

Short communication

Wet effluent diffusion denuder technique and the determination of volatile organic compounds in air II. Monoterpenes

Jana Sklenská, Anna Broškovičová, Zbyněk Večeřa*

Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Veveří 97, CZ-61142 Brno, Czech Republic

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Abstract

The wet effluent diffusion denuder technique (WEDD), for the determination of α - and β -pinenes, *S*-limonene, α -phellandrene, camphene and Δ^3 -carene in air has been tested. These monoterpenes were continuously preconcentrated into a thin film of methanol (ethanol, 1-propanol and heptane) flowing down the inner wall of the cylindrical wet effluent diffusion denuder. The concentrates were analyzed by GC–FID and GC–MS, respectively.

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1. Introduction

Monoterpenes belong to the group of biogenic volatile [1] compounds, originating as metabolites in some plants, mainly trees, and in particular conifers [2,3]. Although the concentration of monoterpenes in the atmosphere varies from a few ppb (v/v) down to a few ppt (v/v) the production of these types of terpenes is significant [4] and influences the chemistry of the atmosphere in a fundamental fashion [5–14].

For the determination of monoterpenes in the atmosphere, gas chromatography is the only technique used. Although at present the reliable determination of monoterpenes in the atmosphere is of

exceptional importance, published data on the level of monoterpenes in the atmosphere are still open to question. An underestimation of content of monoterpenes in air and errors in their determination can be expected [14]. Errors are significant, while the reliability of results depends on the type of monoterpene and is influenced by the presence of ozone and nitrogen dioxide in particular [15]. A further problem with the reliability of results is also linked with enrichment techniques that are an integral part of monoterpene analysis [16–20]. The problem of analytical artifacts arising cannot be resolved by neither reductors removing ozone in front of the sorbent purge trap [21–29] or cryogenic preconcentration techniques [26].

This paper describes the behavior of monoterpenes, namely α - and β -pinenes, *S*-limonene, α -phellandrene, camphene and Δ^3 -carene in an air–methanol (ethanol, 1-propanol, heptane) system with-

*Corresponding author. Tel.: +42-053-229-0168; fax: +42-054-121-2113.

E-mail address: vecera@iach.cz (Z. Večeřa).

in a cylindrical wet effluent diffusion denuder (WEDD) [30]. Use of this WEDD concentrating apparatus could resolve problems of reliability in the course of the determination of monoterpenes, primarily linked both to sampling procedures and in particular the presence of photo-oxidants in sampling air. The employment of denuders with a moving film of absorption liquid can also prevent the destruction of temperature-sensitive compounds in the course of heat desorption of monoterpenes if the adsorption–heat–desorption technique [16,31–34] is applied and make possible the “real-time” analysis of organic analytes in air [35–37].

2. Experimental

2.1. Reagents and solutions

All monoterpenes (α -pinene 99.5%; β -pinene 99.5%; *S*-limonene 99%; Δ^3 -carene 99%; α -phellandrene 97%; and camphene 85%) were gas chromatography grade (Fluka Chemie) and absorbing liquids, methanol 99.8% (Merck); ethanol 99.8% (Scharlau Chemie); 1-propanol 99.8% (Sigma Aldrich); and heptane 99.0% (Sigma Aldrich); gas chromatography grade were used.

2.2. Equipment

The gas chromatographic measurements were carried out with an LP 4600 gas chromatograph (Unicam Analytical Systems) with a flame ionization detector (FID), SPB-1 capillary column (30 m \times 0.75 mm I.D. \times 1.0 μ m film, Supelco), nitrogen as a carrier gas and column temperature 50–100 °C. A GC-8000 series gas chromatograph coupled with a Trio-1000 (Fisons Instruments) mass spectrometer, while a DB-5 (30 m \times 0.32 mm I.D. \times 1 μ m film, J&W Scientific) capillary column was also available for experiments (helium, column temperature 50–150 °C).

