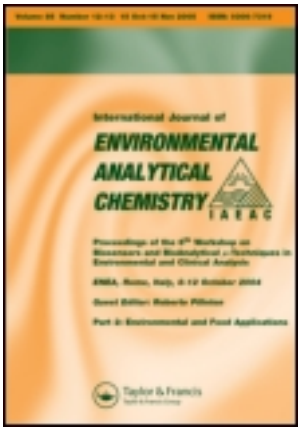

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Accelerated solid-phase dynamic extraction for the analysis of biogenic volatile organic compounds in air

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Accelerated solid-phase dynamic extraction for the analysis of biogenic volatile organic compounds in air

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In this study, accelerated solid phase dynamic extraction (ASPDE) technique was used to identify biogenic volatile organic compounds (BVOCs) emitted from Norway spruce (*Picea abies*). Compounds that were determined in tree samples are: tricyclene, α-pinene, camphene, β-pinene, myrcene, 3-carene, *p*-cymene, limonene, cineole, α-phellandrene, α-terpinene, γ-terpinene and terpinolene. ASPDE showed a potential for the analysis of environmental samples as well as for field applications. This technique was further studied by using a gaseous mixture of BVOCs (sabinene, α-pinene, β-pinene, limonene, linalool, and (Z)-hexenyl acetate) and exhibited a good repeatability during all the experiments in the range of 2.5% (α-pinene) and 14.6% (linalool). However, during the analysis of samples it was observed that desorption at high temperature (230°C) can lead to the formation of artifacts, which were not observed at the desorption temperature of 100°C. Further experimental investigations revealed that monoterpenes appeared as unanticipated compounds during desorption of ASPDE samples; these compounds were degradation products of linalool.

Keywords: accelerated solid phase dynamic extraction; preconcentration techniques; biogenic volatile organic compounds; environmental monitoring

1. Introduction

Over the last few years, volatile organic compounds (VOCs) emitted from vegetation have received much attention due to their vital role in atmospheric processes and their impact on air quality [1,2]. These compounds are highly reactive and their atmospheric lifetime is typically a few hours or less [3]. Atmospheric oxidation of biogenic VOCs (BVOCs) and their reactions with ozone (O_3), hydroxyl ($OH^{\bullet}_3$) and nitrate ($NO^{\bullet}_3$) radicals are considered as important processes in tropospheric formation of secondary organic aerosols and ozone [4,5]. Moreover, Guenther *et al.* [6] have estimated that global emission of BVOCs amounts to 1150 TgC y^{-1} and exceeds the emission of anthropogenic non-methane organic compounds (NMOCs) by a factor of 10.

In this respect an accurate evaluation of BVOC emissions is of high interest. In general, GC-MS technique coupled with preconcentration step is widely used for the analysis of these compounds. Techniques used for the preconcentration of BVOCs are: sorbent tubes

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[7–10], solid phase microextraction (SPME) [11–14], and headspace sorptive extraction (HSSE) [15,16]. An alternative for these methods could be solid phase dynamic extraction (SPDE), primarily introduced by Lipinski [17]. SPDE is a further development of SPME, having increased coating thickness and protected stationary phase. The volume of the SPDE needle coating is 6 times higher than 100 μm SPME fibre (4 μL vs. 0.66 μL); therefore the relatively higher SPDE extraction capacity can result in increased analytical sensitivity. Moreover, an SPDE needle has the coating placed inside a steel needle resulting in a longer coating lifetime because of the higher resistance to destruction. Unlike SPME, SPDE is a dynamic technique for headspace analysis: during sampling the syringe plunger is moved up (aspirating step) and down (dispensing step) several times at a controlled speed resulting in sorption of the analytes into the internal coating.

To date, SPDE has been applied for the headspace determination of different analytes such as: chlorinated pesticides [17], ethers and alcohols [18], furan, xylenes, benzene, toluene, ethylbenzene, n-aldehydes (C_6–C_{10}) and chlorinated VOCs [19–22] from aqueous matrices, cannabinoids, amphetamines and synthetic designer drugs from hair samples [23–25]. Bicchi *et al*. [26] reported the SPDE analysis of the volatile fraction from food matrices and described optimisation of sampling and desorption parameters of SPDE for mixtures β-pinene, isoamylacetate and linalool. In this study [26], SPDE was applied for headspace determination of the compounds in rosemary, banana, green coffee, red and white wine. Kamphoff *et al*. [27] reported application of SPDE for the determination of α-terpineol, (−)-carveol and (S)-carvone. SPDE has also been successfully applied for the analysis of volatile fraction in herbs [16].

Recently, Van Durme *et al*. [28] introduced an innovative accelerated SPDE (ASPDE) technique, characterised by a one large volume aspiration step (50 mL) and elimination of dispensing steps. In this study [28], during analysis of toluene it was reported that application of ASPDE results in improvement of extraction yield and shorter sampling time in comparison with SPDE. So far, ASPDE has not been used in the environmental monitoring of BVOCs. Therefore, the aim of this study was to investigate the applicability of ASPDE for the field experiments in order to determine BVOCs emitted from trees. For further quantitative analysis of BVOCs a dilution system was constructed containing a standard mixture of sabinene, α-pinene, β-pinene, limonene, linalool, and (Z)-hexenyl acetate. In addition, ASPDE and SPME techniques were evaluated with regard to repeatability.

