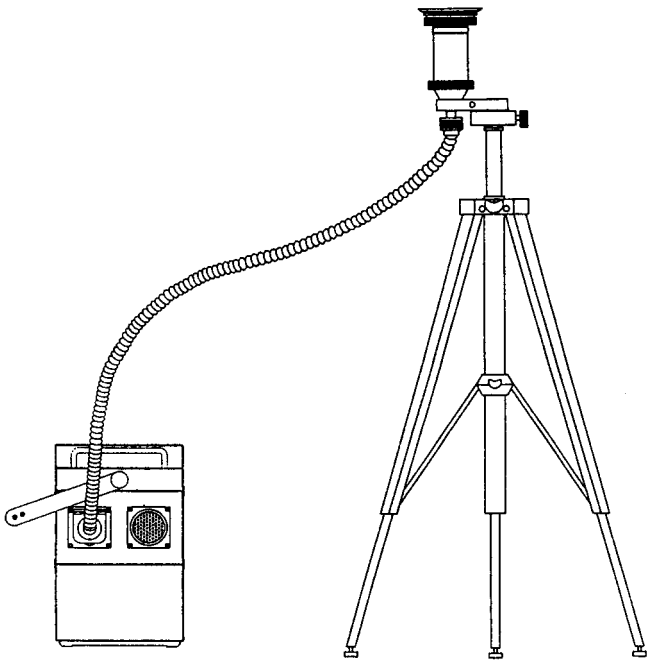

Fig. 1. Sampling apparatus.

PUR foam plug in a 1 l amber glass bottle to protect it from the light
Transport case for the sampling head
Tweezers for removing the foam plug from the amber glass bottle
Tripod and pressure tube for connecting the pump and sampling head
Disposable gloves made of polyethylene

2.1.1 Sampling head

e. g. PM4-G-D according to the Institute for Occupational Safety (BIA) from GSM GmbH, Neuss-Norf

The sampling head itself consists mainly of an omnidirectional, cylindrical inlet and sample holder which are screwed together.

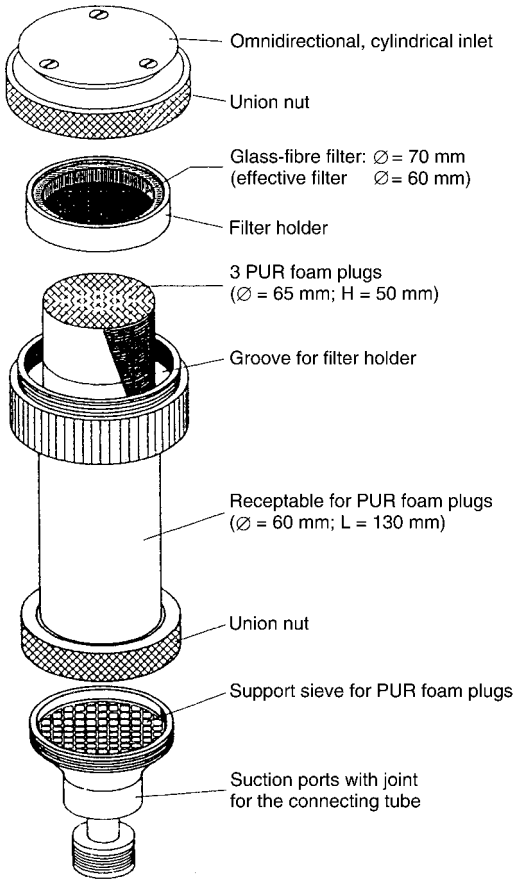

Fig. 2. Sampling head.

The parts in contact with the air sample are made of stainless steel. Before sampling, the sampling head is cleaned in three steps:
the individual parts are cleaned in a dishwasher with commercially available detergent, then rinsed with distilled water,
and the inner side (parts in contact with the gas) of the sampling head is then wiped over with analytical grade acetone.
The sampling heads are stored in the airtight aluminium containers used for transport.

2.1.2 Specimen

Filter:
Binder-free glass-fibre deep bed filter, e. g. of type MN 85/90 PF, Macherey-Nagel.
A glass-fibre deep bed filter with a diameter of 70 mm is used to collect the particulate/particle-bound PCDDs/PCDFs. This filter is placed in a filter holder made of surface-modified aluminium so that an effective filter diameter of 60 mm remains (cf. Fig. 3). A sieve with a thickness of 0.4 mm and a mesh size of 3.5 mm is used to support the filter. To transport the filter holder, lids made of the same material as the filter holders are fitted at the top and bottom. The system is kept together by means of a clamp clip.

PUR foam plugs:
TDI-based polyether urethan foam, e. g. flexible foam from TPC, Klaus Ziemer GmbH.
Cleaned toluene diisocyanate-based polyether flexible foam with a density of 20–25 kg/m^3 and defined porosity is used. The porosity must be equivalent to a counterpressure of 0.20 hPa (100 000 Pa = 1 bar, 100 Pa = 1 hPa = 1 mbar). The individual PUR foam plugs have a diameter of 65 mm and a height of 50 mm; these dimensions can be exceeded by 2 to 3 mm. The PUR foam plugs are cleaned by means of Soxhlet extraction with toluene for 24 hours, followed by Soxhlet extraction with acetone for 24 hours and subsequent drying at 40 °C in a vacuum drying cabinet. This procedure should be carried out in darkness. Three PUR foam plugs are necessary for each analysis.

Note:
Polyester foam should not be used because it is not stable to hydrolysis!

2.1.3 Suction pump

e. g. Gravikon PM4 from GSM GmbH, Neuss-Norf.
The pump runs pulsation-free, regulated with a flow rate of 4 ± 0.1 m^3/h under operating conditions. The flow rate is regulated to be constant so that it is independent of the loading of the filter (underpressure max. 500 mm water column), the ambient pressure (between 500 and 2000 hPa) and the ambient temperature (between –10 °C and 50 °C).
The power for the pump can be supplied by either storage batteries or the mains. The apparatus is therefore suitable for use at mobile workplaces, e. g. in vehicles, in crane cabins or for sample collection at workplaces outdoors.

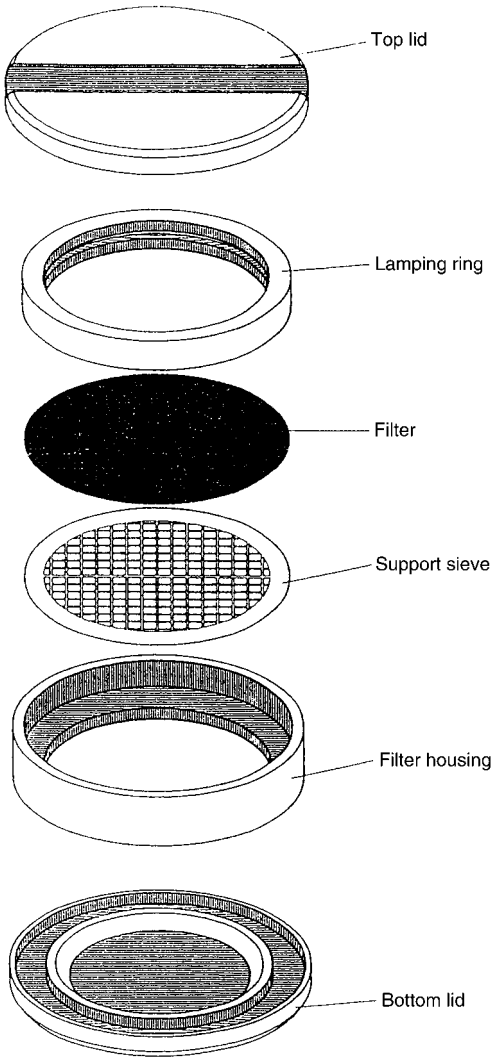

Fig. 3. Filter holder.

2.2 Chemicals, solutions and adsorbents

2.2.1 Solvents

Toluene, analytical grade, for precleaning the foam
Acetone, analytical grade, for precleaning the foam and for cleaning the sampling head

2.2.2 Sampling standards

e. g. Promochem, Cambridge Isotope Laboratories

For the more highly volatile PCDDs/PCDFs:
1,2,3,4-$^{13}C_{12}$-TCDD, or alternatively 1,2,3,4-$^{13}C_6$-TCDD if treatment of the sample extract with oleum is not necessary.

Optionally for the more highly volatile PCDDs/PCDFs:
2,3,7,8-$^{37}Cl_4$-TCDD if treatment of the sample extract with oleum is necessary. (cf. Sect. 3.4.4) (can contain up to 1% native 2,3,7,8-TDCC!)

Optionally for the less volatile PCDDs/PCDFs:
1,2,3,4,6,7,8-$^{13}C_6$-HpCDF.

2.2.3 Spiking solution

Solution of e. g. 1 ng/mL 1,2,3,4-$^{13}C_{12}$-TCDD in toluene.
10 µL of a commercially available standard solution (cf. Sect. 2.2.2) containing e. g. 1 µg/mL 1,2,3,4-$^{13}C_{12}$-TCDD is homogenised in 10 mL toluene.

2.3 Procedure

2.3.1 Applying the sampling standards

In the laboratory 100 µL of the spiking solution is injected into the top surface (e. g. marked with a cut) of one of the three cleaned PUR foam plugs by puncturing the surface several times with a microlitre syringe in such a way that the solution is distributed on the surface as evenly as possible. This is done most easily after the foam plugs have been placed in the sampling head (cf. Sect. 2.3.2), otherwise the previously spiked foam plugs should be stored separate from the untreated plugs in an amber glass bottle.

2.3.2 Setting up the sampling apparatus

The first step in setting up the sampling apparatus (cf. Fig. 1) is the preparation of the sampling system beginning with the PUR foam. The three cleaned PUR foam plugs are taken out of the transport container (amber glass bottles) with the tweezers and placed in the tube opened at both ends. As one of the three PUR foam plugs is spiked, they must be placed in the sampling head in the right order. The spiked plug must be directly behind the filter with the spiked surface facing the filter. How the PUR foam plugs are inserted is of great importance; there should be no space between the foam and the inside walls of the tube. Then the filter is inserted and the sampling system screwed together. After connecting the tube between the suction pump and sampling system and fixing the system on a tripod, the pump is started up for sampling. After

sampling the specimens (filter with filter holder, PUR foam plugs, sampling system) are packed in the transport containers and taken immediately to the laboratory for preparation.

3 Sample preparation

The sample deposited on the glass-fibre filter and three PUR foam plugs is extracted with toluene in a Soxhlet extractor. The PCDDs/PCDFs present in the extract are separated from interfering components using the purification procedures described in detail below as examples.
Air samples from work areas, unlike samples from the product area and emissions, contain only very little extractable matrix. Experience has shown that the matrix components present in the enriched air sample can frequently be removed by passage through the multi-layer column or by adsorption chromatography on aluminium oxide, as described in Sect. 3.4.2 and 3.4.3. For this reason further purification steps are only necessary in exceptional cases. If adequate purification is not achieved in these two steps, additional treatment with sulfuric acid or the use of an activated carbon/Celite disposable column, as described in Sect. 3.4.4 and 3.4.5, can be successful, as well as possibly repeating the purification steps first mentioned.
One of the tested methods of sample preparation validated by the comparative study is described in detail below. Alternative methods of sample preparation are described in the flow diagrams in Sect. 7.4.

3.1 Equipment

3.1.1 Sample extraction

100–500 µL Eppendorf pipettes
250 mL Round bottom flask with ground glass joint
100 mL Soxhlet extractor
Reflux condenser with ground glass joint
250 mL Heating mantle

3.1.2 Extract purification with multi-layer column

Plastic column, 13 cm long, internal diameter 2.7 cm, with frit and outlet, e. g. ICT Order No A1213-1018, (alternatively a glass column with comparable dimensions can be used)
Pasteur pipette
200 mL Wide-necked reagent bottle with conical shoulder

250 mL Erlenmeyer flasks with ground glass joint
250 mL Amber glass bottle with ground glass joint
500 mL Glass bottle with ground glass joint
100 mL Round bottom flask with ground glass joint
1 mL Sample vials with conical interior

3.1.3 Extract purification with aluminium oxide

Disposable plastic column with connection for solvent reservoir, 14.5 cm in length, upper part 2.5 cm in length, internal diameter 1.7 cm and lower part 12 cm in length, internal diameter 1.2 cm, e. g. Muromachi Kagaku Kogyo Kaisha Ltd, Tokyo (Japan), (alternatively a glass column with similar dimensions can be used)
Pasteur pipette

3.1.4 Extract purification with sulfuric acid

Round bottom flask with ground glass joint
Reflux condenser with ground glass joint

3.1.5 Extract purification using column chromatography on activated carbon/ Celite

Metal column, 12.5 cm in length, internal diameter 0.4 cm (e. g. empty HPLC column) or glass column of similar dimensions
Peristaltic pump for conveying the eluent

3.2 Chemicals

The chemicals listed below are particularly free from interfering chlorinated hydrocarbons.