2.3. Standard gas mixtures

A continuous stream of standard monoterpene mixture in nitrogen with a defined content of substances was prepared by forcing of a controlled

stream of dry nitrogen through a thermostated glass vessel containing six miniature glass test-tubes (length 32 mm, I.D. 4 mm, O.D. 6 mm) filled with the monoterpenes (diffusion path 10 mm).

2.4. Wet effluent diffusion denuder

The wet effluent diffusion denuder [30,35–37] consisted of a treated glass tube (40 \times 1.1 cm I.D. \times 1.4 cm O.D.) and untreated inlet and outlet tubes, assembled at two heads. The tubes were sealed in the heads by Teflon tape to avoid leakage. The inlet tube (11 \times 1.1 cm I.D.) was used to adjust the laminar flow of sampled air into the WEDD. A denuder tube of length of 40 cm was chosen to attain satisfactory collection efficiency.

3. Experimental procedure

The main parts of the measuring system are: the wet effluent diffusion denuder and a generator of monoterpene vapor. A detailed illustration of the individual parts of the experimental apparatus is given in Fig. 1 [37], when the saturator is replaced by a generator of monoterpene vapor. So only information concerning the monoterpene vapor generator follows. The diffusion tubes were placed in a special PTFE holder “immersed” in the glass container (I.D. 50 mm, length 70 mm) kept at a

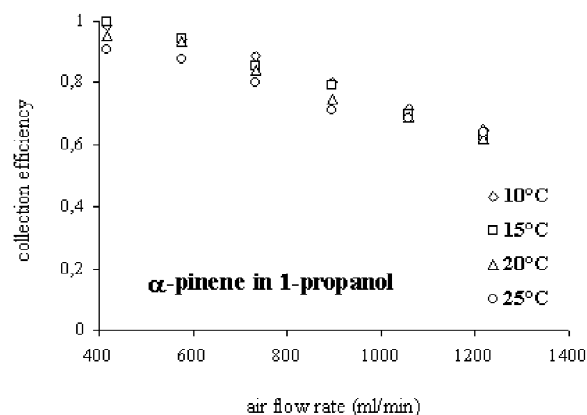


Fig. 1. Experimental values of collection efficiencies of α -pinene in 1-propanol in cylindrical wet effluent diffusion denuder, at temperatures of 10, 15, 20 and 25 °C.

temperature of 8.0 ± 0.2 °C. A controlled stream of pure dry nitrogen (14.4 ml/min) from a pressure flask flows through this glass vessel. The diffusion tubes used were filled with terpenes at the start of experiment, and weighed by means of an analytical microbalance, a Sartorius M5P model sensitive to single units of μg . The weight losses of the diffusion tubes were measured as a function of time and allowed the calculation of the mass flow of monoterpenes in the carrier gas. The mass flows of individual monoterpenes were: 6.21, 3.97, 2.74, 1.69, 1.61 and 1.46 mg/day ($SD \pm 0.05$) for camphene, α -pinene, β -pinene, Δ^3 -carene, α -phellandrene and *S*-limonene within five 5-day sets of experiments. The generated concentrations varied from 10.36 $\mu\text{g}/\text{l}$ (camphene, gas flow-rate 0.416 l/min) to 833 ng/l (*S*-limonene, gas flow-rate 1.217 l/min). The diffusion tubes with monoterpenes were stored in a closed glass bottle in the presence of a desiccating agent (magnesium perchlorate) in the dark at temperature of 4 °C when unused.

The gas outlet of the monoterpene generator is connected by PTFE capillary to the inlet of the denuder, where the vapor of the studied substances was mixed with pure air. The absorbent liquid was fed into the denuder tube through a porous PTFE O-ring located between the outlet tube and the wetted part of the WEDD. It forms a uniform film on the inner wall and falls continuously under gravity. The amount of 1-propanol (ethanol, methanol, heptane) evaporated into the sampled air can be easily calculated from the known vapor pressure for particular temperatures. Based on these calculations, the flow-rate of absorption liquid fed into the denuder was chosen to attain an actual flow-rate of the absorption liquid through the denuder of 500 ± 10 $\mu\text{l}/\text{min}$. The concentrate of monoterpenes was aspirated with a peristaltic pump through a second PTFE O-ring placed between the bottom of the denuder tube and the inlet tube and was taken for further processing. The WEDD was orientated vertically and was immersed in a water-cooling jacket that kept the wetted part of the WEDD at temperatures of 10, 15, 20 or 25 °C. The collection efficiency of analytes in the WEDD was studied for air flow-rates of 416, 576, 736, 897, 1057 and 1217 ml/min, respectively. The amounts of the studied monoterpenes in the air entering the denuder were kept constant within the

