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Calibration system and analytical considerations for quantitative sesquiterpene measurements in air

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Abstract

Sesquiterpenes ($C_{15}H_{24}$, SQT) are semi-volatile organic compounds emitted from vegetation and are of interest for air quality considerations because of their suspected contribution to the formation of secondary aerosol. This article investigates the application of a capillary diffusion method for the generation of standard atmospheres of 16 SQT and four other related semi-volatile compounds. This instrument subsequently has been used in the testing of analytical materials, protocols and calibration of air sampling methods. SQT DB-1 retention indices, vapor pressures at 25 and 75 °C, and diffusion coefficients were determined. A quantitative, on-line GC method yielded improved results (median relative standard deviation of 5.0–6.1%) for the diffusion rate determination in comparison to a gravimetric approach (median relative standard deviation 18%). The GC method also allowed identifying errors in the gravimetric method stemming from residual solvent evaporation, impurities, and chemical analyte losses. Stainless steel, glass, nickel and PTFE tubing that were tested for transfer lines and a sampling loop had to be kept at temperatures in excess of ~110 °C in order to prevent significant analytical errors from the stickiness of SQT to these materials. In addition to SQT analysis, results from this research provide general guidelines for gas-phase analysis of related compounds in the C_{14}–C_{16} volatility range.

Keywords: Calibration; Air analysis; Capillary diffusion; Retention index; Vapor pressure; Sesquiterpenes

1. Introduction

Sesquiterpene hydrocarbons ($C_{15}H_{24}$, SQT) and oxygenated alcohol, aldehyde, and ketone analogous derivatives ($C_{15}H_{22}O$, $C_{15}H_{24}O$, $C_{15}H_{26}O$) (Fig. 1) have been identified in plant materials as well as in studies on biogenic volatile organic compound (BVOC) emissions from vegetation [1–10]. Substantial SQT emissions have been observed from several plant species that have common agricultural uses including sunflower [11], citrus trees [12,13], fungus infected corn [14] and potatoes [15].

Total SQT emission rates on the order of <0.1 to 78 μg gdw^{-1} h^{-1} have been reported [16]. The mean α-humulene and β-caryophyllene emission rates at 25–26 °C from sunflower were measured to be 19

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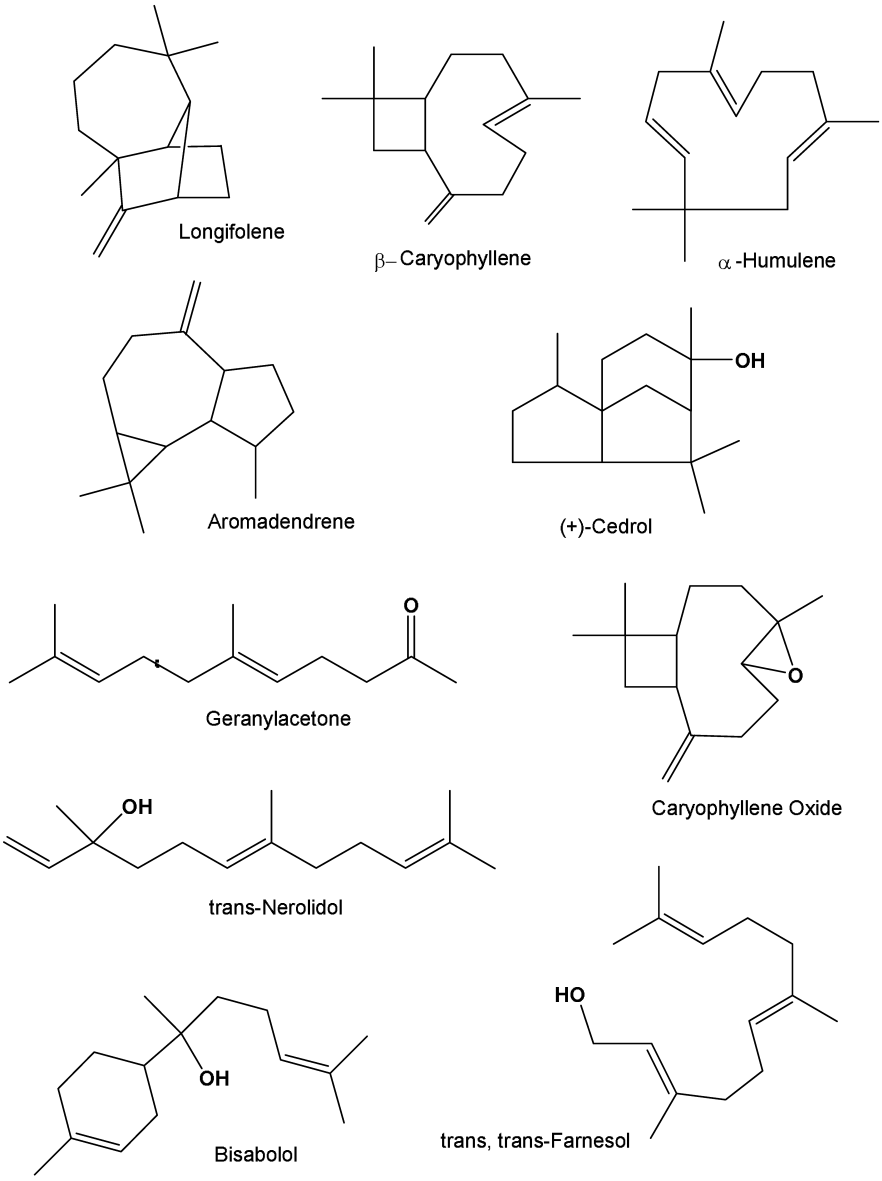

