ELSEVIER

Journal of Chromatography A, 962 (2002) 175–181

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Sensitive indoor air monitoring of monoterpenes using different adsorbents and thermal desorption gas chromatography with mass-selective detection

Juliane Hollender*, Frank Sandner, Manfred Möller, Wolfgang Dott

Institut für Hygiene und Umweltmedizin, RWTH Aachen, Pauwelsstrasse 30, 52074 Aachen, Germany

Received 7 January 2002; received in revised form 18 April 2002; accepted 22 April 2002

Abstract

A simple method using active trapping on adsorbents and thermal desorption followed by GC–MS analysis was developed for the indoor air monitoring of monoterpenes. The study was carried out using a dynamically generated atmosphere consisting of 11 monoterpenes: camphene, camphor, Δ^3-carene, 1,8-cineol, limonene, linalool, α-pinene, β-pinene, α-terpinene, γ-terpinene, fenchyl alcohol. The influence of the different adsorbents Tenax TA, Tenax GR, Carbosieve SIII, Chromosorb 106 on the yield of six selected monoterpenes at indoor air concentrations was studied. The adsorbent Tenax GR gave relatively the best yields followed by Tenax TA. Detection limits of approximately 1 μg m^3 were determined with Tenax GR for most of the monoterpenes.

Keywords: Thermal desorption; Air analysis; Adsorbents; Monoterpenes; Terpenes

1. Introduction

Monoterpenes such as α-pinene, β-pinene, camphene, Δ^3-carene, α-terpinene, and limonene are released into indoor air mainly from building materials of wood, paints and varnishes, cleaning agents and cosmetics. Because of these various exposure sources, monoterpenes are one of the most frequent group of volatile organic compounds (VOCs). In Germany, they contribute 10–60% to the total VOCs with concentrations in the μg m^3 range [1–3]. In contrast to other compounds like benzene, toluene and xylenes, in recent years, the indoor air terpene concentrations are reported to be higher, obviously because of the increasing use of natural products and furniture made of wood. In new dwelling houses, maximal terpene concentrations of 797 μg m^3 were measured [4,5]. Therefore the question arises whether these concentrations lead to health effects and sensitive, simple and valid methods for indoor air monitoring are necessary.

Air sampling, using adsorbents, thermal desorption and gas chromatography, is a common method for identifying and quantifying trace levels of VOCs in the environment [6,7]. However, indoor air sampling of VOCs and monoterpenes during many studies was performed by solvent desorption with carbon disulfide instead of thermal desorption [1,3] although this method is less sensitive, solvent consuming and the

*Corresponding author. Tel.: +49-241-808-8282; fax: +49-241-808-2477.

E-mail address: juliane.hollender@post.rwth-aachen.de (J. Hollender).

0021-9673/02/$ – see front matter
PII: S0021-9673(02)00511-3

procedure is prone to errors. In addition, diffusive sampling is often performed [8], but for this method, longer sampling periods are necessary.

For environmental monitoring of several monoterpenes various adsorbents such as charcoal, Carbopack B [9], Carboxen 569 [10] Tenax TA [8,11,12], Tenax GC [13] or Tenax GR [14] have been used but usually the efficiency of different adsorbents was not compared. Comparing solvent elution and thermal desorption from Tenax TA, Griffiths et al. [15] found broadly similar monoterpene concentrations apart from Δ^3-carene that was detected in consistently lower levels in the thermally desorbed samples. The decrease was possibly caused by breakdown of Δ^3 carene. Decomposition of terpenes especially with several C–C double bonds on various grades of Tenax and Carboxen was described, and had been reported to be caused mostly by reaction with atmospheric ozone [10,16,17].