2. Experimental

2.1 *Chemicals*

β-pinene (99%), limonene (97%), camphene (95%), α-terpinene (98%), terpinolene (90%), *p*-cymene (99%), myrcene (90%), linalool (>95%), α-phellandrene (95%), a series of n-alkanes C_8–C_{15} (99%) were purchased from Sigma-Aldrich (Steinheim, Germany); 3-carene (>90%) and (Z)-hexenyl acetate (>97%) were purchased from TCI Europe (Zwijndrecht, Belgium); and cineole (99%), γ-terpinene (98%), α-pinene (98%) were purchased from Janssen Chimica (Beerse, Belgium). All standards were used as obtained without further purification. Stock and standard solutions were prepared in methanol (HPLC grade, VWR Prolabo, Leuven, Belgium). Toluene-d_8 (99.5+ at.% D) from Acros Organics (Geel, Belgium) was used as an internal standard.

2.2 *Tree samples*

Sampling from Norway spruce (*Picea abies*) was carried out at the campus of Ghent University Belgium, during February and March 2008. A static bag enclosure technique [29] was used to collect samples from tree. One branch of the tree was covered with a Nalophane bag (Dera Food Technology NV, Bornem, Belgium) for 2h, and then samples were taken with SPME and ASPDE. Description of the used ASPDE device can be found elsewhere [28]. Specific sampling parameters for SPME and ASPDE are further described in Section 2.4. Identification of analytes was performed on a ThermoFinnigan Trace GC Ultra coupled with a high resolution mass spectrometer MAT95XP-Trap and conditions of chromatographic analysis are further described in Section 2.5.

2.3 *Dilution system for standard gaseous mixture of BVOC*

A scheme of the dilution system is shown in Figure 1. A certified gaseous mixture of sabinene (0.492 ppm_v), limonene (0.486 ppm_v), α-pinene (0.496 ppm_v), β-pinene

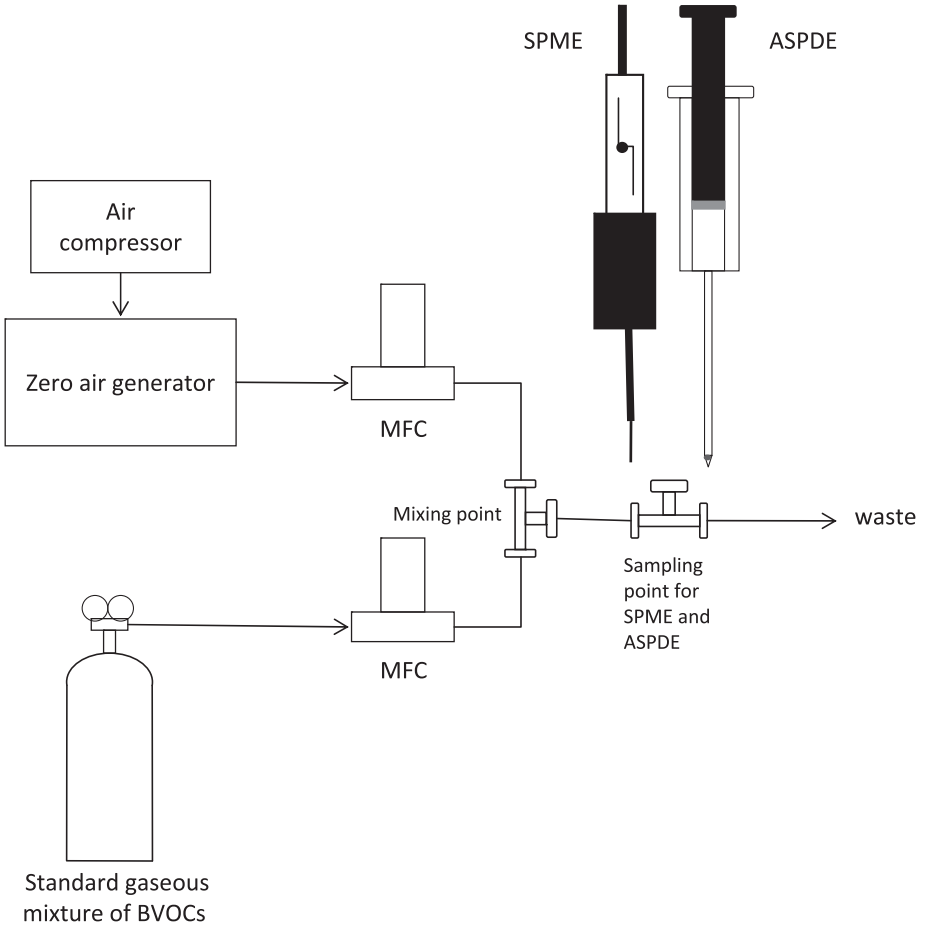

Figure 1. Schematic of dilution system for standard gaseous mixture of BVOCs.