3.2.1 Sample extraction

Toluene, e. g. Promochem, Order No. 8092

3.2.2 Extract purification with multi-layer column

Silica gel, 70-230 mesh ASTM, e. g. Merck, Article No 7734
Sodium sulfate, water-free, e. g. Riedel de Haën, Article No 13464

Silver nitrate, e. g. Baker, Article No 1182
Potassium hydroxide, e. g. Reininghaus, Article No R 222
Sulfuric acid, e. g. Riedel de Haën, Article No 30741
Toluene, e. g. Promochem, Order No 8092
n-Hexane, e. g. Promochem, Order No 4159
Nitrogen, purity 99.998%

3.2.3 Extract purification with aluminium oxide

Aluminium oxide A Super I for dioxin analysis, e. g. ICN, Order No 404592
n-Hexane, e. g. Promochem, Order No 4159
Dichloromethane, e. g. Promochem, Order No 3023
Diethylether, e. g. Promochem, Order No 3434

3.2.4 Extract purification with sulfuric acid

Sulfuric acid, e. g. Riedel de Haën, Article No 30741
n-Hexane, Promochem, Order No 4159

3.2.5 Extract purification using column chromatography on activated carbon/ Celite

Activated carbon AX-21, e. g. Andersen, Adrian, Michigan (USA)
Celite 545, e. g. Bayer AG, Leverkusen
Toluene, Promochem, Order No 8092
Dichloromethane, e. g. Promochem, Order No 3023
n-Hexane, e. g. Promochem, Order No 4159

3.3 Solutions

3.3.1 Clean-up standard

A mixture of 2,3,7,8-^{13}C-labelled PCDDs/PCDFs, which must contain at least one PCDD/PCDF per degree of chlorination, serves as clean-up standard. These PCDD/PCDF congeners must not be used in other steps of the analytical procedure.
Solution of e. g. 1 ng/mL of each 2,3,7,8-^{13}C-labelled PCDD/PCDF in toluene.

Preparation:
10 µL of each of the commercially available standard solutions (cf. Sect. 2.2.2) containing e. g. 1 µg/mL 2,3,7,8-^{13}C-labelled PCDDs/PCDFs are homogenised together in 10 mL toluene.

3.3.2 Injection standard

The injection standard serves to determine the recovery of the internal standards. As injection standard e. g. 3 µL of a solution of 100 pg/µL 1,2,3,4-$^{13}C_6$-TCDD is added to the sample solution, provided this was not already used as sampling standard.
Preparation:
3 µL of a commercially available standard solution (cf. Sect. 2.2.2) containing e. g. 1 µg/mL 1,2,3,4-$^{13}C_6$-TCDD is homogenised in 10 mL toluene.

3.4 Procedure

3.4.1 Sample extraction

The inner walls of the sampling head are rinsed twice with about 25 mL toluene and the rinsing solution is added to the extract from the glass-fibre filter and the PUR foam plugs.
Immediately before extraction the glass-fibre filter or one PUR foam plug is spiked with e. g. 300 µL clean-up standard (cf. Sect. 3.3.1). The PUR foam and the glass-fibre filter are placed in a Soxhlet extractor for extraction. A volume of about 150 mL toluene is necessary for extraction. The duration of extraction is at least 7 hours. The extract together with the rinsing solution is concentrated to a volume of about 1 mL in a rotary evaporator (raw extract).

3.4.2 Extract purification with multi-layer column

Multi-layer column packed with silica gel treated with sulfuric acid, potassium hydroxide and silver nitrate. If greater quantities are necessary the following amounts must be increased correspondingly.

Silica gel/sulfuric acid:
56 g silica gel is weighed into a wide-necked reagent bottle with conical shoulder and 44 g concentrated sulfuric acid is added. The mixture is shaken until a uniform powdery material has formed.

Silica gel/silver nitrate:
50 g silica gel is weighed into a 250 mL Erlenmeyer flask with ground joint and 5.5 g silver nitrate dissolved in 21.5 g water is added a little at a time and shaken. The mixture is allowed to stand for 30 min. The loaded silica gel is transferred under a countercurrent stream of nitrogen to a glass tube heated to about 70 °C and the temperature increased in steps to 120 °C over about 5 hours. After the water has evaporated completely the mixture is heated for a further 15 hours at 12 °C. It is then cooled to room temperature, the stream of nitrogen is interrupted and the loaded silica gel is transferred to an airtight amber glass bottle with ground joint.

Silica gel/potassium hydroxide (40 % KOH):
193 g KOH is dissolved in 700 mL methanol and the resulting solution filtered. 300 g silica gel is added and the mixture stirred for 90 min at 55 °C. The solvent is distilled off in a rotary evaporator until a fine powdery material is left. The loaded silica gel is transferred to an airtight container.

The following reagents are placed in the plastic column one at a time (an evenly packed, pocket-free bed is obtained by tapping the column):
1.5 g silica gel/10 % silver nitrate
1.0 g silica gel
5.0 g silica gel/44 % sulfuric acid
1.0 g silica gel
2.5 g silica gel/40 % KOH
1.0 g silica gel
2.0 g sodium sulfate, water-free

After pre-washing the column with about 50 mL *n*-hexane/toluene (95 : 5 v/v) the concentrated sample extract (raw extract; cf. Sect. 3.4.1) is placed onto the column. The sample vessel is rinsed three times with 5 mL *n*-hexane/toluene (95 : 5 v/v) and the rinsing liquid also added to the column. Elution is carried out with a further 60 mL of the same solvent mixture and the eluate collected in a 100 mL round bottomed flask. The column eluate is reduced to a volume of about 10 mL in a rotary evaporator, transferred to a pear-shaped distilling flask and concentrated further, and after further transferral to a sample vial, with conical interior finally reduced to a volume of about 500 µL in a stream of nitrogen.

3.4.3 Extract purification with aluminium oxide

Adsorption chromatography on aluminium oxide:
The alkaline aluminium oxide of activity level Super I described in Sect. 3.2.3 can be used without previous treatment. It is recommended that it be stored and handled in a moisture-free atmosphere.
The plastic column is filled with 10 g alkaline aluminium oxide. It is then covered with 1 g sodium sulfate. The sample (raw extract; cf. Sect. 3.4.1) dissolved in about 5 mL *n*-hexane is applied to the column; the sample vessel is rinsed three times with 10 mL *n*-hexane/dichloromethane (99 : 1 v/v) and the rinsing solution is also applied. After the solutions have completely entered the carrier material elution is carried out with 150 mL *n*-hexane/dichloromethane (99 : 1 v/v). This eluate can be discarded after completing the analysis.
The PCDD/PCDF fraction is eluted from the column with 75 mL dichloromethane/diethyl ether (9 : 1 v/v).

3.4.4 Extract purification with sulfuric acid

If the preparation steps described in Sect. 3.4.2 and 3.4.3 are not sufficient to eliminate interfering components for GC/HRMS determination, this purification step may be successful.
The raw extract (cf. Sect. 3.4.1) can be treated directly with sulfuric acid. Studies [4] have shown that treatment with sulfuric acid at a higher temperature can remove most of the organic matrix. Silica gel impregnated with concentrated sulfuric acid (preparation cf. Sect. 3.4.2) is added to the raw extract in amounts up to about 50 g. The solvent is evaporated off and the dry residue treated at 70 °C for 20 min. Alternatively the sulfuric acid/silica gel mixture can be added to *n*-hexane to dissolve the PCDD/PCDF fraction; the mixture is heated for 20 min under reflux. The *n*-hexane is then decanted off and the residue washed twice with *n*-hexane.

3.4.5 Extract purification using column chromatography on activated carbon/ Celite

If the preparation steps described in Sect. 3.4.2 and 3.4.3 are not sufficient to eliminate interfering component for GC/HRMS determination, this purification step may be successful.
PCDDs/PCDFs are selectively adsorbed on the activated carbon if *n*-hexane/dichloromethane (1 : 1 v/v) is used as the mobile phase. To achieve higher flow rates Celite is added to the activated carbon. The adsorbed compounds can then be eluted with toluene; for this the column is eluted in the opposite direction to that used for loading. Purification on activated carbon can be carried out after the multi-layer column (cf. Sect. 3.4.2).
To prepare the activated carbon/Celite mixture 82 g Celite and 18 g activated carbon are weighed into with 500 mL round bottom flask. After mixing with 500 mL dichloromethane the solvent is distilled off at a water bath temperature of about 40 °C in a rotary evaporator under vacuum. The adsorbent is then dried at 40 °C for an hour under vacuum. About 0.5 g of the active carbon/Celite mixture is used as the stationary phase; the column should be packed as compactly as possible. The column is washed with 100 mL toluene/dichloromethane (1 : 1 v/v) and then with 50 mL *n*-hexane/dichloromethane (1 : 1 v/v). The sample solution (raw extract; cf. Sect. 3.4.1) is diluted to about 50 mL with *n*-hexane/dichloromethane (1 : 1 v/v) and added to the column. The sample vessel is then rinsed with a further 50 mL and this solution also added to the column. Non-adsorbable components are then eluted with 250 mL *n*-hexane/dichloromethane (1 : 1 v/v). The dioxin and furan fraction can then be eluted by inverse elution with 300 mL toluene (at 80 °C). Alternatively, the PCDD/PCDF fraction can be passed over an activated carbon/glass-fibre column according to the technique of Stalling [3]. 0.5 g of an activated carbon/glass-fibre mixture (1 : 9 w/w) is placed in the chromatography column and 5 to 10 mL sample solution added (dilution of the raw extract (cf. Sect. 3.4.1) with cyclohexane/dichloromethane (1 : 1 v/v). The column is rinsed with 70 mL cyclohexane/dichloromethane (1 : 1 v/v) and then with 50 mL dichloromethane/methanol/toluene (70 : 20:5 v/v/v). It is then rotated by 180 °C and eluted with 50 mL toluene in the opposite direction.

3.4.6 Final sample solution

The collected extracts are in each case concentrated in a stream of nitrogen to a final volume of e. g. about 200 µL and spiked with 3 µL injection standard (cf. Sect. 3.3.2).

4 Analytical determination

4.1 Equipment

Gas chromatograph: Varian 3400 with cold sample introduction Gerstel KAS 2
Mass spectrometer: Finnigan MAT 90

The operating conditions were evaluated with the following gas chromatography column:

Column:	Material:	Quartz capillary
	Length:	60 m
	Internal diameter:	0.25 mm
	Stationary phase:	DB Dioxin, polar, J&W Scientific
	Film thickness:	0.15 µm
Carrier gas:	Helium:	180 kPa

4.2 Operating conditions

4.2.1 Gas chromatography

Determination of the 2,3,7,8-substituted PCDDs/PCDFs is carried out on a polar GC column of type DB Dioxin. Separation can also be carried out on other polar capillary columns such as e. g. Restek Rtx 2330, Supelco SP 2331 or Chrompack CP Sil 88. The column must be replaced if there are significant losses of the hepta-chlorinated and octa-chlorinated PCDDs/PCDFs or poor separation of 2,3,7,8-TCDF and 2,3,4,8-TCDF. Alternatively the HpCDDs/HpCDFs and OCDD/OCDF can be determined on a capillary column with a nonpolar separation phase (e. g. J&W DB-5, HP Ultra 2). The separating performance of the GC columns is tested by injecting a test solution with PCDDs/PCDFs. Determination, if necessary, of the homologue sum parameter can also be carried out on a nonpolar GC column (cf. Tab. 3, Sect. 6.1.2).

Temperature programme for cold sample introduction:

Injection at:		
	Starting temperature:	60 °C
	Initial hold time:	90 s
Solvent flush (toluene) at:		
	Heating rate 1:	2 °C/s
	Intermediate temperature:	80 °C
	Intermediate hold time:	90 s

Splitless injection at:	Heating rate 2:	12 °C/s
	Final temperature:	300 °C
	Final hold time:	600 s
Furnace temperature programme:		
	Starting temperature:	100 °C
	Initial hold time:	3 min
	Heating rate 1:	20 °C/min
	Intermediate temperature:	220 °C
	Heating rate 2:	5 °C/min
	Final temperature:	250 °C
	Final hold time:	90 min
GC/HRMS interface temperature:		250 °C

4.2.2 Mass spectrometry

The HRMS operates in SIM mode with a resolution of at least 5000. Ionisation is carried out under electron impact conditions (70 eV). Two selected ion tracks are registered routinely both for the native isotope-labelled standards and the internal isotope-labelled standards. As verification, further ion tracks from the molecule ion cluster or from the cluster $[M\text{-}COCl]^+$ can be used. An analysis time should be selected which allows each GC peak to consist of at least 10 measuring points. The corresponding fine masses for selective registration of the PCDD/PCDF ions are given in Table 1.

Table 1. Fine masses of the ions for registration of the PCDDs/PCDFs (calibration substance FC43).

Ion	**Mass in amu**
TDCF	303.902 and 305.899
Lock mass	313.984
$^{13}C_{12}$-TCDF	315.942 and 317.939
TCDD	319.897 and 321.894
$^{13}C_6$-TCDD	325.917
$^{37}Cl_4$-TCDD	327.885
$^{13}C_{12}$-TCDD	331.937 and 333.934
Calibration mass	351.981
Lock mass	325.984
PeCDF	339.860 and 341.857
$^{13}C_{12}$-PeCDF	351.900 and 353.897
PeCDD	355.855 and 357.852
Calibration mass	363.981
$^{13}C_{12}$-PeCDD	367.895 and 369.892

Table 1. (continued)

Ion	Mass in amu
Lock mass	363.981
HxCDF	373.821 and 375.818
$^{13}C_{12}$-HxCDF	385.861 and 387.858
HxCDD	389.816 and 391.813
$^{13}C_{12}$-HxCDD	401.856 and 403.853
Calibration mass	414.981
Lock mass	375.981
HpCDF	407.782 and 409.779
$^{13}C_{12}$-HpCDF	419.822 and 421.819
HpCDD	425.774 and 427.771
$^{13}C_{12}$-HpCDD	437.814 and 439.811
Calibration mass	464.978
Lock mass	425.978
OCDF	439.746 and 441.743
$^{13}C_{12}$-OCDF	451.786 and 453.783
OCDD	461.732 and 463.729
Calibration mass	464.978
$^{13}C_{12}$-OCDD	473.772 and 475.769

4.3 Procedure

4.3.1 Calibration

Calibration is carried out with solutions which contain the isotope-labelled standards used and the native standards to be determined (including sampling and injection standards). The calibration range should include the expected concentration range of the sample. The relative response factors of the components to be analysed are calculated using the calibration curve. The calibration frequency depends on the stability of the GC/HRMS system. It can be checked by injecting a control calibration standard.