The aim of this study was to compare different adsorbents which are often used for VOC monitoring for active air sampling of monoterpenes in indoor air concentrations within the lower $\mu g\ m^{-3}$ range. For the best adsorbent the validation parameters such as the detection limits should be determined. Eleven monoterpenes that are detected in indoor air were selected for the study. In order to avoid exceeding the breakthrough volume (BTV) that had been determined for monoterpenes up to several litres [12,18,19] relatively low flow-rates (10 ml min^{-1}) and a short sampling period (1 h) resulting in only 600 ml sample volumes were used. Since no significant effect of the relative humidity on the recovery had been determined for many similar VOCs [20] this parameter was not investigated.

2. Experimental

2.1. Chemicals

The monoterpenes used in the test mixture were Δ^3-carene, α-pinene, β-pinene, α-terpinene, γ-terpinene (Fluka, Bern, Switzerland), 1,8-cineol, limonene, linalool (Merck, Darmstadt, Germany), camphene, camphor and fenchyl alcohol (Aldrich, Milwaukee, WI, USA). Methanol Suprasolv used as solvent for standards was obtained from Merck.

2.2. Adsorbents

The adsorbents tested and their characteristics are presented in Table 1. The sample tubes of quartz glass (Supelco, Deisenhof, Germany, 160 mm length×6 mm O.D.×4 mm I.D.) contained adsorbent (approx. 300 mg/tube) and silanized glass wool at both ends. Apart from Chromosorb 106 tubes, the adsorbent tubes were conditioned before use by heating three times for 10 min at 260 °C in a stream of helium (100 ml min^{-1}) in the thermal desorption injector (ATD 400, Perkin-Elmer). Chromosorb tubes were heated only to 230 °C because of the decomposition at higher temperature. The conditioned tubes were sealed with Swagelok fittings with PTFE ferrules before sampling.

2.3. Generation of test atmosphere

Artificial air samples were prepared by an instrument (KS 1095 D-1, Axel Semrau, Spröckhovel,

Table 1
Characteristics of the adsorbent materials tested

Adsorbent	Material	Particle size (μm)	Surface area ($m^2\ g^{-1}$)	Max. temperature (°C)	Supplier
Tenax GR	2,6-Diphenyl-*p*-phenyleneoxide mixed with 23% graphitized carbon	180–250	24	375	Supelco
Tenax TA	2,6-Diphenyl-*p*-phenyleneoxide	180–250	35	375	Supelco
Carbosieve SIII	Molecular sieve (carbon)	180–250	820	400	Chrompack
Chromosorb 106	Cross-linked polystyrene	180–250	600–700	250	Chrompack

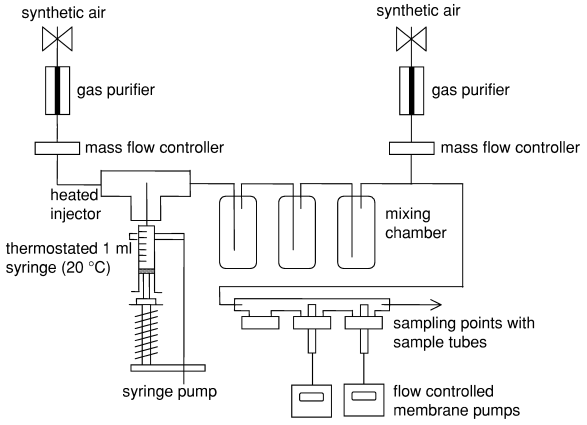

Fig. 1. A schematic view of the gas generation system.

Germany) for the dynamic generation of test gases, using synthetic air and methanol solutions of the monoterpenes (Fig. 1). The methanol solution was automatically injected from a 1-ml syringe at 0.002 ml min^{-1} through the heated syringe needle in a 100 ml flow-controlled stream of synthetic air. The syringe was kept at 20 °C. The synthetic air stream with the monoterpenes was mixed in the glass chamber with an air stream adjusted to 5.0 l min^{-1} by a flow controller. Prior to the generation of test atmosphere, the synthetic air was cleaned using a gas filter cartridge containing a molecular sieve (Lesker, Clairton, PA, USA). Air sampling was carried out after an equilibrium time of 60 min. Four samples were taken on the four different adsorbents by four pumps at the same time in the generation equipment. For each terpene concentration generated two samples for each adsorbent were taken.