($0.501\,ppm_v$), linalool ($0.473\,ppm_v$) and (Z)-hexenyl acetate ($0.499\,ppm_v$) was obtained from AiR Environmental (Denver, CO, USA). Air was used as dilution gas and according to the supplier (Air Liquide, Luik, Belgium) the trace gases concentrations in the air were as follows: $[H_2O] < 3.0\,ppm_v$, $[O_2] < 2\,ppm_v$, $[C_xH_y] < 0.5\,ppm_v$. Prior to mixing with the stream of BVOCs mixture, supplied air was additionally purified with a zero-air generator (Model 10001, Parker Balston, Haverhill, MA, USA). Both air and standard mixture flows were controlled by mass flow controllers (SLA 5850S, Brooks Instrument, Ede, The Netherlands) placed before the mixing point. In the described dilution system the concentration of the standard gaseous mixture of BVOCs could be set in the range between 0.0025 and $0.500\,ppm_v$. Tubing, connections and sampling point were made of Teflon to prevent losses of compounds by sorption on the material.

2.4 *Sampling techniques*

Both techniques, SPME and ASPDE, were studied by using the same standard gaseous mixture of BVOCs at the concentration in the range of $0.473\,ppm_v$ for linalool and $0.501\,ppm_v$ for β-pinene.

A SPME device supplied by Supelco (Bornem, Belgium) consisting of a manual holder and 1 cm fused silica fibre coated with polydimethylsiloxane (PDMS) (film thickness 100 μm) was used. The fibre was conditioned for 30 min at 250°C. During sampling, the fibre was exposed under stable flow ($25\,mL\,min^{-1}$) of the BVOCs standard gaseous mixture for 20 min.

A commercially available SPDE stainless steel needle coated inside with 4 μL of PDMS (Chromtech, Idstein, Germany; length 56 mm, outer diameter 800 μm, internal diameter 400 μm, film thickness 50 μm) was connected to a 60 mL plastic syringe (BD Plastipak) and placed in a syringe pump (NE-1000 ProSense, Oosterhout, The Netherlands). The sample volume, aspirating and dispensing plunger speed could be controlled and adjusted by a syringe pump. Prior to extraction, the SPDE needle was flushed with He at a rate of 4 mL/min for 30 min at 250°C. After connecting the needle to the 60 mL syringe, the BVOCs standard gaseous mixture was sampled just in one aspirating cycle at the speed of $3\,mL\,min^{-1}$.

2.5 *Chromatographic analysis*

2.5.1 *SPME*

After sampling, the SPME fibre was immediately inserted into a GC injector for 2 min. Measurements were carried out with a GC 8000 Top Series (CE Instruments, Milan, Italy) coupled with flame ionisation detector (FID). This GC was fitted with a 60 m capillary column CP-624 CB (length 60 m, internal diameter 0.25 mm, outer diameter 0.39 mm, film thickness 1.4 μm). Injector temperature was kept at 230°C and the GC oven temperature programme was as follows: initial temperature 35°C hold for 5 min, $15°C\,min^{-1}$ up to 140°C, $6°C\,min^{-1}$ up to 220°C and then hold for 5 min. The GC was set with a constant pressure of 220 kPa and in splitless mode (3 min). Identification of compounds was effected by comparing the retention times with those of pure standards.

2.5.2 *ASPDE*

For the desorption step, the SPDE needle was connected with a 0.5 mL gastight syringe Hamilton 1750 (Bonaduz, Switzerland). A 0.5 mL of toluene-d_8 headspace ($T = 25°C$) as

an internal standard or helium was aspirated through the loaded SPDE needle. Then, the needle was completely inserted into injector port and the plunger was immediately manually moved down with a speed of about 0.5 mL min^{-1}. Description of preparation of the internal standard toluene-d_8 headspace as a closed two-phase system (CTS) can be found elsewhere [30]. The analyses of ASPDE samples were performed with the a 8000 Top Series GC (CE Instruments, Milan, Italy) coupled with a flame ionisation detector (FID). Chromatographic conditions were as described previously (Section 2.5.1.). Identification of compounds in tree samples was performed on a ThermoFinnigan Trace GC Ultra coupled with high resolution mass spectrometer MAT95XP-Trap on DB-5 capillary column (length 30 m, internal diameter 0.25 mm, film thickness 0.50 μm). The initial GC oven temperature was held at 30°C for 3 min, then at 5°C min^{-1} up to 220°C and kept for 5 min. The injections were done in splitless mode (3 min) at 230°C and a constant pressure of 68kPa. The mass spectrometer ($m/z = 35$–250) was operated in electron impact mode ionisation energy of 70 eV. Compound identification was based on comparison with retention index (RI) and mass spectra of pure standards and analysis of spectral data obtained from NIST library.

3. Results and discussion

3.1 *SPME and ASPDE for tree samples analysed by GC-MS*

SPME and ASPDE were used to identify compounds emitted from Norway spruce. Figure 2 shows profiles of BVOCs obtained by sampling with both techniques and analyzed by GC-MS. Following BVOCs were identified in SPME samples: tricycylene, α-pinene, camphene, β-pinene, myrcene, 3-carene, *p*-cymene, limonene, and cineole. In ASPDE samples four additional compounds (α-phellandrene, α-terpinene, γ-terpinene, terpinolene) were observed.