The calibration factor for each native PCDD/PCDF to be determined is calculated separately with reference to a corresponding given isotope-labelled PCDD/PCDF.

The calibration factor f_c for the PCDD/PCDF congener c with reference to its assigned isotope-labelled standard i is calculated according to Equation (1):

$$f_c = \frac{F_{is} \cdot w_c}{F_c \cdot w_{is}} \tag{1}$$

Legend:

F_c Calibration factor for the PCDD/PCDF congener c

F_{is} Peak area of the corresponding isotope-labelled standard i from the ion mass chromatogram of the calibration solution
w_c Mass of the PCDD/PCDF congener c in the calibration solution
F_c Peak area of the PCDD/PCDF congener c from the ion mass chromatogram of the calibration solution
w_{is} Mass of the corresponding isotope-labelled standard i in the calibration solution.

The mean value of the calibration factor from several analyses of the calibration solutions should be used for calculation of the analytical result.

4.3.2 Identification of the PCDDs/PCDFs

A PCDD/PCDF is identified and can be determined if the following criteria are fulfilled:
The relationship between the signals for the two selected isotope peaks corresponds with the theoretical value within a range of 20 %.
The difference in retention time between native and isotope-labelled PCDD/PCDF is less than 3 seconds. When determining heptaCDDs/heptaCDFs and octaCDD/octaCDF with polar columns, the tolerance is 5 seconds. The signal–noise ratio is at least 3 : 1 on the ion track of lower intensity.

4.3.3 Determination of recovery and blank values

The recovery rate of the internal standard added for sampling and sample preparation should always be above 0.5.
When using this procedure it should be checked regularly whether selective losses of individual congeners occur (cf. also Sect. 6).
During each step of sample preparation, including the sampling heads, the blank value must also be checked.
To be able to monitor at the workplace a concentration of e. g. 50 pg TE/m^3 PCDDs/PCDFs, the summed blank value should not be above 0.5 pg TE/m^3 taking into account the quantification limits.

5 Calculation of the analytical result

5.1 Analytical result

The concentration (w/v) of an individual PCDD/PCDF congener in the air sample is calculated according to Equation (2):

$$c_{\mathrm{p}} = \frac{F_{\mathrm{p}} \cdot w_{\mathrm{qs}} \cdot f_{\mathrm{p}}}{F_{\mathrm{qs}} \cdot V} \tag{2}$$

Legend:

F_{p} Area of the PCDD/PCDF congener p from the ion mass chromatogram of the final sample solution

w_{qs} Mass of the isotope-labelled internal standard q in the final sample solution in pg

F_{qs} Area of the isotope-labelled internal standard q from the ion mass chromatogram of the final sample solution

f_{p} Mean response factor of the PCDD/PCDF congener p according to formula (1) related to the isotope-labelled standard q

c_{p} Concentration of the PCDD/PCDF congener p in the air sample in pg/m^3

V Air sample volume in m^3

By using the clean-up standards according to Sect. 3.3.1 before extraction, the recovery during sample preparation is taken into account in the results. The recovery of the sampling standards is only given for information.
From the known calibration factors for the injection standard (expressed in terms of the spiked isotope-labelled PCDD/PCDF congeners) the individual recovery of these PCDD/PCDF congeners is calculated for the individual steps of the procedure.

5.2 Toxicity equivalents

The total amount of PCDDs/PCDFs in the air is calculated according to formula (3) using the toxicity equivalent factors (TEFs) according to NATO/CCMS (cf. Tab. 2). If the concentration of a congener is below the quantification limit, its TE concentration is calculated by taking half of the quantification limit [5].
To calculate the toxicity equivalent concentration c_{TE} in pg/m^3 first the concentration determined for the PCDD/PCDF congener c_{n} is multiplied by the corresponding TE factor $\mathrm{TEF_n}$. Then these products for all 2,3,7,8-substituted PCDD/PCDF congeners in Table 2 (m = 17) are added together.

$$c_{\mathrm{TE}} = \sum_{n=1}^{m} c_{\mathrm{n}} \cdot TEF_{\mathrm{n}} \tag{3}$$

Legend:

c_{n} Concentration of the PCDD/PCDF congener n in the air sample in pg/m^3

c_{TE} Toxicity equivalent concentration in the air sample in pg TE/m^3

TEF_{n} TE factor for the PCDD/PCDF congener n

m 17, the total number of PCDD/PCDF congeners (with TEFs)

Table 2. Toxicity equivalent factors (TEFs) according to NATO/CCMS (1988) [7].

PCDD congener	TEF	PCDF congener	TEF
2,3,7,8-TCDD	1.0	2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDD	0.5	1,2,3,7,8-PeCDF	0.05
1,2,3,4,7,8-HxCDD	0.1	2,3,4,7,8-PeCDF	0.5
1,2,3,6,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDD	0.01	1,2,3,7,8,9-HxCDF	0.1
OCDD	0.001	2,3,4,6,7,8-HxCDF	0.1
		1,2,3,4,6,7,8-HpCDF	0.01
		1,2,3,4,7,8,9-HpCDF	0.01
		OCDF	0.001

5.3 Presentation of the results

The congener-specific concentration of PCDDs/PCDFs in the air is given in pg/m^3 according to formula (2) rounded to two significant figures. The amount of PCDDs/PCDFs in air is given as the toxicity equivalent concentration in pg TE/m^3 according to formula (3) rounded to a maximum of two significant figures.

6 Reliability of the method

To determine the relative uncertainty of the procedure described above, a comparative study was carried out in which six laboratories took part. Six air samples were taken simultaneously. The air sample volume was 32 m^3 with sampling for eight hours. Sampling was carried out in the factory hall of an aluminium-recycling plant where homogenous distribution of PCDDs/PCDFs could be assumed. The filter samples were conditioned to constant temperature and humidity and then reweighed to determine the dust weight in each case. Then they were sent together with the corresponding three PUR foam plugs to the participating laboratories.

The samples were analysed by the laboratories at different times within twelve weeks after sampling. Each laboratory received an unloaded set of PUR foam plugs with a filter to determine the blank values of the specimens and the total analytical procedure. To determine the sample values and blank values the filter with the three PUR foam plugs were prepared together and analysed. A detailed description has been published [1].

The results of the comparative study show that the procedure is suitable for monitoring a concentration of e. g. 50 pg TE/m^3 PCDDs/PCDFs in the workplace air.

Table 3. PCDF concentrations and standard deviations from the comparative study [1].

PCDF congeners	Laboratory I	Laboratory II	Laboratory III	Laboratory IV	Laboratory V	Laboratory VI	Mean value	Standard deviation s	Standard deviation (rel.) $s_{rel.}$
	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	%
sum of tetra-CDFs	190.12		396.75	390.0	327	150.2			
sum of penta-CDFs	92.64		103.1	182.0	154	76.7			
sum of hexa-CDFs	34.43		43.75	73.80	63	29.0			
sum of hepta-CDFs	4.43		24.38	32.80	21	35.8			
sum of tetra to octa-CDFs	322.33		572.58	683.6	571	295.5			
2,3,7,8-tetra-CDF	5.16	8.31	5.86	7.35	6.6	3.8	6.18	1.61	26
1,2,3,7,8/1,2,3,4,8-penta-CDF	7.83	13.4	9.69	5.85	10.3	3.9	8.50	3.39	40
2,3,4,7,8-penta-CDF	7.89	9.97	7.59	12.9	9.7	5.5	8.93	2.53	28
1,2,3,4,7,8/1,2,3,4,7,9-hexa-CDF	2.85	6.44	6.29	6.49	7.2	4.1	5.56	1.69	30
1,2,3,6,7,8-hexa-CDF	3.17	6.92	5.79	8.57	5.8	3.7	5.66	2.01	35
1,2,3,7,8,9-hexa-CDF	<0.25	<0.359	0.6	0.41	0.5	<0.5	0.50	0.09	19
2,3,4,6,7,8-hexa-CDF	5.79	9.13	7.36	8.36	8.1	5.0	7.29	1.59	22
1,2,3,4,6,7,8-hepta-CDF	4.21	18.9	16.53	22.7	14.7	11.2	14.71	6.44	44
1,2,3,4,7,8,9-hepta-CDF	<0.14	2.03	2.02	2.21	2.0	1.5	1.95	0.27	14
octa-CDF	0.72	4.63	4.6	4.96	5.0	3.8	3.95	1.64	42

Table 3. (continued) PCDD concentrations and standard deviations from the comparative study [1].

PCDD congeners	Laboratory I	Laboratory II	Laboratory III	Laboratory IV	Laboratory V	Laboratory VI	Mean value	Standard deviation s	Standard deviation (rel.) $s_{rel.}$
	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	%
sum of tetra-CDDs	87.52		114.35	134	119	93.1			
sum of penta-CDDs	76.41		76.53	108	106	82.2			
sum of hexa-CDDs	71.92		83.44	115	107	72.4			
sum of hepta-CDDs	38.48		48.44	66.4	54	16.6			
sum of tetra to octa-CDDs	297.35		342.4	449.7	413	277.9			
2,3,7,8-tetra-CDD	<0.09	0.766	0.66	0.46	0.5	0.5	0.58	0.13	23
1,2,3,7,8-penta-CDD	0.8	3.52	2.5	2.07	2.8	3.9	2.60	1.11	43
1,2,3,4,7,8-hexa-CDD	0.71	2.61	2.71	3.04	2.7	4.6	2.73	1.24	45
1,2,3,6,7,8-hexa-CDD	2.42	6.24	5.43	9.83	5.3	3.1	5.39	2.63	49
1,2,3,7,8,9-hexa-CDD	0.49	3.98	3.17	3.88	3.2	2.0	2.79	1.33	48
1,2,3,4,6,7,8-hepta-CDD	18.23	30.2	23.62	31.2	25.3	16.7	24.21	5.97	25
octa-CDD	23.03	25.7	20.0	26.3	27	13.6	22.61	5.11	23
sum of tetra to octa-CDFs/CDDs	619.68		915.02	1133.3	984	573.4			

6.1 Accuracy

6.1.1 Dust concentration

The mean concentration of the inhalable dust fraction was 0.24 mg/m^3. The relative standard deviation was 1.2%. This correlation of the dust values shows that no systematic error was made during sampling with regard to the location of the individual sampling systems.

6.1.2 PCDD/PCDF congeners

The PCDD/PCDF concentrations determined by the various laboratories can be found in Table 3.
In Table 4 these concentrations are converted to toxicity equivalent concentrations according to NATO/CCMS [7] and these concentrations added together to yield an end result. The values refer to the sum of the particulate or particle-bound PCDD/PCDF fractions and those which passed the filter.
The separate evaluation of the filter and PUR foam by one of the participating laboratories revealed that at the workplace investigated about 30% of the total weight of PCDDs/PCDFs(TE) was present as a fraction which passed the filter. This is confirmed by results from metal-recycling plants [6]. Another column shows similarity parameters of the congener profiles. Further details and the calculation are given in Sect. 6.1.3.

Table 4. TE concentrations of PCDDs/PCDFs and similarity parameters of the congener profiles (cf. Sect. 6.1.3) from the comparative study to validate the procedure.

Laboratory	PCDDs/PCDFs pg TE/m^3	Congener profile similarity parameter
I	7.08	18.1°
II	13.11	4.6°
III	10.35	5.4°
IV	13.62	8.7°
V	11.7	4.4°
VI	8.4	9.8°
Mean value	**10.71**	**0°**
s	2.60	–
s_{rel}	24.3%	–

From the results a relative standard deviation for the total procedure of about 25% was calculated as the uncertainty associated with the analysis. Also the uncertainty values associated with the mean concentration values from Table 3 for the 17 2,3,7,8-substituted congeners determined were still below 50%, many even in the range of deviation of the above named TE concentrations from Table 4.

6.1.3 Congener profile

The results of the comparative study were checked with a mathematical procedure to see whether the correlation of the congener profile, as related to the values reduced to TE units could have been random values. From a qualitative point of view, with simultaneous sampling the congener distribution should be identical. Recognisable differences in the concentration distribution of the PCDD/PCDF congeners can indicate selective losses of individual congeners.
The similarity in congener distribution can be calculated by interpretation of the measured values of a congener collective as a vector (e. g. values of the 17 PCDD/PCDF congeners of a laboratory column in Tab. 3) [10]. The angle of intersection between two of these vectors is defined as the similarity parameter, which is calculated according to Equation (4) via the scalar products:

$$x = \cos\varphi = \frac{\sum_{n=1}^{m} a_n \cdot b_n}{\sqrt[2]{\sum_{n=1}^{m} a_n^2 \cdot \sum_{n=1}^{m} b_n^2}} \tag{4}$$

$$\text{with } \varphi = \frac{\arccos x \cdot 180^\circ}{\pi}$$

Legend:
a_n Value of the PCDD/PCDF congener of row n in column a of Table 5
b_n Value of the PCDD/PCDF congener of row n in column b of Table 5
x Cosine of the angle between the measured value columns regarded as directional vectors
φ Angle between the measured value columns regarded as directional vectors
n Index numbers of the rows in Table 5
m Total number of congeners in a laboratory column in Table 5 included in the comparison of similarity (m = 17)

This procedure is a mathematical procedure of vector transformation. Full similarity (correlation, dependence) corresponds with an angle of intersection of 0 °, total dissimilarity (independence, orthogonality) an angle of intersection of 90 °. The advantage of the mathematical view of similarity is that the results yield figures which are moreover independent of calculation factors (e. g. TE factors) as long as these refer to the same PCDD/PCDF congeners.
To illustrate this, in Table 5 using two columns from Table 3 in Sect. 6.1.2 the similarity parameters between the congener profiles (here laboratories V and VI) are determined with rounded values. The values below the analytical quantification limit are taken as 0, as in this procedure they are of negligible effect on the result.
Table 6 lists the angles of intersection calculated in the way described between the vectors of the laboratories in Table 3 and with the vector of the mean values.