Table 2
Retention times and main fragments of terpenes found using the GC–MS method

	Terpene	Retention time (min)	Main fragments[a] (m/z)
1	α-Pinene	18.23	77, **93**, 121, 136
2	Camphene	19.05	79, **93**, 121, 107
3	β-Pinene	20.21	69, **93**, 121, 136
4	Δ^3-Carene	21.45	77, 79, 91, **93**
5	α-Terpinene	21.59	77, **93**, 121, 136
6	Limonene	22.29	53, **67**, 93, 121
7	1,8-Cineol	22.37	**69**, 81, 89, 108, 139
8	γ-Terpinene	23.41	**93**, 121, 136
9	Linalool	25.14	55, 69, **71**, 93, 121
10	Fenchyl alcohol	25.53	69, 80, **81**, 111
11	Camphor	27.05	81, **95**, 108, 152

[a] Mass fragments (in bold) were used for quantitation.

2.4. Air sampling

Immediately before sampling the adsorbent tubes were opened and active air sampling was done by calibrated flow controlled membrane pumps (224-PCEX 8, SKC, Eighty Four, PA, USA). A sampling time of 60 min and a sampling rate of 10.0 ml min^{-1} resulted in a total sample volume of 600 ml. Afterwards the tubes were sealed with Swagelok fittings with PTFE ferrules and stored at 20 °C in the dark for a few days until analysis.

2.5. Thermal desorption and GC–MS analysis

Thermal desorption (purge and trap) of the monoterpenes from the adsorbents was performed with a thermal desorption injector (ATD 400, Perkin-Elmer). The monoterpenes were desorbed for 10 min at 250 °C with a helium 5.0 flow of 100 ml min^{-1} from the Tenax and Carbosieve SIII material and at 220 °C from Chromosorb 106. Tenax TA was used as adsorbent for the secondary cold trap at −30 °C. Desorption of this trap was performed with 10 ml min^{-1} outlet flow of the helium at 270 °C for 3 min. The transfer line to the GC system (Perkin-Elmer GC 8500) was kept at 225 °C and the pressure on the injector and column was 170 kPa (helium). Chromatographic separation was carried out with a fused-silica capillary column (Restek Type Rtx-5, 60 m× 250 μm I.D., film thickness 0.25 μm). The GC temperature program was 8 min isotherm at 40 °C, with 5 °C min^{-1} up to 90 °C, 0.1 min isotherm, then 10 °C min^{-1} up to 280 °C, 12.3 min isotherm. Mass-selective detection was carried out on an ion trap (Finnigan MAT ITD 800). Identification of the terpenes was based on retention time and matching of the mass spectra with reference spectra. Quantitation was carried out by the specific main mass fragments of the monoterpenes (Table 2).

3. Results and discussion

3.1. Comparison of different adsorbents

The adsorption of the six selected monoterpenes α-pinene, β-pinene, Δ^3-carene, limonene, linalool and camphor on the four different adsorbents Tenax GR, Tenax TA, Carbosieve SIII, and Chromosorb 106 was compared using the dynamically generated artificial atmosphere. Six different concentrations in the range from 1.0 up to 100 μg m^{-3} were sampled using methanol standard solutions with monoterpene concentrations of 0.0025–0.25 mg ml^{-1}. The resulting high methanol concentrations in the generated atmospheres are not present in true indoor environments but cannot be avoided using this gas generation instrument for calibration. Methanol was used because the adsorbents have only a low affinity for this polar solvent as one supplier of the adsorbents (Supelco) stated and it does not interfere with the GC–MS analysis. In Fig. 2 the peak area of the monoterpenes at a concentration of 10 μg m^{-3} are shown for the different adsorbents. The best yields were reached with Tenax GR followed by Tenax TA for all terpenes tested independent of their different functional groups. In contrast, comparing Chromosorb 106 and Tenax TA for diffusive sampling, Sunesson et al. [8] reported lower results with Tenax TA for some monoterpenes. Perhaps these differences are caused by the different sampling procedures. Peters et al. [12] found irreproducible results and loss of terpenes with Tenax GR which were attributed to the graphite in the adsorbent. Sunesson et al. [20] described breakdown of geosmin and 2-methylisoborneol during thermal desorption from Tenax GR. In this study, such effects were not observed, perhaps because of the high desorption temperature (270 °C) and high helium flow (100 ml min^{-1}) used or the improvement of the adsorbent material by the supplier. The effect of the adsorbents on the yield was for the six investigated monoterpenes independent of the concentration as shown in Fig. 3 for the example compound α-pinene. The relation between the terpene yields with the different adsorbents remained constant for all monoterpenes at increasing concentrations (data not shown). Sunesson et al. [8] reported that sampling with Tenax TA were affected by the concentration as well as the sampling