Fig. 1. Chemical structures of selected SQT and related compounds used in this study. α-Humulene is synonymous to α-caryophyllene.

and 190 ng gdw^{-1} h^{-1}, respectively [11]. Agelopoulos et al. [17] noted that emissions of β-caryophyllene increased significantly from damaging of plants. Hansen and Seufert [12] measured β-caryophyllene emission rates from citrus trees of 410 ng gdw^{-1} h^{-1} and noted that emissions increased 7.8-fold from a flowering branch. Using bag enclosure data combined with a landscape biomass survey [16,18], the total SQT landscape flux for an urban forest site near Atlanta, GA was estimated at 320 μg C m^{-2} h^{-1} or 16% of the overall measured BVOC flux.

SQT have also garnered attention because of their role in attracting flower pollinators and in plant responses to environmental stress conditions. For instance, several SQT, including α-farnesene, β-farnesene and nerolidol, have been identified among several compounds that are produced and released

in-novo as a form of protection against herbivores. These compounds can act directly as toxins and feeding deterrents or, interestingly, attract insects that will feed on the herbivores [19–23].

Kinetic and product studies of a few selected SQT gas phase reactions imply that atmospheric SQT are highly reactive, consequently have very short atmospheric lifetimes (on the order of a few minutes), and that SQT oxidation results in remarkably high (close to quantitative) aerosol yields [24–26]. Therefore, SQT are anticipated to play an important role in aerosol-forming processes and heterogenic reactions in the lower troposphere.

The magnitude of SQT landscape scale emissions and their relative contribution in atmospheric chemistry processes remain highly uncertain. This uncertainty is mainly due to the lack of quantitative emission and flux data on both the plant and the ecosystem levels. Many questions regarding reliable SQT analysis remain unresolved. Most published reports on SQT emissions from vegetation lack thorough descriptions of SQT analytical parameters. In a study of 36 VOCs and BVOCs in a diffusion system [27], the generated mixing ratios of SQT in gas standards for four included SQT were about 2–4 times less precise than those for monoterpenes. This study also revealed further analytical problems by an inconsistent GC response factor for the SQT *trans*-caryophyllene. Our own previous observations (unpublished results and Ref. [16]) suggest substantial SQT losses on materials commonly used in analytical systems as well as the potential for chemical losses from SQT decomposition and rearrangement reactions. SQT preconcentration on solid adsorbents has been the preferred method for sample collection; however, systematic recovery studies have not yet been reported. For instance, particular problems that require more attention include interferences from co-adsorbed water on multi-bed adsorbent cartridges during enclosure studies, recovery rates during thermal desorption from adsorbent materials and potential SQT losses during ambient sampling from reactions with atmospheric oxidants [13,28].