Table 5. Calculation of the similarity parameter.

PCDD/PCDF congener	Laboratory V (a) pg/m^3	Laboratory VI (b) pg/m^3	ab	a^2	b^2
2,3,7,8-TCDF	6.6	3.8	25.08	43.56	14.44
1,2,3,7,8-PeCDF	10.3	3.9	40.17	106.09	15.21
2,3,4,7,8-PeCDF	9.7	5.5	53.35	94.09	30.25
1,2,3,4,7,8-HxCDF	7.2	4.1	29.52	51.84	16.81
1,2,3,6,7,8-HxCDF	5.8	3.7	21.46	33.64	13.69
1,2,3,7,8,9-HxCDF	0.5	0	0	0.25	0
2,3,4,6,7,8-HxCDF	8.1	5.0	40.5	65.61	25
1,2,3,4,6,7,8-HpCDF	14.7	11.2	164.64	216.09	125.44
1,2,3,4,7,8,9-HpCDF	2.0	1.5	3	4	2.25
OCDF	5.0	3.8	19	25	14.44
2,3,7,8-TCDD	0.5	0.5	0.25	0.25	0.25
1,2,3,7,8-PeCDD	2.8	3.9	10.92	7.84	15.21
1,2,3,4,7,8-HxCDD	2.7	4.6	12.42	7.29	21.16
1,2,3,6,7,8-HxCDD	5.3	3.1	16.43	28.09	9.61
1,2,3,7,8,9-HxCDD	3.2	2	6.4	10.24	4
1,2,3,4,6,7,8-HpCDD	25.3	16.7	422.51	640.09	278.89
OCDD	27	13.6	367.2	729	184.96
Sum			1232.85	2062.97	771.61
Root				45.41992	27.77786
cos φ (V,VI)			0.98		
Similarity parameter φ (V,VI)			12.3°		

Table 6. Similarity matrix of the congener profiles, similarity parameters of the congener profile vectors.

	Lab I	Lab II	Lab III	Lab IV	Lab V	Lab VI	Mean values
Lab I	0	20.0°	22.7°	24.5°	15.6°	25.4°	18.1°
Lab II	20.0°	0	3.9°	10.8°	7.1°	11.2°	4.6°
Lab III	22.7°	3.9°	0	9.3°	8.0°	9.6°	5.4°
Lab IV	24.5°	10.8°	9.3°	0	12.1°	10.8°	8.7°
Lab V	15.6°	7.1°	8.0°	12.1°	0	12.3°	4.4°
Lab VI	25.4°	11.2°	9.6°	10.8°	12.3°	0	9.8°
Mean values	18.1°	4.6°	5.4°	8.7°	4.4°	9.8°	0

The angle of intersection of the vectors of the laboratories which took part with the vector of the mean values (row and column "Mean values" in the table above) are represented graphically in Figure 4. The mean value vector is the horizontal line.
The similarity of the congener profiles is within the range of 4.4° to 18.1° to the vector of the mean values. This is a range which still represents satisfactory correlation.

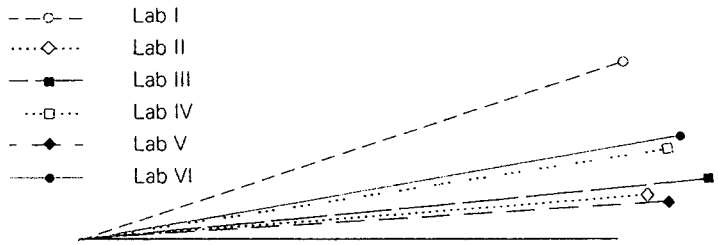

Fig. 4. Similarity between the congener profiles, angle of intersection.

6.2 Recovery

The recovery for the whole procedure can be assumed to be constant for all congeners within a homogenous series.
The recovery is taken into account in the calculation of the result due to the evaluation process without being explicitly determined. The recovery rate of the sampling standard was determined separately and, with one exception, was above 0.7 [1].

6.3 Quantification limits

6.3.1 Blank values

Suitable procedures should usually allow monitoring of a tenth of the threshold limit value. With a threshold limit value in the air of 50 pg TE/m^3 this corresponds to a PCDD/PCDF concentration of 5 pg TE/m^3. The results of the blank value analyses are listed in Table 7. They show that with the procedure described enough PCDDs/PCDFs can be accumulated with sampling for eight hours from a 32 m^3 air sample to obtain the necessary distance between the threshold limit value [9] and blank value for work-place determinations.

Table 7. TE blank value concentrations of PCDDs/PCDFs from the comparative study for a 32 m^3 air sample volume.

Laboratory	**PCDDs/PCDFs*** pg TE/m^3
I	0.05
II	0.52
III	0.51
IV	0.09
V	0.38
VI	1.31

* For congeners not detected the corresponding quantification limits were taken.

6.3.2 Quantification limits of the PCDD/PCDF congeners

Under optimum conditions the chromatographic separation system combined with a high-resolution mass spectrometer with a resolution of R = 10,000 allows the following absolute quantification limits:
0.3 pg TCDD/TCDF, PeCDDs/PeCDFs, HxCDDs/HxCDFs
1 pg HpCDDs/HpCDFs and
3 pg OCDD or OCDF

The following relative quantification limits were found for 30 µL final sample solution, a 3 µL injection volume and a 20 m^3 air sample volume:
0.15 pg/m^3 TCDD/TCDF, PeCDDs/PeCDFs, HxCDDs/HxCDFs
0.5 pg/m^3 HpCDDs/HpCDFs and
1.5 pg/m^3 OCDD or OCDF

6.4 Selectivity

The selectivity of the procedure depends above all on the mass spectrometric resolution, on the type of column used and the interfering matrix components. In practice the named GC columns have proved reliable.

7 Comments

7.1 Quality control

Blank values must be checked regularly and the values determined recorded. With comparatively high determined values it is sufficient that the blank value is lower by at least a factor of 10 than the lowest value determined in a sampling series.
Checking of individual steps of the procedure (in particular extraction, extract purification steps and GC/HRMS analysis, and reference standards) can be carried out by regular investigation of certified reference or control materials and standard solutions. The overall recovery rate for the part of the procedure that can be checked should not be below 0.5.

7.2 Shelf life

A tested shelf life for the samples of at least 12 weeks can be assumed from the comparative study.

7.3 Parallel determination of other substances

The procedure described can also serve as the basis for determination of polybrominated dibenzodioxins and polybrominated dibenzofurans. There are no comparable results from investigations available on procedure characteristics, particularly for sample preparation, calibration and recovery. They must be individually elaborated.

7.4 Alternative procedures for sample preparation (Figures 5 to 10, appendix)

The preparation procedures used by the individual laboratories which participated in the comparative study offer alternatives and supplements to the procedure described here as example.

7.5 Alternative conditions for analytical determination (Table 8, appendix)

The conditions for the apparatus used by the individual laboratories which participated in the comparative study listed in the table offer alternatives and supplements to the procedure described here as example.

8 Suppliers

Suppliers for Sect. 2, sampling

Sampling head Gravikon PM 4 GD and sampling pump Gravikon PM 4,
GSM GmbH,
Neuss-Norf
GSA Meßgerätebau GmbH
Gut Vellbrüggen
41499 Neuss

Binder-free glass-fibre deep bed filter type MN 85/90 PF,
Macherey-Nagel
Postfach 101352
52313 Düren

TDI-based polyether flexible foam, density: 20–25 kg/m^3,
TPC, Klaus Ziemer GmbH
Pommernstr. 96
68309 Mannheim

Suppliers for Sect. 3, sample preparation

Promochem
Postfach 101340
46469 Wesel

Cambridge Isotope Laboratories,
50 Frontage Road, Andover
Mass. 01810–5413 U.S.A

Merck KGaA
Frankfurter Str. 250
64271 Darmstadt

ICT Handelsgesellschaft GmbH
Norsk-Data-Str. 3
61352 Bad Homburg

Riedel de Haën AG
30926 Seelze

Baker
Im Leuschenpark 4
64347 Griesheim

ICN-Biomedicals GmbH
Mühlengrabenstr. 10
53090 Meckenheim

Andersen
1415 E. Michiganstreet
Adrian, Michigan
49221–3499 (USA)

Reininghaus-Chemie
Joachimstr. 122
45309 Essen

Muromachi Kagaku Kogyo Kaisha Ltd
Tokyo (Japan)

Suppliers for Sect. 4, analytical determination

Gerstel cold sample introduction system KAS 2,
Gerstel GmbH
Aktienstr. 232–234
45473 Mühlheim/Ruhr

Mass spectrometer MAT 90 or MAT 95,
Finnigan MAT GmbH
Barkhausenstr. 2
28197 Bremen

Column DB Dioxin,
J & W Scientific Products GmbH
Horbeller Str. 15
50858 Köln

9 References

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[8] *European Committee for Standardization (CEN)* (1994) DIN EN 482, Workplace atmospheres – General requirements for the performance of procedures for the measurement of chemical agents. Brussels. Beuth Verlag, Berlin

[9] *Bundesministerium für Arbeit und Sozialordnung* (1997) TRGS 402: Ermittlung und Beurteilung für der Konzentrationen gefährlicher Stoffe in der Luft in Arbeitsbereichen. BArbBl. 11/1997: 27–33.