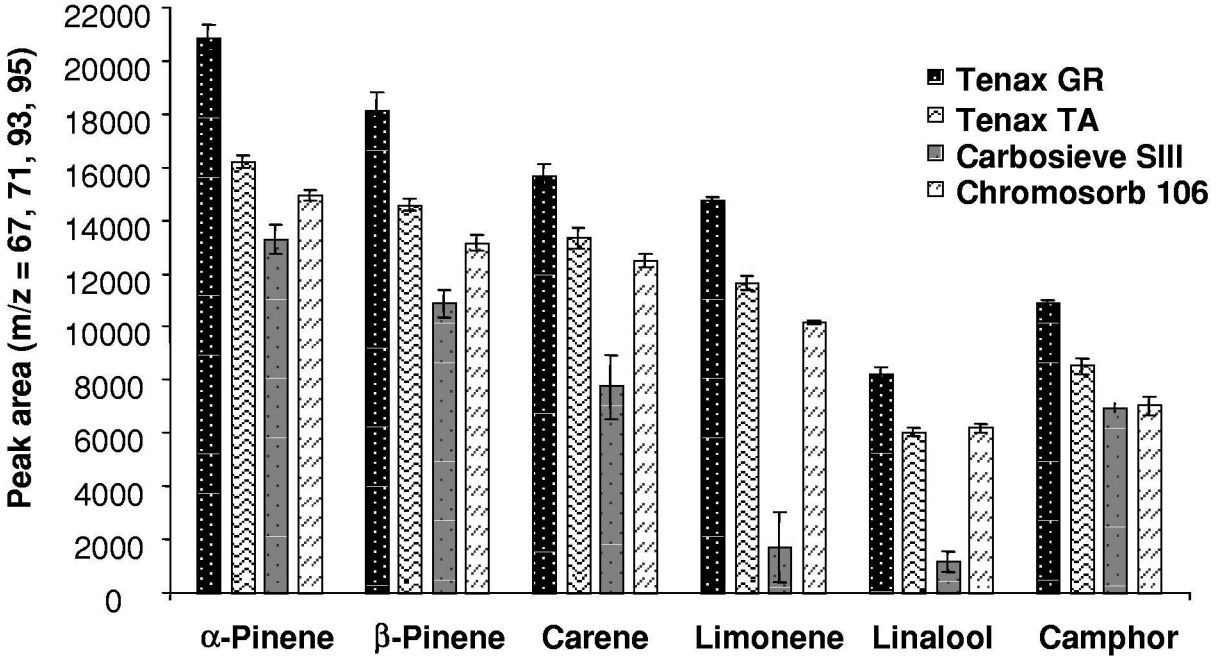

Fig. 2. Influence of the adsorbent material on the yield of terpenes.