above-mentioned flow-rates. The monoterpene concentrates were analyzed by GC–FID. The GC–MS technique has been used to confirm the reliability of results. One microliter of concentrate was injected onto the column in both the GC–FID and GC–MS techniques. The signal of both FID and MS detectors was evaluated based on a two-point calibration graph.

4. Results and discussion

When alcohols (methanol, ethanol, 1-propanol) and heptane are fed in as an absorption liquid at a flow-rate of 500 $\mu\text{l}/\text{min}$ there was no wetting problem of the denuder tube observed over the measuring period, whether the temperature of the WEDD was 10, 15, 20 or 25 °C.

It is well known that in contrast to highly soluble gases, the collection efficiency (ϵ) of less soluble vapors of organic compounds depends on the effective distribution coefficient K_{eff} ($K_{\text{eff}} = C_{\text{A}}/C_{\text{G}}$) which takes account of the surface accommodation, solvating and/or reactions compounds of interest within the absorbing process [38,39]. The relationship between the collection efficiency of preconcentration process and the effective distribution coefficient can be exhibited as follows:

$$\epsilon = C_{\text{A}}F_{\text{A}} / (C_{\text{A}}F_{\text{A}} + C_{\text{G}}F_{\text{G}}) \quad (1)$$

where C_{A} and C_{G} are the analyte concentrations (mol/cm^3) in the concentrate and gaseous phase leaving the denuder, and F_{A} and F_{G} are the flow-rates (ml/min) of the aqueous and gaseous phases, respectively. The introduction of the effective distribution coefficient into Eq. (1) leads to ϵ formularization:

$$\epsilon = F_{\text{A}} / (F_{\text{A}} + (F_{\text{G}}/K_{\text{eff}})) \quad (2)$$

So application of the Gormley–Kennedy equation [40], written for the cylindrical wet effluent diffusion denuder tube in simplified form:

$$\epsilon = 1 - 0.819 \exp^{-11.4919 DL/F_{\text{G}}} \quad (3)$$

could be misguided (D is the diffusion coefficient of the gaseous analyte in sampled air, L is the denuder tube length, and F_{G} is the volume flow-rate of sampled air).

The experimental values of collection efficiency of α -pinene in 1-propanol as an absorption liquid are shown in Fig. 1. The temperature (10–25 °C) does not essentially effect collection efficiency, since the ϵ values measured for different temperatures are very similar. Such relationships were also observed for other monoterpenes and the remainder of the absorption liquids. The collection efficiencies' dependence on temperature for the same flow-rate is ranged within $\pm 5\%$, but is not greater than $\pm 10\%$.

On the other hand the preconcentration is remarkable influenced by air flow-rate. Increasing air flow-rate decreases collection efficiency. Selected ex-

perimental data representing the behavior of monoterpenes in the cylindrical wet effluent diffusion denuder at different air flow-rates (416, 897 and 1217 ml/min) are in Table 1. These data indicate that preconcentration is not influenced by the nature of absorption liquid, but more likely by the physical-chemical properties of individual monoterpenes. Since α -pinene is excellently absorbed in all solvents, the collection of Δ^3 -carene is relatively poor. These two monoterpenes were chosen for further sets of experiments, which served also as a data field for a comparison of the experimental data and calculated data. The theoretical collection efficiencies of the

Table 1
Collection efficiencies of six monoterpenes at the cylindrical wet effluent diffusion denuder at four temperatures and three flow-rates of air