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10 Appendices

Appendix to Section 7.4
Alternative sample preparation procedures

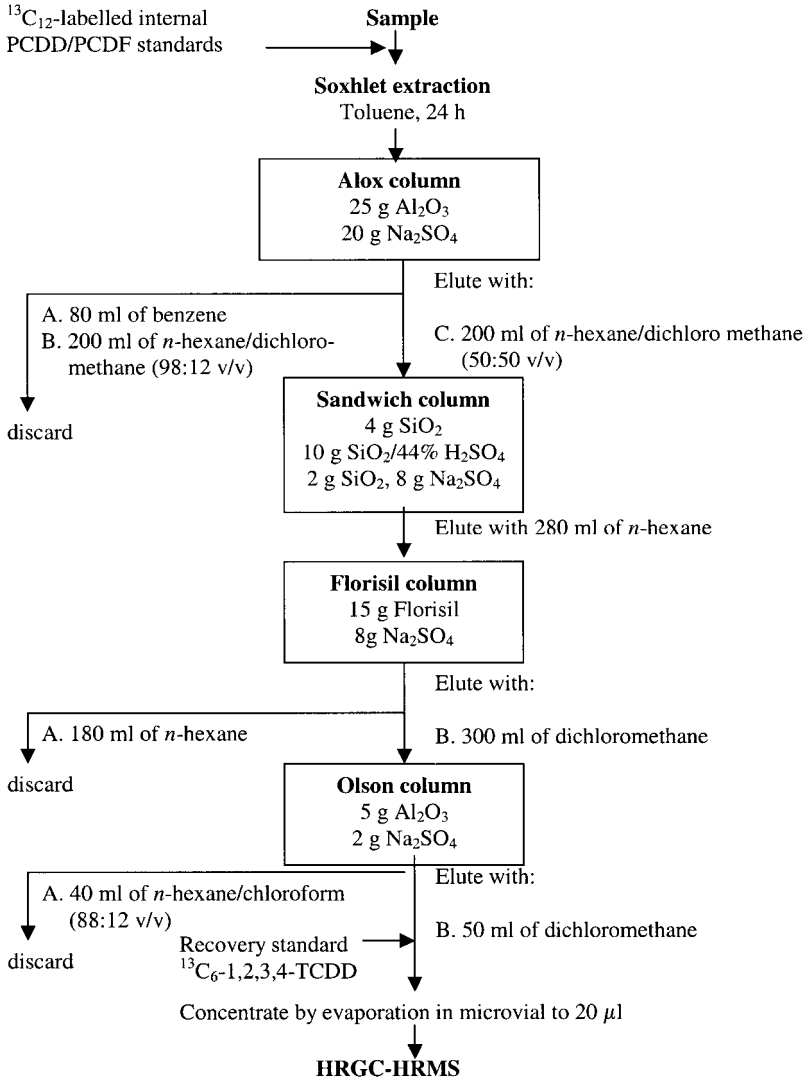

Figure 5

Appendix to Section 7.4
Alternative sample preparation procedures

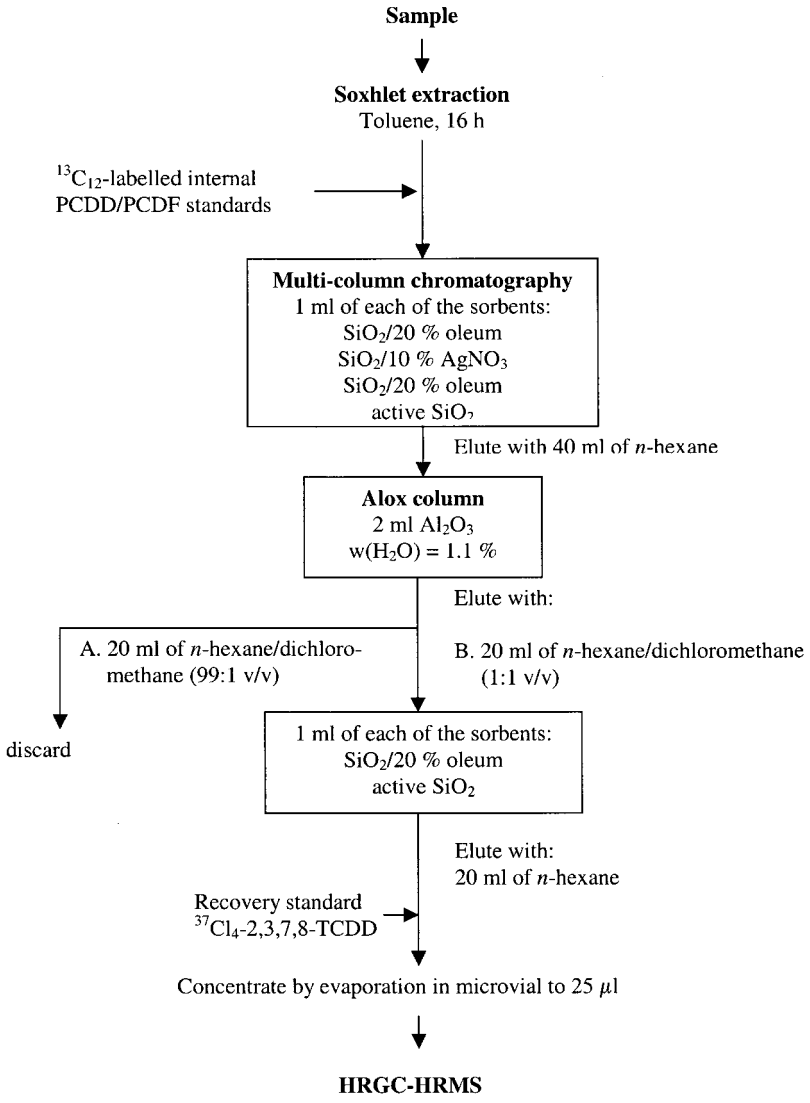

Figure 6

Appendix to Section 7.4
Alternative sample preparation procedures

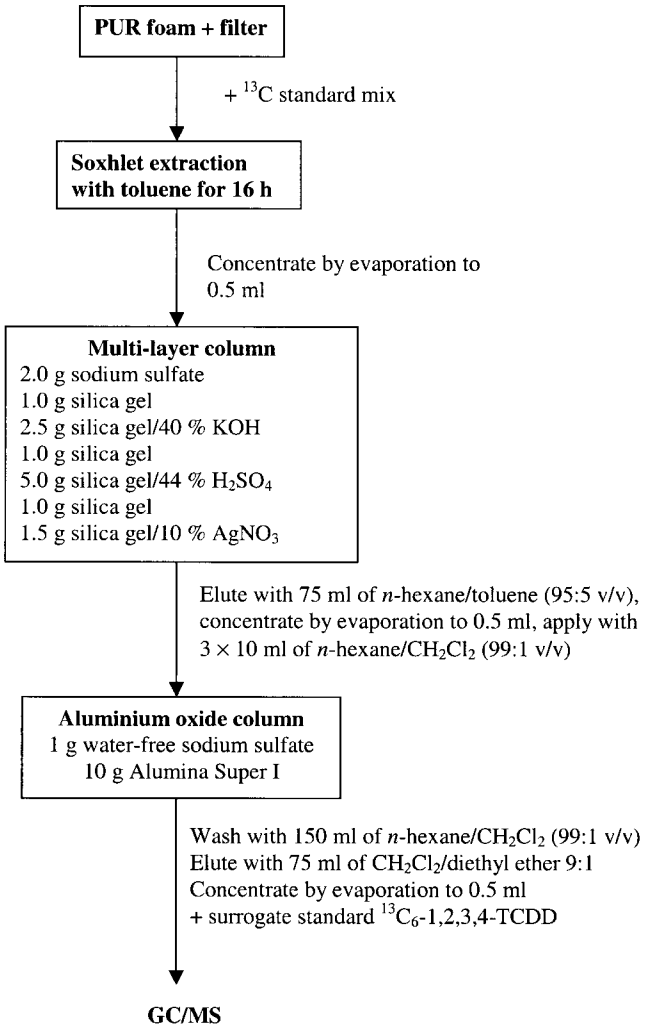

Figure 7

Appendix to Section 7.4
Alternative sample preparation procedures

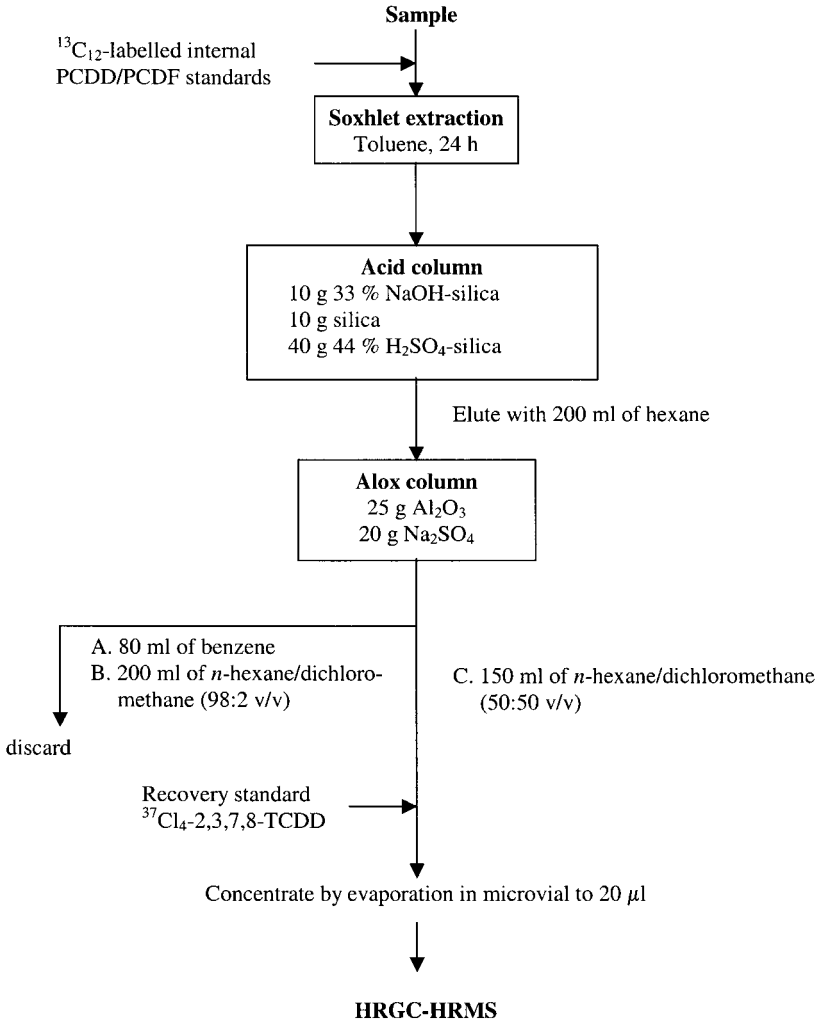

Figure 8

Appendix to Section 7.4
Alternative sample preparation procedures

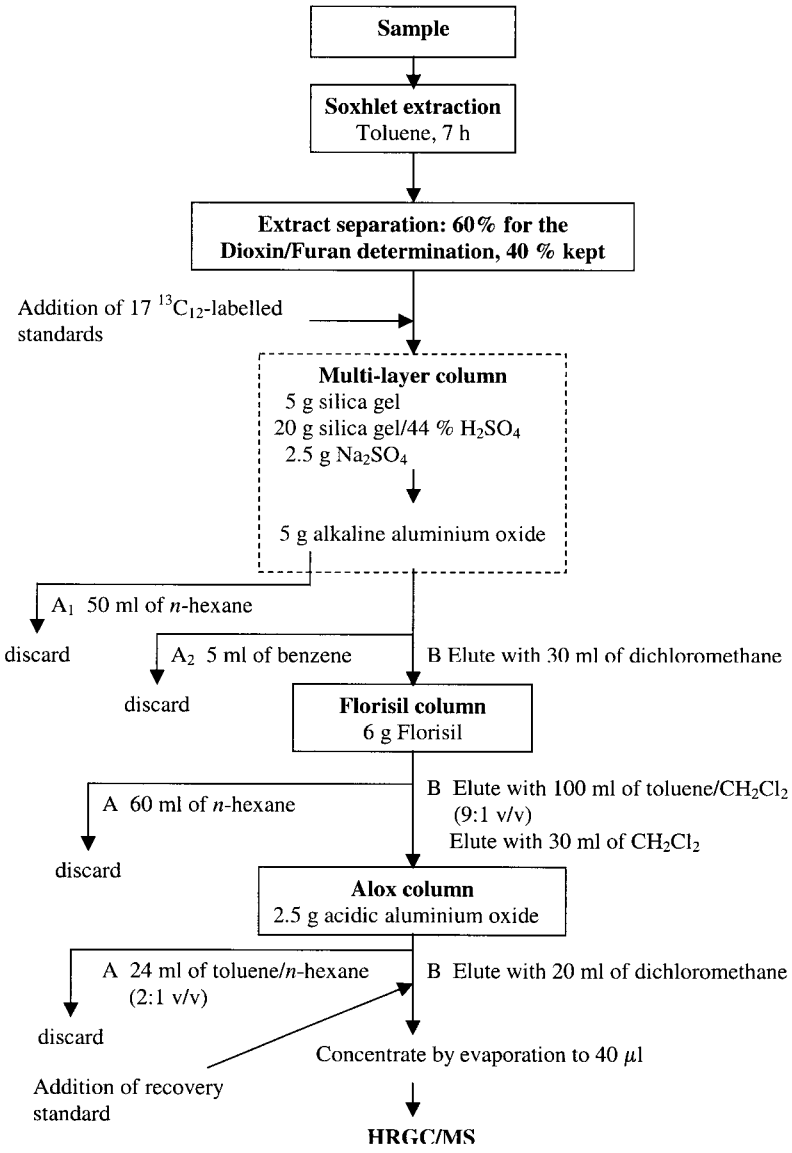

Figure 9

Appendix to Section 7.4
Alternative sample preparation procedures

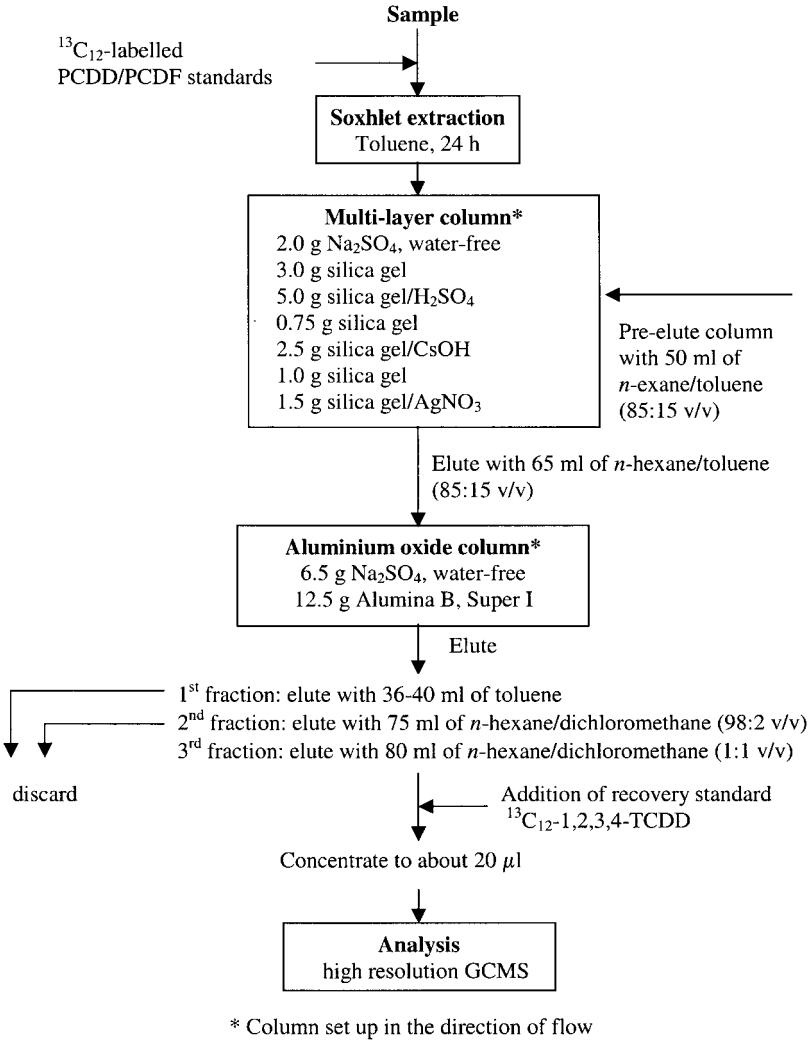

Figure 10

Appendix to 7.5

Alternative operating conditions for analytical determination.