Identification of α-pinene, β-pinene and limonene from Norway spruce has been already described in the literature [31,32], which is in an agreement with the results of this study. Moreover, in our qualitative investigation other compounds, such as *p*-cymene, cineole, α-phellandrene and terpinolene were identified, which have not been reported in relation to Norway spruce.

A higher number of analytes identified in ASPDE samples, compared to the other studies, indicates that this technique has a potential as a sampling method and can be successfully used in field application. Considering the above results, the dilution system for standard gaseous mixture of BVOCs was constructed for further investigation of both sampling methods.

3.2 *Repeatability of BVOC sampling techniques*

The repeatability of the two sampling techniques expressed as the relative standard deviation (RSD) determined from peak areas is presented in Table 1. The SPME technique shows a good repeatability with RSD between 5.9% for β-pinene and 8.6% for linalool ($n = 3$). Repeatability of ASPDE is similar for all compounds with the exception of linalool. There is noticeable difference in repeatability of linalool (14.6%) and the other analytes (2.3% for β-pinene).

Internal standardisation is essential for quantitative analysis to improve the precision and accuracy of experiments. In this study, we proposed the use of headspace of an

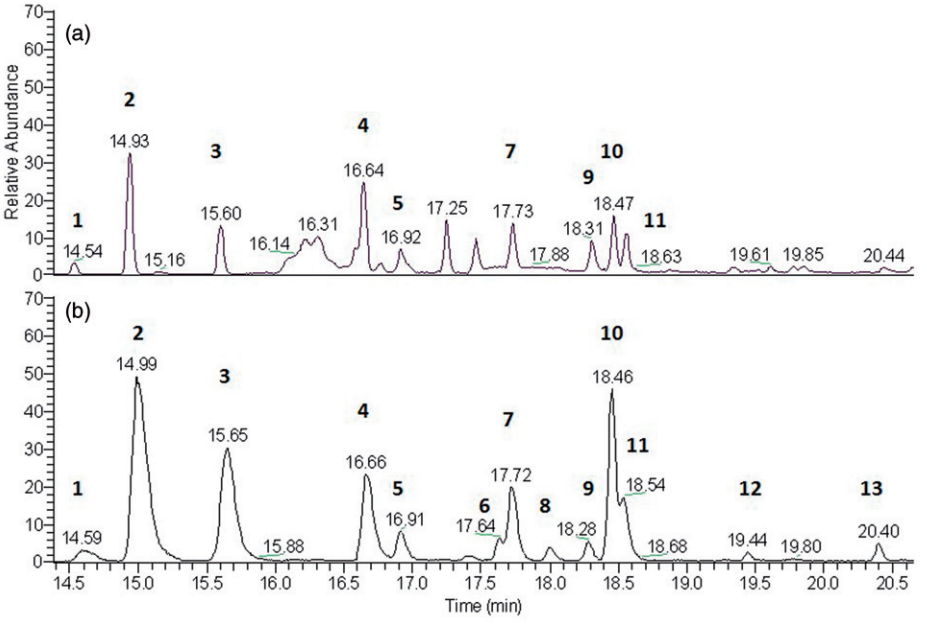

Figure 2. Full-scan chromatograms of Norway Spruce sampled by (a) SPME; (b) ASPDE. List of identified compounds: 1. tricycylene 2. α-pinene 3. camphene 4. β-pinene 5. myrcene 6. α-phellandrene 7. 3-carene 8. α-terpinene 9. *p*-cymene 10. limonene 11. cineole 12. γ-terpinene 13. terpinolene.

Table 1. Repeatability of two sampling techniques: ASPDE desorbed at 230°C with ($n=3$) and without ($n=3$) use of internal standard; and SPME desorbed at 230°C ($n=3$) for standard gaseous mixture of BVOCs.

	Repeatability %		
Compounds	SPME without I.S.[a]	ASPDE without I.S.	ASPDE with I.S.
α-pinene	7.6	2.5	3.6
sabinene	7.7	5.5	5.1
β-pinene	5.9	2.3	4.3
(Z)-hexenyl acetate	6.4	4.8	4.3
limonene	7.8	3.4	2.3
linalool	8.6	14.6	12.8

[a]Internal standard.

internal standard as a desorption gas. Therefore, after loading of the sample on the SPDE needle, 0.5 mL of the gaseous toluene-d_8 was aspired through the needle and then the sample was desorbed in GC injector. No difference in repeatability of the ASPDE technique was noticed with application of an internal standard. However, the experiments revealed that the use of headspace of toluene-d_8 as a desorption gas is an easy and workable method to introduce the internal standard to ASPDE samples.