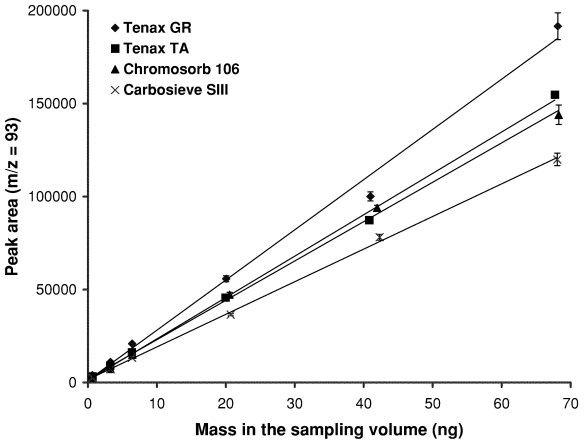

Fig. 3. Calibration curves of α-pinene for different adsorbents.

time but they had used higher concentrations and longer sampling times.

3.2. Validation of the GC–MS method

A chromatogram of a prepared artificial air sample with 11 terpenes is shown in Fig. 4. All peaks are separated well within the time range of 18–27 min. For quantitation the main fragments were selected from the mass spectra (Table 2). The background sampling of artificial synthetic air without monoterpenes was performed. The background values were very low, in the range of the noise showing no interference with the monoterpene peaks.

In order to prove the reliability of the method and the application limits, the correlation coefficients, detection and quantitation limits were determined using artificial air samples with at least 10 different concentrations for each compound in the range of 0.05 up to 56.1 μg m^{-3} using the best adsorbent, Tenax GR (Table 3). The *F*-test proved that the calibration functions were linear. Detection and quantitation limits were calculated from the calibration curves according to DIN 32645 [21] and compared with the values obtained using the signal-to-noise ratio method (Table 3). The values of almost all terpenes are below 1 μg m^{-3} with both determination methods. Only 1,8-cineol and linalool showed significantly higher detection limits determined by the DIN 32645. The RSD values are relatively high, obviously caused by the variation of the mass detection sensitivity on different days. Therefore it is recommended to measure standards each day. The quantitation limits are similar to the values received by a method using activated charcoal as adsorbent for 450 l air volume and carbon disulfide as desorption solvent [3]. The detection limits could be further improved using higher sampling rates and longer sampling times resulting in air volumes higher than 600 ml. By using this procedure, the sample volume must be taken into account in order to avoid breakthrough.

3.3. Indoor air samples

The described sampling and analysing procedure for monoterpenes was applied to real indoor air

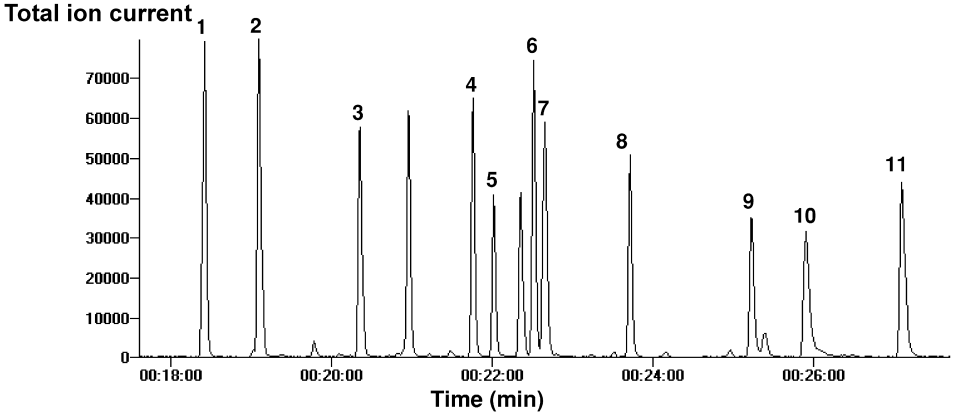

Fig. 4. GC–MS chromatogram of an artificial air sample (each monoterpene 50 μg m^{-3}), terpene standards as in Table 2.