	Laboratory I	Laboratory II	Laboratory III	Laboratory IV	Laboratory V	Laboratory VI
Gas chromatograph	HP 5890 series II	HP 5890 series II	HP 5890 series II	Varian GC 3400	HP 5890 series II	Varian GC 3400
Column	60 m Rtx-2330 ID 0.25 mm, FT 0.1 μm	60 m Rtx-2330 ID 0.25 mm, FT 0.1 μm	60 m Rtx-2330 ID 0.32 mm, FT 0.1 μm	60 m DB-Dioxin ID 0.25 mm, FT 0.15 μm	60 m SP 2331 ID 0.25 mm, FT 0.20 μm	60 m DB-Dioxin ID 0.25 mm, FT 0.2 μm
Temperature programme	90 °C (1.5 min)- 180 °C (25 °C/min)- 260 °C (2 °C/min)- 260 °C (30 min)	140 °C (10 °C/min)- 200 °C (4 °C/min)- 260 °C	120 °C (1 min)- 197 °C (10 °C/min)- 197 °C (0.3 min)- 247 °C (2.4 °C/min)- 247 °C (15 min)	100 °C (3 min)- 220 °C (20 °C/min)- 250 °C (5 °C/min)- 250 °C (90 min)	80 °C (2 min)- 80 °C (20 °C/min)- 200 °C (4 °C/min)- 250 °C (60 min)	130 °C (3 min)- 180 °C (50 °C/min)- 220 °C (15 °C/min)- 220 °C (47 min)- 270 °C (15 °C/min)- 270 °C (36 min)
Injector	Cold on-column Gerstel KAS 3 120 °C-280 °C (12 °C/s)- 280 °C (10 min)- 300 °C (12 °C/s)- 300 °C (10 min)	270 °C splitless Split/Splitless (HP)	290 °C Split/Splitless	Cold on-column Gerstel KAS 2 60 °C-80 °C (2 °C/s)- 80 °C (90 s)- 300 °C (12 °C/s)- 300 °C (10 min)	Cold on-column Gerstel KAS 3 50 °C-80 °C (2 °C/s)- 80 °C (90 s)- 320 °C (12 °C/s)- 320 °C (10 min)	Varian SPI injector 100 °C-300 °C (300 °C/min)- 300 °C (36 min)
Carrier gas	Helium, 200 kPa	Helium, 160 kPa	Helium, 120 kPa	Helium, 180 kPa	Helium, 200 kPa	Helium, 140 kPa
Injection volume	2 μl, splitless	2 μl, splitless	2 μl, splitless	3 μl, splitless	5 μl, splitless	1 μl, splitless
GC/MS interface	260 °C	260 °C	260 °C	250 °C	260 °C	270 °C
MS	Finnigan MAT 95	Finnigan MAT 95	Finnigan MAT 95	Finnigan MAT 90	VG Autospec, Ultima	Finnigan MAT 95
Resolution (valley level of 10 % peak height)	10,000	9,500	10,000	5,000	9,000	9,000
Source temperature	260 °C	260 °C	260 °C	250 °C	260 °C	250 °C
Ionisation energy	70 eV	70 eV	70 eV	70 eV	40 eV	65 eV
Evaluation	SIM $M^{\oplus}$ and $(M+2)^{\oplus}$ or $(M+4)^{\oplus}$	SIM $M^{\oplus}$ and $(M+2)^{\oplus}$ or $(M+4)^{\oplus}$	SIM $M^{\oplus}$ and $(M+2)^{\oplus}$ or $(M+4)^{\oplus}$	SIM $M^{\oplus}$ and $(M+2)^{\oplus}$ or $(M+4)^{\oplus}$	SIM $M^{\oplus}$ and $(M+2)^{\oplus}$ or $(M+4)^{\oplus}$	SIM $M^{\oplus}$ and $(M+2)^{\oplus}$ or $(M+4)^{\oplus}$

ID = internal diameter, FT = film thickness

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Styrene

Method number 2

Application Air analysis

Analytical principle Gas chromatography

Completed in November 1994

Summary

This method permits the determination of styrene after active or passive sampling. With active sampling, measured air volumes are drawn with a sampling pump through sampling tubes filled with Tenax TA. With passive sampling, collection of the hazard substances is carried out via diffusion processes and adsorption on the adsorbent. The adsorbed styrene is thermally desorbed and analysed by a gas chromatograph equipped with a flame ionisation detector. Quantitative evaluation is carried out using calibration standards of known composition. Toluene is used to test the stability of the standards. The peak areas are linearly dependent on the styrene concentrations.

Precision of the whole procedure:	(Active and passive sampling) Standard deviation (rel.): s = 1.98% and 15.55% Mean variation: u = 4.85% and 38.09% for n = 6 determinations and c = 9.9 mg/m^3 Standard deviation (rel.): s = 1.78% and 12.49% Mean variation: u = 4.37% and 30.85% for n = 6 determinations and c = 82 mg/m^3 Standard deviation (rel.): s = 1.52% and 7.82% Mean variation: u = 3.73% and 19.15% for n = 6 determinations and c = 172 mg/m^3
Limit of quantification:	1 mg/m^3 (active sampling) 2 mg/m^3 (passive sampling)
Recovery:	$\eta > 0.98$ (>98%)
Sampling recommendation:	Active sampling: sample volume of about 200 mL with a flow rate of 1–4 mL/min Passive sampling: 4–8 hours

Styrene [C_6H_5–CH=CH_2]

Styrene is a starting material for the synthesis of plastics (polystyrene, copolymers) and polystyrene insulation materials. It is also used as a solvent and reactant in the processing of unsaturated polyester resins.
The MAK-value (1995) was 86 mg/m^3 or 20 mL/m^3 (ppm) [4]. At present (2001) the same MAK-value apply [5].

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Styrene

Method number	2
Application	Air analysis
Analytical principle	Gas chromatography
Completed in	November 1994

Contents

1 General principles

The gaseous styrene is drawn through a sampling tube with a sampling pump (active sampling) or it is collected by diffusion (passive sampling) on sampling tubes containing Tenax TA as adsorbent. During sampling the gas phase is collected quantitatively on the adsorbent.
The analytical determination is carried out by means of gas chromatography after thermal desorption including an intermediate enrichment step in a packed cooling trap. The gas chromatograph is equipped with a flame ionisation detector. Quantitative evaluation is carried out using calibration standards of known composition. Toluene is used to test the stability of the standards. The method has proved successful with active sampling as well as passive sampling [1, 2].

2 Equipment and chemicals

2.1 Equipment

Adsorption tubes made of stainless steel, 6.3 mm x 90 mm, 5 mm internal diameter
Sampling pump, flow rate 1–4 mL/min (e. g. SKC type 224 PCEx 7 from MTC, Müllheim)
Thermometer
Barometer
Diffusion caps (passive sampling) (e. g. from Perkin-Elmer, order number 407-0207)
Gas chromatograph equipped with thermal desorber unit (e. g. ATD 400, Perkin-Elmer) and flame ionisation detector
Computerised data collection and integration system
Apparatus for dynamic calibration or test gas apparatus
Caps (e. g. Swagelock, Teflon or aluminium)

2.2 Chemicals

Styrene, analytical grade or test gas
Toluene, analytical grade
Methanol, analytical grade
Helium (carrier gas) 99.996%
Nitrogen 99.999%
Tenax TA, 60–80 mesh (e. g. Chrompack, Frankfurt)

2.3 Pretreatment of the adsorption tubes

The adsorption tubes are packed with 230 mg of Tenax TA. The adsorbent is fixed between 2 stainless steel sieves. One of the sieves is situated exactly 15 mm from the end of the tube. This side of the sampling tube can therefore be used for passive sampling. Before use the tubes are heated at 250 °C in the thermal desorber and tested for blank values. For storage they are closed with appropriate caps.

2.4 Solutions

A mixture of styrene and toluene is prepared with a ratio between 1 : 1 and 1 : 5. For direct loading of the tubes to prepare the calibration samples the solution is diluted with methanol.

2.5 Calibration standards

Using the solution described in Section 2.4 the adsorption tubes are loaded in a dynamic test gas apparatus (e. g. continuous injection [3]) and closed.

3 Sample collection

Sample collection can be performed as stationary sampling or as personal air sampling. The parameters which are important for the determination of the concentrations in air such as sample air volume, temperature, atmospheric pressure and relative humidity are noted in a sampling protocol. Sampling is carried out in the breathing area. The opening of the adsorption tube should be easily accessible.

3.1 Active sampling

With a sampling pump the air to be analysed is drawn continuously through the adsorption tube at a flow rate of 1–4 mL/min. After sampling, the loaded sampling tube is closed at both ends with suitable caps. A sample volume of at least 200 mL is recommended. The method has been tested with relative humidity of 5–80 %.

3.2 Passive sampling

Before sampling, the cap at the end of the tube intended for passive sampling is replaced by a diffusion cap. The beginning and end of sampling are noted. A sampling time of 4–8 hours is recommended.

4 Analytical determination

4.1 Thermal desorption

The adsorption tubes are put into a thermal desorber, heated and the adsorbed components are transferred to a cooling trap by a carrier gas. After complete desorption the cooling trap is heated. A substance reaches the column as a narrow band.
The following instrumental parameters should be set on the ATD 400 apparatus:

Desorption temperature:	250°C
Desorption time:	5 min
Transfer tubing:	100 °C
Cooling trap (adsorption):	–30 °C
Cooling trap (injection):	300 °C
Weight of the adsorbent in the cooling trap:	20 mg Tenax TA (60–80 mesh)
Carrier gas:	Helium
Input split:	41 mL/min
Desorb flow:	10 mL/min
Output split:	28 mL/min

The instrumental conditions have to be changed if other types of thermal desorbers are used.

4.2 Operating conditions for gas chromatography

Column:	30 m DB-Wax (internal diameter: 0.25 mm, film thickness: 0.5 μm)	
Detector:	FID	
Temperatures:	Furnace:	10 min at 50 °C isothermal, 8 °C/min up to 120 °C, hold for 1 min
	Detector:	200 °C
Carrier gas:	Helium:	column pressure 1.25 kPa (1.7 mL/min)

Under the experimental conditions described the following retention times are obtained:

Methanol	3.95 min
Toluene	8.10 min
Styrene	17.20 min

5 Analytical determination and calibration

To check the functioning of the analytical procedure 100 mL of test gas (calibration gas) from a prepared calibration atmosphere is drawn through adsorption tubes. The concentrations of the test gases should be between 10 and 500% of the limit values

(e. g. test gas preparation according to the VDI guideline 3490, Blatt 8 – Kontinuierliche Injektion [3]). The parameters during the accumulation of the calibration gas (pressure, temperature) are recorded. As an alternative the tubes can also be loaded by injection of aliquots (e. g. 1–10 µL) [1].
After setting up the desorber and the gas chromatograph (see Sections 4.1 and 4.2) the calibration samples and the samples for analysis are analysed. The measured peak areas are plotted against the concentrations used.

6 Calculation of the analytical result

The concentration in the sample is calculated from the peak areas of the calibration samples and the samples for analysis with the following equation:

$$\rho = \frac{A_p \cdot p_k \cdot V_k}{A_k \cdot V_p}$$

where:
ρ Concentration of the analyte in the air sample (mg/m^3)
A_p Peak area of the analyte in the sample
A_k Peak area of the analyte in the calibration gas
ρ_k Concentration of the analyte in the calibration gas (mg/m^3)
V_k Used volume of the calibration gas (mL)
V_p Used volume of the sample (mL), for passive sampling: sampling time (min) × flow rate (0.536 mL/min)

7 Reliability of the method

7.1 Precision

To determine the precision of the method test gas concentrations of 9.9, 82 and 172 mg/m^3 of styrene were generated using a dynamic test gas apparatus. Active and passive sampling were each performed six times. The samples were then prepared and analysed. The following data were obtained:

	Active sampling	Passive sampling
Standard deviation (rel.) Mean variation for $n = 6$ determinations and $c = 9$ mg/m^3	$s = 1.98\%$ $u = 4.85\%$	$s = 15.55\%$ $u = 38.09\%$
Standard deviation (rel.) Mean variation for $n = 6$ determinations and $c = 82$ mg/m^3	$s = 1.78\%$ $u = 4.37\%$	$s = 12.49\%$ $u = 30.85\%$
Standard deviation (rel.) Mean variation for $n = 6$ determinations and $c = 172$ mg/m^3	$s = 1.52\%$ $u = 3.73\%$	$s = 7.82\%$ $u = 19.15\%$

7.2 Recovery rate

The recovery rate was determined by multiple desorption experiments with loaded tubes. The concentrations were between 1/10 and five times the limit value. The recovery rate for both active and passive sampling is over 98%.

7.3 Quantification limit

The quantification limit for active sampling is 1 mg/m^3 with a sample volume of 200 mL. In the case of passive sampling and a sampling time of 4–8 hours the quantification limit is 1–2 mg/m^3.

7.4 Specificity

The specificity of the method depends especially on the type of the column used. In practice the column described has proved successful. If particular interfering components are present another separation phase must be selected.

8 Discussion of the method

The method described permits rapid, automatic determination of styrene. Generally Tenax TA can be used for sampling. If additional substances are to be determined at the same time which are not quantitatively adsorbed on Tenax TA (e.g. acetone and dichloromethane used in UP-resin processing), a more effective adsorbent has to be used (e.g. XAD-4, Chromosorb 106). The adsorption tubes can be used for active and passive sampling. It must be remembered that the retention volume of the analytes is over 100 L/g of adsorbent at 20 °C.

In laboratory tests and in field experiments a collection rate of 0.536 mL/min was determined for Tenax TA.
If other adsorbents or adsorption tubes of other sizes are used the breakthrough volumes and the analytical characteristics must be checked.
The adsorption tubes must be heated in the thermal desorber just before sampling. This is necessary because interfering substances released from the sealing material of the caps can be adsorbed on the collection phase after longer periods of storage.
Water vapour (about 60 % relative humidity) in the air hardly displaces the components from the surface of the collection phase. The loaded adsorption tubes remain stable for one week at temperatures of 20–25 °C (Table 1) without any substance loss.

Table 1. Stability of styrene on Tenax TA (storage at room temperature), theoretical value 132.4 mg/m^3.

Storage period Days	Concentration mg/m^3
0	135.2/134.2
3	132.1/133.1
4	137.1/138.9
5	138.2/138.8
6	137.9/140.1
7	140.8/140.3

Apparatus: ATD 400 and gas chromatograph 8700 from Perkin-Elmer.