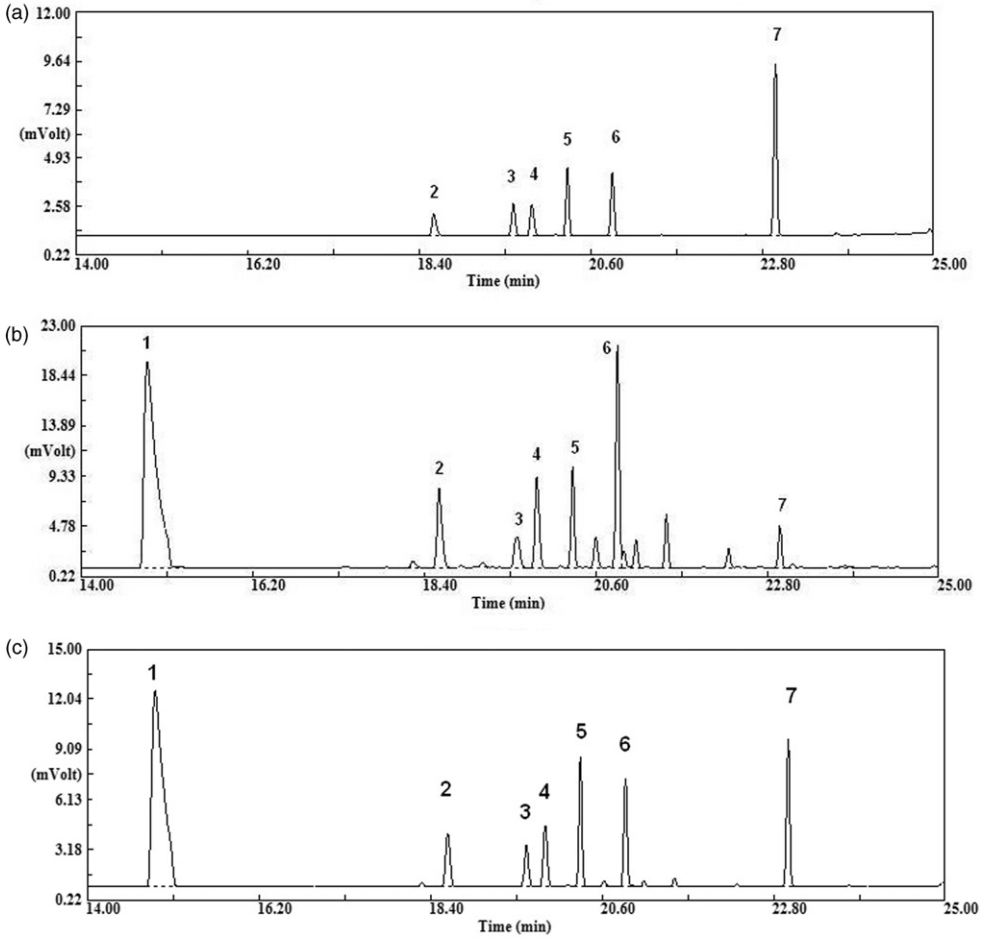

Figure 3. GC-FID chromatograms of gaseous standard mixture of BVOCs sampled by ASPDE and SPME: (a) SPME sample desorbed at 230°C; (b) ASPDE sample desorbed at 230°C; (c) ASPDE sample desorbed at 100°C. Identified compounds: 1. toluene-d_8 2. α-pinene 3. sabinene 4. β-pinene 5. (Z)-hexenyl acetate 6. limonene 7. linalool.

3.3 *Detection of target analytes by GC-FID*

Figure 3 presents the typical chromatograms obtained for SPME (Figure 3a) and ASPDE (Figure 3b) samples of the standard gaseous mixture of BVOCs containing the six analytes under study. Samples were desorbed at 230°C and analysed by GC-FID. In samples of SPME and ASPDE all investigated analytes (α-pinene, sabinene, β-pinene, (Z)-hexenyl acetate, limonene, and linalool) were detected. As can be seen from Figure 3b a few unanticipated peaks were observed in chromatograms of ASPDE samples, which might be considered as degradation products.

3.4 *Parameters of ASPDE desorption*

Given the low repeatability of ASPDE technique for linalool as well as the appearance of additional compounds in ASPDE samples, desorption parameters were pointed out for

further investigation. Regarding to the desorption process of ASPDE, the following parameters were carefully studied: syringe plunger speed, influence of geometry of GC injector and different desorption temperatures.

First, the influence of injection technique was studied. Therefore, a predesorption time of 30 s and desorption plunger speed of $1\,mL\,min^{-1}$ were applied. During these experiments no changes were observed in peak patterns. However, the obtained all peak areas were lower than those achieved with predesorption time 0 s and desorption plunger speed $0.5\,mL\,min^{-1}$. This is most likely due to incomplete desorption of analytes from the PDMS coating into the helium stream when higher plunger speed is applied.

In addition, in order to investigate the influence of the GC injector geometry injections were also carried out on a GC-FID Agilent 4890D. The inlet nut of this GC was modified in order to adapt for SPDE needles with a diameter of 0.8 mm. This GC and the initially used GC 8000 Top Series differ in injector geometry, which can affect the heat capacity of the injector and heat transfer from the injection port to the needle. However, it was proven that the presence of unanticipated peaks is independent of the equipment used for the desorption of samples. Moreover, during all experiments three SPDE needles were used and the obtained peak patterns were always the same, so it is clear that the unanticipated products are directly attributed to ASPDE technique.