Table 3
Detection limit, quantitation limit and correlation coefficient of the terpenes determined

	Terpene	Detection limit		Quantitation limit ($\mu g\ m^{-3}$)	Method RSD (%)	Method SD ($\mu g\ m^{-3}$)	Correlation coefficient
		DIN 32645 ($\mu g\ m^{-3}$)	$S/N>3$[a]				
1	α-Pinene	0.32	0.52	1.02	14.6	0.07	0.975
2	Camphene	0.54	0.55	1.62	17.2	0.10	0.927
3	β-Pinene	0.48	0.74	1.45	14.0	0.09	0.943
4	Δ^3-Carene	0.32	0.65	0.96	11.7	0.07	0.976
5	α-Terpinene	0.21	1.07	1.53	16.3	0.10	0.968
6	Limonene	0.47	0.55	1.42	20.9	0.10	0.936
7	1,8-Cineol	3.32	0.71	9.69	7.7	0.61	0.998
8	γ-Terpinene	0.59	0.86	1.77	18.4	0.10	0.943
9	Linalool	4.74	1.22	14.22	6.0	0.90	0.997
10	Fenchyl alcohol	0.81	1.28	2.44	7.7	0.11	0.970
11	Camphor	0.87	0.94	2.74	13.9	0.17	0.974

[a] Signal-to-noise ratio >3.

samples. Storage of indoor air samples on the adsorbents until analysis was possible because no significant decrease in the terpenes was found during storage of the capped sample tubes at room temperature in the dark for 3 weeks (data not shown). As an example, the chromatogram of the indoor air atmosphere of a new dwelling-house is shown in Fig. 5. The five terpenes α-pinene, β-pinene, Δ^3-carene, camphene and limonene could be identified clearly in addition to other volatile organic compounds. The concentrations are similar to the 50 percentile values measured by active air sampling in newly built private homes in Germany shown by analysis after solvent desorption [3]. Camphene concentrations were not determined in this study. The high β pinene, α-pinene, and Δ^3-carene concentrations can be caused by the parquet floor covering. The concentrations of the other monoterpenes investigated are below the detection limits.

During ambient air sampling, unsaturated monoterpenes may undergo decomposition through reaction with atmospheric ozone [12,16,22]. In order to investigate whether this is also relevant for indoor air with higher monoterpene and lower ozone concentrations, sampling with the qualified ozone scrubber noXon (polyphenylenesulfide, Hoechst, Frankfurt am Main, Germany) [23] was carried out simultaneously. No significant decomposition was observed for

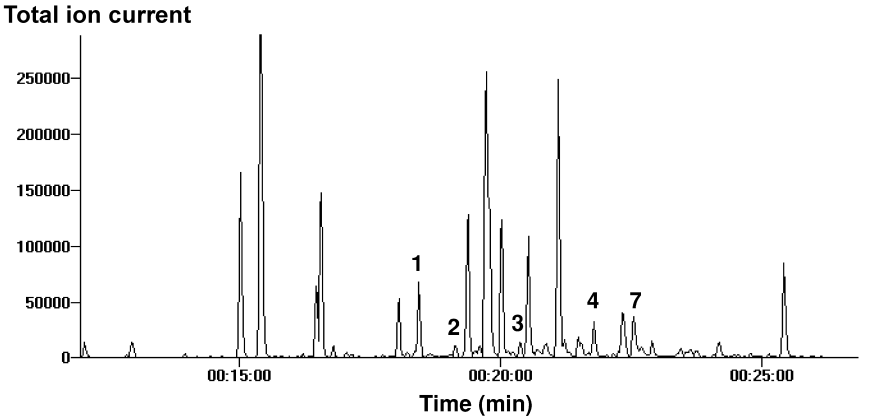

Fig. 5. Chromatogram of an indoor air sample from a new dwelling. 1, 26.4 $\mu g\ m^{-3}$ α-pinene; 2, 9.4 $\mu g\ m^{-3}$ camphene; 3, 13.0 $\mu g\ m^{-3}$ β-pinene; 4, 14.2 $\mu g\ m^{-3}$ Δ^3-carene; 7, 18.2 $\mu g\ m^{-3}$ limonene.

the five compounds. This indicated that ozone removal is not necessary for indoor terpene monitoring if no ozone sources are present but further investigations have to be performed.