9 References

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[2] *Health and Safety Executive* (Ed.): Methods for the Determination of Hazardous Substances: MDHS 43 Styrene in air – diffusive sampling –, HSE March 1985
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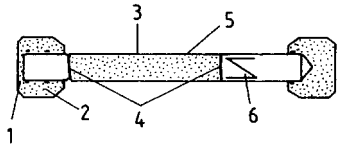

Fig. 1. Sampling tube (type ATD).
Adsorption tube made of stainless steel 6.3 mm × 90 mm, 5 mm internal diameter
1 Cap or
2 Diffusion cap
3 Adsorbent
4 Stainless steel sieves
5 Adsorption tube
6 Spring

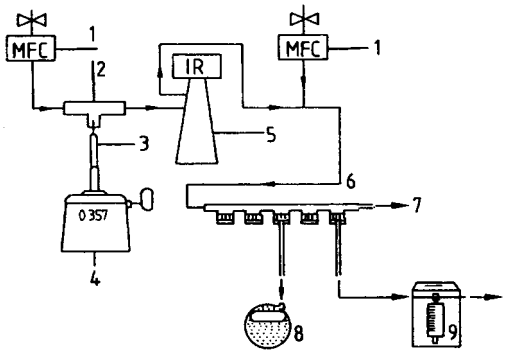

Fig. 2. Dynamic test gas apparatus.
1 Pressure control for zero-gas
2 Injector
3 Piston
4 Piston burette
5 IR monitor or buffer vessel
6 Sampling manifold
7 Excess test gas
8 Sampling pump or
9 Piston pump

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Styrene

Method number 3

Application Air analysis

Analytical principle Gas chromatography

Completed in November 1994

Summary

The method permits the determination of styrene in the air at workplaces as an average concentration during a shift and also as a peak value.
Styrene vapour which is found in the workplace air, for example during the processing of polyester resin [1], is adsorbed on activated carbon tubes. It is desorbed by carbon disulfide and analysed by gas chromatography using a flame ionisation detector. Quantitative evaluation is carried out using *p*-xylene as an internal standard. The calibration standards are prepared by adding the appropriate weight of activated carbon.

Precision of the gas chromatographic analysis:	Standard deviation (rel.):	$s = 0.05\%$
	Mean variation:	$u = 0.1\%$
	for a styrene concentration of 23.6 mL/m^3 and $n = 10$ determinations	
Precision of the complete method:	Standard deviation (rel.)	$s = 1.0\%$
	Mean variation	$u = 2.0\%$
	for a styrene concentration of 23.6 mL/m^3 and $n = 10$ determinations	
Recovery rate:	$\eta = 0.97$ (97%)	
Detection limit:	0.12 µL styrene absolute 1 mL/m^3 styrene for a 25 L air sample volume	
Sampling recommendation:	Personal air sampling:	8 h
	Sampling time:	25 L
	Sampling to determine short-term exposure:	
	Sampling time:	30 min
	Sample volume:	15 L

Styrene [C_6H_5–CH=CH_2]

Styrene is a starting material for the synthesis of plastics (polystyrene, copolymers) and polystyrene insulation materials. It is also used as a solvent and reactant in the processing of unsaturated polyester resins.
The MAK-value (1995) was 20 mL/m^3 (ppm) and corresponds to 86 mg/m^3 [2]. At present (2001) the same MAK value apply [3].

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Styrene

Method number	3
Application	Air analysis
Analytical principle	Gas chromatography
Completed in	November 1994

Contents

1 General principles

Styrene vapour which is found in the workplace air, for example, during the processing of polyester resin [1] is adsorbed on activated carbon tubes. It is desorbed by carbon disulfide and analysed in the solution with a gas chromatograph equipped with a flame ionisation detector. Quantitative evaluation is carried out using *p*-xylene as an internal standard. The calibration standards are prepared by adding the corresponding weight of activated carbon.

2 Equipment, chemicals and solutions

2.1 Equipment

Gas chromatograph equipped with flame ionisation detector (FID)
Capillary column
Integrator for the integration of the peak areas
Flow-stabilised sampling pump (if necessary explosion-proof), suitable for flow rates up to 100 mL/min (personal air sampling) or up to 1 L/min (peak value, stationary sampling at workplaces)
Activated carbon tubes, for example type B from Dräger (collection phase 300 mg, control phase 700 mg activated carbon)
5 mL Vials (or other types of vessels which can be closed tightly)
1 mL Vials (if necessary appropriate for the autosampler)
10 and 50 µL Injection syringes
100 mL Volumetric flasks
Distillation apparatus
Shaking machine

2.2 Chemicals

Styrene, for synthesis, (freshly distilled)
p-Xylene, analytical grade (internal standard)
Carbon disulfide, analytical grade (free of styrene and *p*-xylene)
Toluene, analytical grade (free of styrene and *p*-xylene)

2.3 Solutions

Styrene stock solution: 10 mL of freshly distilled styrene is pipetted into a 100 mL volumetric flask containing about 50 mL of toluene. The solution is diluted up to the mark with toluene (100 µL/mL).

The solution is stable for several weeks. The stability can be checked using gas chromatography by determining the ratio of the peak areas.
p-Xylene (internal standard): 50 µL of *p*-xylene is pipetted into a 100 mL volumetric flask containing about 50 mL carbon disulfide. The solution is diluted up to the mark with carbon disulfide (0.5 µL/mL).

2.4 Calibration standards

The calibration standards are prepared according to the following pipetting scheme:

Styrene stock solution µL	Internal standard solution mL	Activated carbon mg	Weight of styrene in the standard mg	Styrene concentration for a 1 L air sample mL/m^3
1.5	2.0	300	0.14	32.94
2.5	2.0	300	0.23	54.11
6.0	2.0	300	0.55	129.41
10.0	2.0	300	0.91	214.11
25.0	2.0	300	2.28	536.47
50.0	2.0	300	4.55	1070.59

For a 25 L air sample volume (average shift value) this corresponds with a concentration range of 1.26–42.8 mL/m^3 and for a 15 L air sample volume (peak value) with a concentration range of 2.1–71.3 mL/m^3.

3 Sample collection and preparation

3.1 Sample collection

At the workplace a previously labelled activated carbon tube is connected to the sampling pump in such a way that the short phase serves as a collection phase. For personal air sampling over a complete shift a flow rate of about 50 mL/min (3L/h) is set. To determine the peak values a flow rate of about 500 mL/min (30 L/h) is set.
After sampling, the flow rate, the sampling time, the atmospheric pressure at the sampling location and if necessary the temperature are noted. From these parameters the sample volume can be calculated with the following equation:

$$V = \frac{\Delta h \cdot q \cdot 1013 \cdot (273 + t)}{p \cdot 293}$$

where:
V Air sample volume (L)
Δh Sampling time (h)
q Flow rate (L/h)
t Temperature (°C)
p Atmospheric pressure (hPa)

The activated carbon tube is removed from the pump, closed with plastic caps and stored. Under normal ambient conditions it can be kept in the dark for at least two weeks without substance losses.

3.2 Sample preparation

The activated carbon tube is opened in the laboratory using a glass cutter. The carbon from the short collection phase is quantitatively transferred to a 5 mL glass vial. (It is recommended that a funnel be used). About 300 mg of the control phase next to the collection phase is handled in the same manner and transferred to another vial. The remaining carbon is stored for further investigations if substances are detected on the analysed control phase. (Under the sampling conditions described this is unlikely for styrene. However, it is probable for the solvents acetone and dichloromethane which are often used for cleaning purposes during polyester processing).
The separated charcoal phases are each covered with a layer of 2.0 mL of the internal standard (see Section 2.3) and shaken for 2 hours in closed vessels. Immediately afterwards the desorption solution is completely or partially decanted into glass vials intended for sampling the injection solution. (If the samples remain in this solution for a longer time the desorption equilibrium may be shifted. This results in decreasing styrene concentrations in the solution).

4 Operating conditions for gas chromatography

Column:	Material:	Quartz (fused silica)
	Length:	25 m
	Internal diameter:	0.32 mm
	Film thickness:	0.17 µm
	Stationary phase:	5% PhMeSilicone cross linked (Ultra 2 from Hewlett Packard)
Detector:	FID	
Temperatures:	Column:	100 °C
	Injector:	250 °C
	Detector:	250 °C
Carrier gas:	Helium 4.6 (99.996%)	column pressure: 70 kPa
	Split:	1:20 (2 mL/min)

Injection volume: 1 µL
Analysis time: 6 min

5 Analytical determination

1 µL of each of the decanted desorption solutions is injected at least twice (manually or automatically) into the gas chromatograph. The peak areas of the substance and of the internal standard are recorded and the ratios calculated. Using this quotient the corresponding volume (µL) or weight (mg) of styrene can be read off the calibration curve. If styrene was detected in the tested part of the control phase, the remaining control phase must also be analysed. If significant amounts of styrene are also detected here, the reliability of the method can no longer be guaranteed. Otherwise the determined weights of styrene from the collection phase and from the control phase must be added when calculating the result. If necessary the sources of error have to be considered.
If the gas chromatograph is connected to a computer and the calibration is set up to express the styrene concentration in the air, the air sample volume of each sample can be entered as the sample amount and the result can be given directly as the concentration in the air (the correct position of the decimal comma should be checked). The quotient of the peak areas should be within the linear range of the calibration curve.

6 Calibration

Immediately after preparation and after adding 300 mg of carbon the calibration standards (see Section 2.4) are also shaken for two hours, decanted and analysed as described in Section 5. To create the calibration curve the quotients of the peak areas are plotted against the corresponding amounts of styrene (see Fig. 1.). The calibration is linear in the range indicated.
If the gas chromatograph is connected to a computer and the styrene concentration is to be calculated directly the calibration curve is created using the concentrations of the calibration standards recalculated for the used sample volume (for calculation see Section 7).

7 Calculation of the analytical result

Using the quotients of the peak areas of styrene and the internal standard obtained from the analysis of the desorption solutions the corresponding styrene concentrations can be read from the calibration curve. The result is calculated using the following equation:

$$\sigma = \frac{v \cdot d \cdot MV}{MG \cdot V \cdot \eta}$$

$$\rho = \frac{\sigma \cdot MG}{MV}$$

where:

σ	Styrene concentration in the ambient air in mL/m^3
ρ	Styrene concentration in the ambient air in mg/m^3
v	Amount of styrene in the sample in µL
d	Density of styrene (0.91 g/mL)
MV	Molecular volume at 20 °C (24100 mL/mole)
MG	Molecular weight of styrene (104.14 g/mole)
V	Sample volume in L
η	Recovery rate

8 Reliability of the method

The following way describes the validation procedure of this method: Ten activated carbon tubes were loaded twice from the vapour phase at an interval of 15 min with 7 µL of styrene stock solution (20 % styrene by volume) with a flow rate of 500 mL/min and a sampling time of 30 min. This procedure was carried out using a special dosing device connected to a pump (see Fig. 2. of Method number 1 "Styrene" or Fig. 8 on page 7 of the "Special Foreword"). This corresponds with a total amount of 2.8 µL styrene per tube or 23.6 mL/m^3 for a sample volume of 25 L. The tubes were loaded within a period of two weeks. Afterwards the tubes were prepared and analysed on the same day according to Sections 3.2, 4 and 5. The *p*-xylene content in the internal standard solution was 2.5 µL in 2 mL of carbon disulfide (not in accordance with the data in Section 2.3).

The calibration standards containing the same amounts of styrene were prepared twice with and without the addition of 300 mg of carbon. The test solutions were injected automatically into the gas chromatograph twice, one after the other alternately with the calibration solutions, so that each of the four calibration standards was injected five times.

Styrene (and also toluene) were found only on the collection phase.

8.1 Precision

To check the precision of the analytical method (gas chromatographic determination) the standard deviation of the calibration standards was calculated using the following equation [4]:

$$s = \sqrt{\frac{\Sigma\Sigma\,(x_{ij} - \bar{x}_j)^2}{N - M}}$$

where:
s Standard deviation
x_{ij} Measuring value i of the jth group
$\bar{x}_j$ Mean of the jth group
N Number of measurements
M Number of samples

This resulted in a standard deviation (rel.) of s = 0.05% and a mean variation of u = 0.1% with a styrene concentration of 23.6 mL/m^3 and a sample volume of 25 L.
To check the precision of the method (adsorption on activated carbon, preparation and analysis) the desorption solutions from the loaded activated carbon tubes were each injected twice and the results were determined. The standard deviation was calculated from the mean values according to the following equation [3]:

$$s = \sqrt{\frac{\Sigma\,(x_i - \bar{x})^2}{N - 1}}$$

where:
s Standard deviation
x_i Mean value of the ith repeated determination
$\bar{x}$ Mean value of all x_i
N Number of all repeated determinations

After 10 repeated determinations the standard deviation (rel.) was s = 1.0%, the corresponding mean variation u = 2.0%.

8.2 Recovery rate

For the calibration standard with 300 mg of added carbon a recovery rate of 97.2% (η = 0.97) was obtained in the range of 1/20 up to twice the MAK value.

8.3 Desorption rate

For the calibration standard without added carbon a desorption rate of 84.6% was obtained. This corresponds to equilibrium after covering with the desorption agent and shaking for two hours.

8.4 Shelf-life

The concentration values of the tubes loaded at the beginning of the two weeks sample collection were not significantly lower than those of the tubes loaded at the end of the sample collection. The collection phases can therefore be stored in the dark for at least two weeks at ambient temperature conditions. While testing the method, a concentration loss of >10% was observed in the course of the two weeks storage due to the influence of light.