Further, the influence of desorption temperatures was tested: the standard mixture was desorbed at 230°C, 180°C, 140°C, and 100°C. As shown in Figure 4, the desorption temperature effect is not the same for all the compounds under study. It was found that for α-pinene, sabinene, β-pinene, limonene, and (Z)-hexenyl acetate the peak areas increase with increasing desorption temperature whereas for linalool the highest peak area was obtained at the desorption temperature 140°C. At a desorption temperature 230°C the peak areas of α-pinene, sabinene, β-pinene, limonene and (Z)-hexenyl acetate were about 2 times higher than at 100°C. Repetition of the desorption step at 230°C revealed that all compounds were already completely desorbed from the needle after the first desorption.

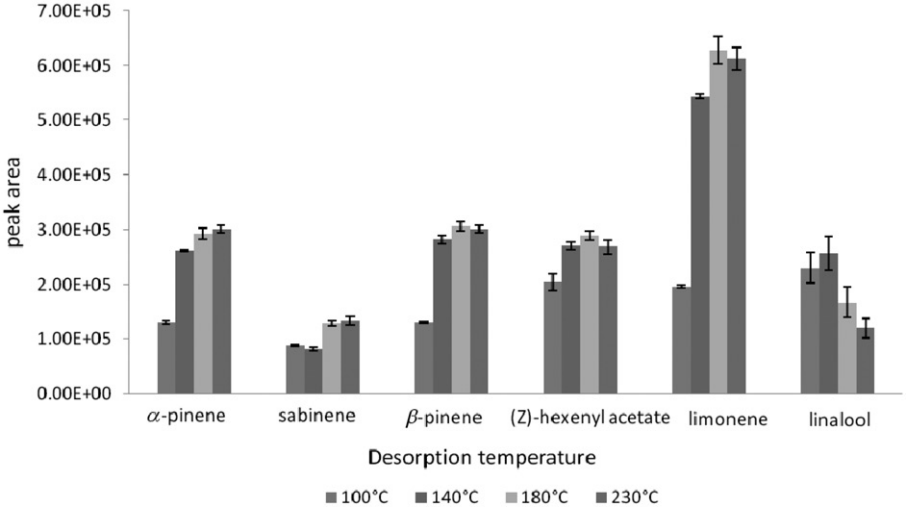

Figure 4. Influence of desorption temperatures (230°C, 180°C, 140°C, 100°C) on the recovery of the ASPDE technique.

A similar approach at 100°C showed that depending on the compound the peak areas obtained during a second desorption amounted 9–14% of the peak areas obtained after the first one, which proved incomplete desorption of analytes from the SPDE needle when using low desorption temperature. The injections with ASPDE at different temperatures showed that the higher desorption temperatures lead to the formation of the unanticipated peaks, which were not observed at 100°C (Figure 2b and 2c). Interestingly, no extra peaks were noticed in the chromatogram of the SPME sample, though it was also desorbed at 230°C (Figure 2a).

3.5 *Identification of unanticipated peaks in ASPDE samples*

In order to determine which compound undergoes degradation, the commercially available standards were injected individually. No unanticipated peaks were noticed during desorption of standards of α-pinene, β-pinene, limonene, and (Z)-hexenyl acetate at 230°C. However, for the standard of linalool desorbed at 230°C artifacts were observed (Figure 5a) whereas only one peak was obtained at desorption temperature 100°C, i.e. linalool (Figure 5b). Thus, it can be concluded that the extra peaks result from linalool and appear at high desorption temperature.

In the next step, analyses of ASPDE samples were performed on ThermoFinnigan Trace GC Ultra coupled with high resolution mass spectrometer MAT95XP-Trap. A total 12 compounds were identified by comparison with the retention index and mass spectra of pure standards and analysis of spectral data obtained from NIST library (Table 2). Since the additional compounds found in samples of standard mixture are monoterpenes