4. Conclusions

The simple method developed using trapping on an adsorbent and thermal desorption followed by GC–MS analysis is suitable for the determination of the 11 selected monoterpenes in indoor air.

The adsorbent Tenax GR gave the best yields for trapping of monoterpenes.

The detection limits of 1 $\mu g\ m^{-3}$ are sufficient for the determination of the most frequently found monoterpenes in indoor air such as α-pinene, β-pinene, carene and limonene but not low enough for the less frequently detected monoterpenes.

Acknowledgements

Financial support was provided by the Deutsche Bundesstiftung Umwelt.

References

[1] C. Krause, M. Chutsch, M. Henke, M. Huber, C. Kliem, M. Leiske, M. Mailahn, C. Schulz, E. Schwarz, B. Seifert, D. Ullrich, Umwelt-Survey, Vol. IIIc, WaBoLu-Hefte, Bundesgesundheitsamt, Berlin, 1991.
[2] K. Hoffmann, R. Schwabe, C. Krause, C. Schulz, B. Seifert, D. Ullrich, Umwelt-Survey 1990/91, Vol. IV, WaBoLu-Hefte, Bundesgesundheitsamt, Berlin, 1996.
[3] W. Lux, S. Mohr, B. Heinzow, G. Ostendorp, Bundesgesundheitsblatt 44 (1991) 619.
[4] J.P. Heisel, VDI-Report, Vol. 1122, VDI Verlag, Düsseldorf, Germany, 1994, p. 329.
[5] U. Kaiser, Umweltmed. Forsch. Prax. 1 (1996) 47.
[6] M. Harper, J. Chromatogr. A 885 (2000) 129.
[7] G.B. Lockwood, J. Chromatogr. A 936 (2001) 23.
[8] A.-L. Sunesson, M. Sundgren, J.O. Levin, K. Eriksson, R. Carlson, J. Environ. Monit. 1 (1999) 45.
[9] T. Hoffman, Fresenius J. Anal. Chem. 351 (1995) 41.
[10] C. Coeur, V. Jacob, I. Denis, P. Foster, J. Chromatogr. A 786 (1997) 185.
[11] T. Hoffman, P. Jacob, M. Linscheid, D. Klockow, Int. J. Environ. Anal. Chem. 52 (1993) 29.
[12] R.J.B. Peters, J.A.D.V. Renesse, V. Duivenbode, J.H. Duyzer, H.L.M. Verhagen, Atmos. Environ. 28 (1994) 2413.
[13] E.D. Morgan, N. Bradley, J. Chromatogr. 468 (1989) 339.
[14] C.R. He, F. Murray, T. Lyons, Atmos. Environ. 34 (2000) 645.
[15] D.W. Griffiths, G.W. Robertson, A.N.E. Birch, R.M. Brennan, Phytochem. Anal. 10 (1999) 328.
[16] A. Calogirou, B.R. Larsen, C. Brussol, M. Duane, D. Kotzias, Anal. Chem. 68 (1996) 1499.
[17] W. Schrader, J. Geiger, D. Klockow, E.-H. Korte, Environ. Sci. Technol. 35 (2001) 2717.
[18] V. Simon, M.-L. Riba, A. Waldhart, L. Torres, J. Chromatogr. A 704 (1995) 465.
[19] R.H. Brown, Analyst 121 (1996) 1171.
[20] A.-L. Sunesson, C.-A. Nilsson, B. Andersson, J. Chromatogr. A 699 (1995) 203.
[21] DIN 32645, Chemical analysis: decision limit, detection limit and determination limit; estimation in case of repeatability, terms, methods, evaluation, Beuth Verlag, Berlin, 1994.
[22] D. Helmig, Atmos. Environ. 31 (1997) 3635.
[23] A. Calogirou, M. Duane, D. Kotzias, M. Lahaniati, B.R. Larsen, Atmos. Environ. 31 (1997) 2741.