		Collection efficiency (%)											
		Methanol			Ethanol			1-Propanol			Heptane		
Air flow-rate (ml/min)	→	416	897	1217	416	897	1217	416	897	1217	416	897	1217
α -pinene	10 °C	90.8	77.2	62.6	98.1	84.0	67.7	98.6	80.4	64.5	98.6	82.3	69.3
	15 °C	90.4	73.8	60.4	89.7	74.9	63.3	99.5	79.1	63.0	85.5	66.5	52.7
	20 °C	97.2	76.2	59.3	87.5	71.8	57.1	95.4	74.3	61.9	98.0	79.8	61.2
	25 °C	85.8	65.5	51.0	91.7	72.8	51.1	90.6	70.6	64.2	98.1	81.1	62.5
Camphene	10 °C	59.3	52.1	42.6	68.4	57.5	46.9	71.2	61.0	51.4	78.9	67.6	53.6
	15 °C	59.2	50.9	41.2	59.7	50.7	44.0	72.3	60.7	51.1	59.9	48.8	36.9
	20 °C	63.0	50.9	41.2	59.0	48.1	39.2	72.1	59.0	51.0	66.2	52.6	40.5
	25 °C	56.4	44.6	35.2	61.2	49.3	35.7	63.5	52.1	46.8	65.6	54.6	42.1
β -pinene	10 °C	68.7	59.3	48.9	84.8	72.5	59.6	76.6	66.9	55.6	81.7	68.6	55.8
	15 °C	69.7	61.1	51.6	74.3	62.7	56.2	77.4	67.6	56.2	62.5	49.2	38.2
	20 °C	79.4	64.8	52.9	72.6	60.9	51.3	79.3	65.7	57.2	65.3	52.7	41.4
	25 °C	72.5	59.3	48.8	81.6	63.1	45.9	71.6	57.7	52.7	67.7	56.2	42.5
Δ^3 -carene	10 °C	44.5	42.0	35.4	59.7	46.6	36.5	33.8	29.9	26.8	41.7	32.8	26.2
	15 °C	51.6	45.0	38.8	58.8	50.7	44.2	32.4	31.4	26.1	28.2	22.2	22.9
	20 °C	53.0	44.0	34.7	57.9	50.5	44.6	36.4	30.8	29.0	25.1	24.9	17.5
	25 °C	52.2	40.9	33.0	61.6	51.9	38.4	36.0	30.5	28.5	28.9	23.5	18.2
α -phellandrene	10 °C	56.8	51.3	44.3	74.3	63.1	54.0	57.8	51.1	45.1	70.3	57.6	48.1
	15 °C	60.9	53.7	45.4	66.9	57.7	51.5	60.7	52.6	45.0	51.2	42.2	40.6
	20 °C	65.1	69.0	52.0	65.4	55.9	47.9	60.4	51.5	45.7	51.3	48.6	37.1
	25 °C	61.4	60.6	51.6	71.1	58.2	43.1	54.9	48.6	45.9	54.9	47.7	40.2
<i>S</i> -limonene	10 °C	61.5	59.6	51.1	94.2	82.3	65.0	51.1	49.7	48.0	60.5	51.7	39.3
	15 °C	73.7	64.8	50.8	87.0	72.4	66.0	58.0	51.6	44.0	46.0	33.9	27.3
	20 °C	80.8	68.4	56.8	84.8	74.8	63.0	60.9	51.7	46.2	39.8	36.5	27.9
	25 °C	78.2	66.0	56.9	96.0	77.6	54.8	58.9	50.2	45.3	48.8	39.7	30.3

investigated monoterpenes were calculated using Eq. (3) employing the Fuller, Schettler, and Giddings [41] method for diffusion coefficient calculation. It can be clearly seen (Figs. 2a, b) that the experimental data are far from the theoretical values, whether using the results from Eq. (2) and Gormley–Kennedy Eq. (3). Only the absorption efficiency of α -pinene more or less complies with the assumption of the expected values of the Gormley–Kennedy Eq. (3). The relationships for methanol and ethanol are similar. The maximum experimental collection efficiency ($98.6 \pm 4.5\%$) was obtained for α -pinene in 1-propanol and heptane at 416 ml/min and the minimum value ($17.5 \pm 2.3\%$) for Δ^3 -carene in heptane at 1217 ml/min. The reproducibility of ϵ results

was checked over a two-day measurement period. All of the single points of the relationships (Figs. 2a, b and the data in Table 1) present a mean value of eight measurements.