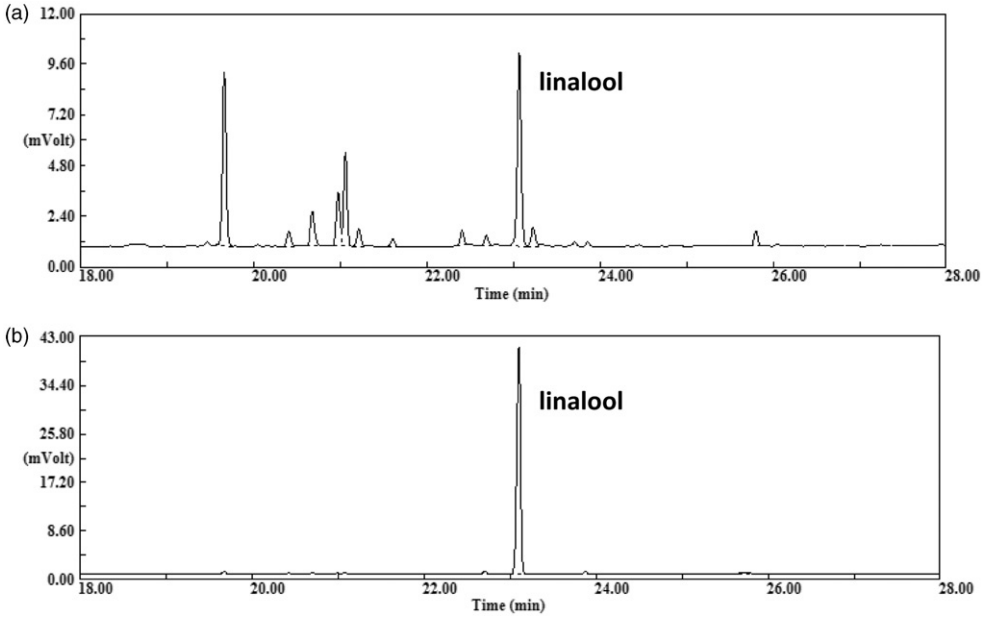

Figure 5. Chromatograms obtained from injection of linalool standard sampled by ASPDE: (a) desorption temperature 230°C; (b) desorption temperature 100°C. Notice that for both analyses the concetration of linalool was the same.

Table 2. Compound identification of standard gaseous mixture of BVOCs sampled by ASPDE and desorbed at 230°C on GC-MS.

Retention index on DB-5	Compound
937	α-pinene
955	Camphene*
978	Sabinene
983	β-pinene
987	β-myrcene*
1006	(Z)-hexenyl acetate
1011	α-phellandrene*
1022	α-terpinene*
1035	Limonene
1064	γ-terpinene*
1091	Terpinolene*
1102	Linalool

*Compounds not present in the standard gaseous mixture of monoterpenoids.

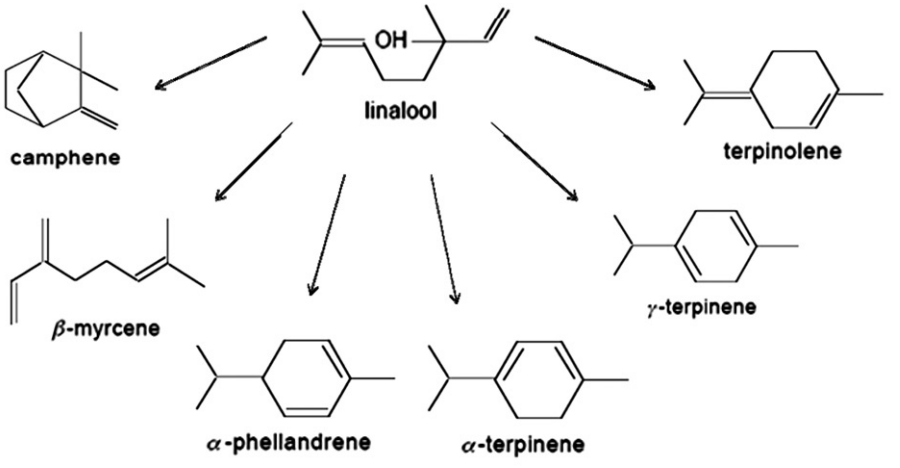

Figure 6. Chemical structures of the degradation products of linalool.

(Figure 6), namely camphene, β-myrcene, α-phellandrene, α-terpinene, γ-terpinene and terpinolene, it can be concluded that during injection of the sample, decomposition reactions of linalool occur.

Wolff *et al.* [16] and Bicchi *et al.* [26] optimised SPDE technique for BVOCs and applied 230°C as desorption temperature. However, in these studies degradation of linalool was not reported. This observed difference between published results [16,26] and the present study could possibly be explained by different properties of sampling devices and/or sampling procedure. However, it could be concluded that ASPDE used in this study is a suitable extraction technique for the mixture of monoterpenes excluding linalool, which needs further investigations.

4. Conclusions

In this study, analysis of BVOCs emitted from Norway spruce was performed. Several BVOCs were identified in SPME samples: tricycylene, α-pinene, camphene, β-pinene, myrcene, 3-carene, *p*-cymene, limonene, and cineole. In ASPDE samples four more compounds (α-phellandrene, α-terpinene, γ-terpinene, terpinolene) were observed.

Several experiments using a dilution system for gaseous mixture of BVOCs were carried out to determine the repeatability of SPME and ASPDE techniques. All six compounds from standard gaseous mixture of BVOCs (sabinene, limonene, α-pinene, β-pinene, linalool and (Z)-hexenyl acetate) were identified in SPME and ASPDE samples. Repeatability was lower than 10% except for linalool. During desorption of ASPDE samples unanticipated compounds were observed at temperatures above 100°C. Further analysis of samples revealed degradation products of linalool. Nevertheless, further investigation of reactions leading to degradation products is necessary in order to assure qualitative and quantitative results of ASPDE technique. Overall, the ASPDE technique has a potential to analyse BVOCs especially monoterpenes but samples containing hydroxyterpenes should be treated with caution.