8.5 Detection limit

The lowest amount of calibration standard used was 0.15 µL of styrene. This corresponded with a peak area ratio of 0.12. For an air sample volume of 25 L this is equivalent to 1.26 mL/m^3. From this value a detection limit of about 1 mL/m^3 (ppm) can be estimated.
The detection limit of the analytical method is at least one order of magnitude lower. However, in this concentration range the desorption rate of the sample preparation must be checked. The examiner determined a detection limit of 0.1 mL/m^3 (ppm). The recovery rate was 88%.

8.6 Specificity

The solvents acetone and dichloromethane used as cleaning agents in the polyester processing industry are completely separated from styrene and the internal standard under the described operating conditions for gas chromatography. However, they are not separated from the carbon disulfide peak.

9 Discussion of the method

The method described permits a precise determination of styrene concentrations in the air.
If possible, the loaded tubes should be kept in the dark.
Furthermore, the desorption solution covering the adsorbent must be decanted after 2 h because longer periods lead to a decrease in the styrene concentration.

Apparatus used: Gas chromatograph HP 5890 series II equipped with autosampler and HP 3365 series II ChemStation as a control and evaluation unit from Hewlett Packard.

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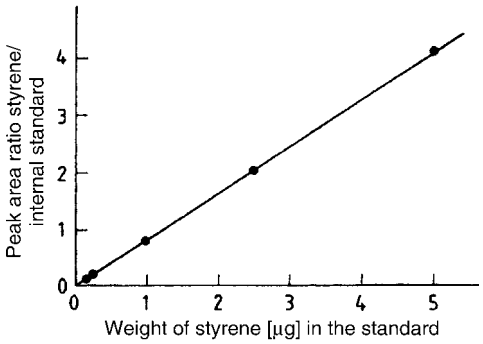

Fig. 1. Example of a calibration curve for the determination of styrene in the air.

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Federation of the Employment Accidents Insurance Institutions of Germany
(Hauptverband der Berufsgenossenschaften)
Centre for Accident Prevention and Occupational Medicine
Alte Heerstraße 111, 53757 Sankt Augustin
Expert Committee Chemistry

Carcinogenic substances Order number: BGI 505-61E
Established methods Issue: December 1996

Method for the determination of α,α,α-trichlorotoluene

Method tested and recommended by the Berufsgenossenschaften for the determination of α,α,α-trichlorotoluene (benzotrichloride) 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 adsorption on Tenax,
gas chromatography after desorption.
"α,α,α-Trichlorotoluene-1-GC"
(Issue: December 1996)

IUPAC name:	**CAS No:**
α,α,α-trichlorotoluene	98-07-7

1 Sampling with a pump and adsorption on Tenax, gas chromatography after desorption

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

Principle: With a pump a measured air volume is drawn through a Tenax tube. The adsorbed α,α,α-trichlorotoluene is desorbed with *n*-hexane and determined by gas chromatography.

Technical data:

Quantification limit: absolute: 0.5 ng α,α,α-trichlorotoluene,
relative: 0.01 mg/m^3 α,α,α-trichlorotoluene for 48 L air sample, 1 mL desorption solution and 1 µL injection volume.

Selectivity: Interfering components may cause too high values. In general, interference can be eliminated by selecting a column with different separating characteristics.

Advantages: Both personal and selective sampling are possible.

Disadvantages: No indication of concentration peaks.

Apparatus: Pump,
gas meter or flow meter,
Tenax tubes,
gas chromatograph (GC) with flame ionisation detector (FID).

Detailed description of the method

Contents

1 Equipment, chemicals and solutions

1.1 Equipment

For sampling:
Pump, suitable for a flow rate of 100 mL/min (e.g. PP1 from Gilian, supplier in Germany: DEHA-Haan & Wittmer GmbH, 71288 Friolzheim)
Gas meter or flow meter
Adsorption tubes with Tenax, standardised, consisting of two Tenax fillings of about 50 mg and 100 mg separated with glass wool (e.g. Catalogue No 226–35-03 from SKC, supplier in Germany: MTC-GmbH, Müllheim)
Caps for the opened Tenax tubes

For sample preparation and analysis:
2 mL Beaded rim vials with polytetrafluoroethylene (PTFE)-coated septa and crimp caps
Crimper
Shaking machine
50 mL Volumetric flask
0.2, 0.5, 1, 2 and 5 mL Pipettes
10 and 50 µL Injection syringes
Gas chromatograph with FID
Data analysis device

1.2 Chemicals

n-Hexane, purity at least 99%, water-free
α,α,α-Trichlorotoluene, purity at least 99%
Gases for operating the gas chromatograph: Helium, purity 99.995%
Hydrogen, purity 99.995%
Synthetic air, free from hydrocarbons

1.3 Solutions

α,α,α-Trichlorotoluene stock solution:
Solution of 10 mg/mL α,α,α-trichlorotoluene in *n*-hexane.
Approx. 500 mg α,α,α-trichlorotoluene is weighed into a 50 mL volumetric flask to the nearest 0.1 mg. The volumetric flask is filled to the mark with *n*-hexane.

Calibration solutions:
Solutions of 1.0 µg/mL, 4 µg/mL, 10 µg/mL, 40 µg/mL, 0.1 mg/mL, 0.4 mg/mL and 1 mg/mL α,α,α-trichlorotoluene in *n*-hexane.
5 µL, 20 µL, 50µL, 0.2 mL, 0.5 mL, 2 mL and 5 mL of the α,α,α-trichlorotoluene stock solution are each transferred to 50 mL volumetric flasks already containing about 10 mL *n*-hexane. The volumetric flasks are filled to the mark with *n*-hexane.
With these solutions and an air sample volume of 48 L and 1 mL desorption solution a concentration range of 21 µg/m^3 to 21 mg/m^3 α,α,α-trichlorotoluene in air is covered.

2 Sampling

The flow rate of the pump is set to a maximum of 100 mL/min. With sampling for 8 hours this corresponds to a maximum air sample volume of 48 L. A Tenax tube is opened and connected to the pump. During working hours the pump and tube are worn by a person or used in a stationary position. After sampling, the tube is closed with caps.

3 Analytical determination

3.1 Sample preparation and analysis

The contents of the loaded Tenax tube are transferred to a 2 mL beaded rim vial and 1 mL *n*-hexane is added. The beaded rim vial is closed and shaken for 30 minutes. 1 µL of the supernatant solution (desorption solution) is injected into the gas chromatograph.

To ensure that the desorption solvent and the Tenax tube do not contain any impurities, the filling of an unloaded Tenax tube is treated with 1 mL *n*-hexane (blank solution). 1 µL of the blank solution is injected into the gas chromatograph.

3.2 Operating conditions for gas chromatography

The method was characterized under the following experimental conditions:

Apparatus:	Gas chromatograph, Hewlett-Packard 5890 with FID	
Column:	Material:	Quartz capillary
	Length:	50 m
	Internal diameter:	0.32 mm
	Stationary phase:	SE-54
	Film thickness:	0.5 µm
Temperatures:	Injector:	200 °C
	Detector:	300 °C
	Furnace temperature programme:	
	Starting temperature:	60 °C, 2 min isothermal
	Heating rate:	10 °C/min
	Final temperature:	280 °C
Injection mode:	Splitless, 0.5 min	
Carrier gas:	Helium, approx. 2.5 mL/min	
Detector gases:	Hydrogen, 35 mL/min	
	Air, 400 mL/min	
Make-up gas:	Helium, 15 mL/min	
Injection volume:	1 µL	

4 Evaluation

4.1 Calibration

1 mL of each of the calibration solutions described in Sect. 1.3 are added to the contents of an unloaded Tenax tube in beaded rim vials and analysed as described in Sect. 3.1.
The calibration curve is obtained by plotting the measured peak areas or peak heights against the α,α,α-trichlorotoluene weights contained in the various calibration solutions. The calibration curve is linear in the given concentration range.

4.2 Calculation of the analytical result

Quantitative evaluation of the chromatograms is carried out according to the external standard method. The concentration by weight c_w in the air sample in mg/m^3 is calculated according to Equation (1):

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

The concentration by volume c_v in mL/m^3 calculated from c_w for 20 °C and 1013 hPa is:

$$c_v = 0.12 \cdot c_w \tag{2}$$

Legend:
c_w Concentration by weight of α,α,α-trichlorotoluene in the air sample in mg/m^3
c_v Concentration by volume of α,α,α-trichlorotoluene in the air sample in mL/m^3
w Weight of α,α,α-trichlorotoluene in the desorption solution in µg
V Air sample volume in L
η Recovery rate

5 Reliability of the method

5.1 Accuracy and recovery

To determine the relative standard deviation of the method, different weights of α,α,α-trichlorotoluene were each loaded onto six Tenax tubes by means of a syringe. Six tubes were prepared with 0.5 µL of the calibration solution with the highest concentration, 0.5 µL stock solution and 1 µL stock solution. Under the sampling conditions described in Sect. 2, 48 L of air were drawn through each of the tubes. The tubes were then analysed. This loading corresponded to air sample concentrations of 0.01, 0.1 and 0.2 mg/m^3 α,α,α-trichlorotoluene.
Under the given conditions the 6 independent measurements yielded the relative standard deviations and recoveries listed in Table 1.

Table 1. Standard deviation (rel.) *s* and recovery rate.

Concentration mg/m^3	Standard deviation (rel.) *s* %	Recovery rate
0.01	7.6	1.06
0.1	3.9	0.90
0.2	4.0	0.93

5.2 Quantification limit

The absolute quantification limit is 0.5 ng α,α,α-trichlorotoluene. It was determined from the signal noise ratio of the chromatograms.
The relative quantification limit is 0.01 mg/m^3 α,α,α-trichlorotoluene for a 48 L air sample, 1 mL desorption solution and a 1 µL injection volume.

5.3 Selectivity

The selectivity of the method depends on the type of column used. In practice the given column has proved reliable. If interfering components are found, a column with other separation characteristics should be used.

6 Discussion

As the quality of the Tenax tubes varies greatly, the blank value of each Tenax tube used should always be checked.
The loaded tubes can be stored at 5–7 °C for at least 7 days without any loss of adsorbed α,α,α-trichlorotoluene.
The stock solution and calibration solutions must be freshly prepared each day due to the sensitivity of α,α,α-trichlorotoluene to hydrolysis.

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Working Group "Analytical Chemistry" of the Commission of the Deutsche Forschungsgemeinschaft for the Investigation of Health Hazards of Chemical Compounds in the Work Area

Organization

The Working Group "Analytical Chemistry" was established in 1969. Under the chairmanship of Prof. Dr. J. Angerer at the present it includes two Working Subgroups:

"Air Analyses"
(Leader: Prof. Dr. rer. nat. Dr. h.c. A. Kettrup)

"Analyses of Hazardous Substances in Biological Materials"
(Leaders: Prof. Dr. J. Angerer and Chem.-Ing. K.H. Schaller).

The participants, who have been invited to collaborate on a Working Subgroup by the leaders, are experts in the field of technical and medical protection against chemical hazards at the workplace. A list of members and guests of "Analyses of Hazardous Substances in Air" is given at the end of this volume.

Objectives and operational procedure

The two analytical subgroups are charged with the task of preparing methods for the determination of hazardous industrial materials in the air of the workplace or to determine these hazardous materials or their metabolic products in biological specimens from the persons working there. Within the framework of the existing laws and regulations, these analytical methods are useful for ambient monitoring at the workplace and biological monitoring of the exposed persons.
In addition to the working out the analytical procedure, these subgroups are concerned with the problems of the preanalytical phase (specimen collection, storage, transport), the statistical quality control, as well as the interpretation of the results.

Development, examination, release, and quality of the analytical methods

In its selection of suitable analytical methods, the Working Group is guided mainly by the relevant scientific literature and the expertise of the members and guests of the Working Subgroup. If appropriate analytical methods are not available they are worked out within the Working Group. The leader designates an author, who assumes the task of developing and formulating a method proposal. The proposal is examined experimentally by at least one other member of the project, who then submits a written report of the results of the examination. As a matter of principle the examination must encompass all phases of the proposed analytical procedure. The examined method is then laid before the members of the subgroups for consideration. After hearing the judgement of the author and the examiner they can approve the method. The method can then be re-

leased for publication after a final meeting of the leader of the Working Group "Analytical Chemistry" with the subgroup leaders, authors, and examiners of the method.
Under special circumstances an examined method can released for publication by the leader of the Working Group after consultation with the subgroup leaders.
Only methods for which criteria of analytical reliability can be explicitly assigned are released for publication. The values for inaccuracy, imprecision, detection limits, sensitivity, and specificity must fulfil the requirements of statistical quality control as well as the specific standards set by occupational health. The above procedure it meant to guarantee that only reliably functioning methods are published, which are not only reproducible within the framework of the given reliability criteria in different laboratories, but also can be monitored over the course of time.
In the selection and development of a method for determining a particular substance the Working Group has given the analytical reliability of the method precedence over aspects of simplicity and economy.

Publications of the working group

Methods released by the Working Group are published in the Federal Republic of Germany, by the Deutsche Forschungsgemeinschaft as a loose-leaf collection entitled "Analytische Methoden zur Prüfung gesundheitsschädlicher Arbeitsstoffe" (WILEY-VCH Verlag, Weinheim, FRG). The collection at present consists of two volumes:

Volume I	"Luftanalysen"
Volume II	"Analysen in biologischem Material".

These methods are also to be published in an English edition. Volume 1 to 7 of "Analyses of Hazardous Substances in Biological Materials" have already been published. The work at hand represents the fifth English issue of "Analyses of Hazardous Substances in Air".

Withdrawal of methods

An analytical method that is made obsolete by new developments or discoveries in the fields of instrumental analysis or occupational health and toxicology can be replaced by a more efficient method. After consultation with the membership of the relevant project and with the consent of the leader of the Working Group, the subgroup leader is empowered to withdraw the old method.

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