The results indicate that the above-mentioned alcohols as well as heptane are good absorption media for the preconcentration of monoterpenes, but that the alcohols create problems in the GC analyses of monoterpenes (distortion, broadening and tailing of peaks).

It is easy to calculate the degree of preconcentration ($D_w = C_L/C_G$, where C_L is the concentration of analyte leaving and C_G represents the concentration of analyte entering the WEDD), which for α -pinene in heptane at 20 °C (0.5 ml/min of heptane, 897 ml/min of air, $\epsilon = 79.8 \pm 4.5\%$) is about 1400. Under the same conditions the degree of preconcentration for Δ^3 -carene is 450, but its collection efficiency ($24.9 \pm 2.7\%$) is still sufficient to allow the measurement of the airborne concentration of this monoterpene at the minimum detectable level (a signal-to-noise ratio of 3) 50 ppb (v/v) for (GC–FID) and about 0.5 ppb (v/v) for GC–MS, respectively (the injection volumes were 1 μ l).

5. Conclusion

Alcohols (methanol, ethanol, 1-propanol) and heptane have been found to be good absorption media for the preconcentration of monoterpenes from air in the cylindrical wet effluent diffusion denuder. In spite of this, from the point of view of the Gormley–Kennedy theory, the absorption of monoterpenes is characteristic of no perfect sorptin. The experimental data fit with great precision and so the preconcentration in the wet effluent diffusion denuder followed by the large volume technique and GC–MS analysis could be successfully used for the “on-line” determination of monoterpenes in ambient air.

The WEDD technique can also avoid problems arising from the presence of biogenic aerosol and/or oxidizing species. This WEDD technique could be fruitful when high time-resolution of the gas concentration of monoterpenes is necessary, although to prove this idea a lot of work has to be done in the near future.

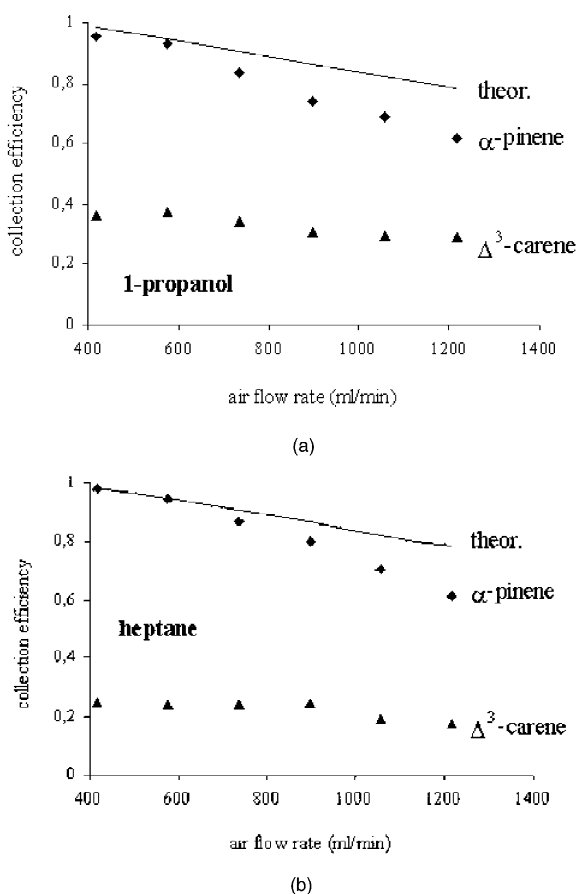


Fig. 2. (a, b) Comparison of theoretical and experimental collection efficiencies of α -pinene and Δ^3 -carene, at temperature 20 °C, in 1-propanol and heptane.

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