Acknowledgements

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References

[1] A. Kiendler-Scharr, J. Wildt, M. Dal Maso, T. Hohaus, E. Kleist, T.F. Mentel, R. Tilmann, R. Uerlings, U. Schurr, and A. Wahner, Nature **461**, 381 (2009).
[2] J. Peñuelas and J. Llusià, Trends in Plant Sci. **3**, 105 (2003).
[3] R. Atkinson and J. Arey, Atmos. Environ. **37** (Supp. No. 2), S197 (2003).
[4] J.D. Fuentes, M. Lerdau, R. Atkinson, D. Baldocchi, J.W. Bottenheim, P. Ciccioli, B. Lamb, C. Geron, L. Gu, A. Guenther, T.D. Sharkey, and W. Stockwell, Bulletin of the American Meteorological Society **81**, 1537 (2000).
[5] M. Claeys, B. Graham, G. Vas, W. Wang, R. Vermeylen, V. Pashynska, J. Cafmeyer, P. Guyon, M.O. Andreae, P. Artaxo, and W. Maenhaut, Science **303**, 1173 (2004).
[6] A. Guenther, C.N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W.A. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, and P. Zimmerman, J. Geophys. Res. **100**, 8873 (1995).
[7] S. Moukhtar, B. Bessagnet, L. Rouil, and V. Simon, Atmos. Environ **39**, 3535 (2005).
[8] C. Holzke, T. Hoffmann, L. Jaeger, R. Koppmann, and W. Zimmer, Atmos. Environ. **40**, 3174 (2006).
[9] P. Dominguez-Taylor, L.G. Ruiz-Suarez, I. Rosas-Perez, J.M. Hernández-Solis, and R. Steinbrecher, Atmos. Environ. **41**, 2780 (2007).
[10] E. Ormeño, C. Fernandez, and J.P. Mévy, Phytochemistry **68**, 840 (2007).
[11] N.C. Bouvier-Brown, R. Holzinger, K. Palitzsch, and A.H. Goldstein, Atmos. Environ. **43**, 389 (2009).
[12] N. Yassaa and J. Williams, J. Chromatogr. A **1141**, 138 (2007).
[13] N.C. Bouvier-Brown, R. Holzinger, K. Palitzsch, and A.H. Goldstein, J. Chromatogr. A **1161**, 113 (2007).

[14] B. Schäfer, P. Hennig, and W. Engewald, J. High Resol. Chromatogr. **18**, 587 (1995).
[15] C. Bicchi, C. Cordero, C. Iori, P. Rubiolo, and P. Sandra, J. High Resol. Chromatogr. **23**, 539 (2000).
[16] AC. Wolff, I. Schellenberg, and D. Bansleben, Z. Arzn. Gew. Pfl **12**, 147 (2007).
[17] J. Lipinski, Fresenius J. Anal. Chem. **369**, 57 (2001).
[18] M.A. Jochmann, M.P. Kmiecik, and T.C. Schmidt, J. Chromatogr. A **1115**, 208 (2006).
[19] K. Ridgway, S.P.D. Lalljie, and R.M. Smith, J. Chromatogr. A **1124**, 186 (2006).
[20] M.A. Jochmann, X. Yuan, and T.C. Schmidt, Anal. Bioanal. Chem. **387**, 2163 (2007).
[21] K. Ridgway, S.P.D. Lalljie, and R.M. Smith, J. Chromatogr. A **1174**, 20 (2007).
[22] K. Sieg, E. Freis, and W. Püttmann, J. Chromatogr. A **1178**, 178 (2008).
[23] F. Musshoff, D.W. Lachnemeier, L. Kroener, and B. Madea, J. Chromatogr A **958**, 231 (2002).
[24] F. Musshoff, D.W. Lachenmeier, L. Kroener, and B. Madea, Forensic Sci. Int. **133**, 32 (2003).
[25] D.W. Lachenmeier, L. Kroener, F. Musshoff, and B. Madea, Rapid Commun. Mass Spectrom. **17**, 472 (2003).
[26] C. Bicchi, C. Cordero, E. Liberto, P. Rubiolo, and B. Sgorbini, J. Chromatogr. A **1024**, 217 (2004).
[27] M. Kamphoff, T. Thiele, and B. Kunz, J. AOAC Int. **90**, 1623 (2007).
[28] J. Van Durme, K. Demeestere, J. Dewulf, F. Ronsse, L. Braeckman, J. Pieters, and H. Van Langenhove, J. Chromatogr. A **1175**, 145 (2007).
[29] M.L. White, R.S. Russo, Y. Zhou, J.L. Ambrose, K. Haase, E.K. Frinak, R.K. Varner, O.W. Wingenter, H. Mao, R. Talbot, and B.C. Sive, Atmos. Chem. Phys. **9**, 8 (2009).
[30] K. Demeestere, J. Dewulf, K. De Roo, P. De Wispelaere, and H. Van Langenhove, J. Chromatogr. A **1189**, 348 (2008).
[31] K. Kempf, E. Allwine, H. Westberg, C. Claiborn, and B. Lamb, Atmos. Environ. **30**, 1381 (1996).
[32] C.S. Christensen, P. Hummelshøj, N.O. Jensen, B. Larsen, C. Lohse, K. Pilegaard, and H. Skov, Atmos. Environ. **34**, 3057 (2000).