Generally, for volatile organic compound (VOC) analysis in air samples, calibration procedures rely on gravimetrically prepared ppm-level gas standards in pressurized cylinders. Subsequently, the ppm standards are dynamically or statically diluted to ppb-levels. Storage stability and recovery of VOC standards from compressed gas cylinders depend on various parameters including the choice of cylinder and valve materials, cylinder cleaning and pre-treatment procedure, standard humidity, pressure, concentration and the individual compound property [29,30]. With proper attention to these parameters, compressed gas cylinders have been shown to yield quantitative VOC recovery after several years of storage [31–33]. Conclusively, it has been found that polar compounds and hydrocarbons beyond C_{10}–C_{11} do not meet these criteria [31]. SQT are considered semi-volatile C_{15} hydrocarbons with vapor pressures at ambient temperature conditions on the order of 10^{-5}–10^{-2} kPa. Consequently, SQT are expected to be unsuitable for preparation and storage of standards in pressurized cylinders.

The alternative approach of in-situ standard generation by capillary diffusion was investigated in this study for SQT analysis. Capillary diffusion has been used in several previous studies, and the principles of this method have been well documented [34–38]. Briefly, in this method, the headspace of a liquid reservoir with the respective compound under investigation is connected to a dilution gas flow via a capillary diffusion resistor. The diffusion rate can be controlled by the length and diameter of the capillary as well as the temperature of the capillary diffusion vial and is determined by:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{DMp}{RT}\frac{A}{l}\ln\left(\frac{p}{p-p_s}\right) \quad (1)$$

with D = diffusion coefficient, M = molecular mass, p = total pressure in the system, R = gas constant, T = temperature in K, A = cross-sectional area of the diffusion capillary, l = capillary length, and p_s = saturation vapor pressure of the analyte at T. This relationship is valid provided that the partial pressure of the analyte is low in the dilution gas and that the saturation partial pressure in the vial is maintained. The diffusion coefficient of the organic compound of interest can either be experimentally determined, derived from the literature (e.g. Refs. [39,40]) or be calculated by theoretical approaches (e.g. Refs. [38,41,42]). Diffusion coefficients depend on temperature, pressure and carrier gas. Differences of diffusion coefficients in air, nitrogen and oxygen are subtle [34]. Temperature and pressure dependencies

can be calculated [39,41]. Another, more practical approach for determining the diffusion rate is to monitor the weight loss of the analyte vials on a regular schedule for determination of the mass loss d*m*.

In addition to this gravimetric approach, a quantitative on-line GC reference method was used in this study for quantification of SQT diffusion rates. The developed capillary diffusion system provides a steady output of several 100 parts-per-billion (ppbv) level SQT standard mixing ratios that can be diluted to ~100 parts-per-trillion (pptv) levels. SQT mixing ratios in air samples from vegetation enclosure experiments or in ambient air are expected to be in the low ppbv and tens to hundred pptv range, respectively. SQT analysis at such levels requires sample enrichment, which most favorably has been accomplished by preconcentration on solid adsorbents. Consequently, the output of this instrument is currently being used in the research of experimental adsorbent sampling techniques for enclosure and ambient SQT. This manuscript focuses on the technique for generating the SQT standards.

2. Experimental

An important consideration in the design of a capillary diffusion calibration system (CDS) is the saturation vapor pressure of the analytes. Under all conditions applied downstream from the capillary vials, SQT vapor pressures need to be below their saturation values in order to avoid losses by condensation. SQT vapor pressure data were not available in the literature and instead, an analytical approach was used to estimate SQT vapor pressures. SQT vapor pressures were determined by correlating their linear programmed GC retention index [43] with the calculated vapor pressures of an *n*-alkane series. This assumption relies on Kovats' second rule of a linear correlation between retention indices on non-polar stationary phases and the boiling temperature of similar organic compounds. Several previous studies have confirmed that retention index data can yield reasonable predictions of physico-chemical properties including compound vapor pressure [44–47].

The SQT used in this study, their sources, and available phase transition data are listed in Tables 1 and 2. Several non-SQT VOC were included in these experiments for comparison purposes. The selected aromatic VOC (1,3,5-tri-isopropylbenzene, diphenylmethane, nonylbenzene) have similar ranges of molecular mass, boiling points and GC retention as the SQT. The comparison with these compounds was meant to yield information whether the observed SQT results were specific for this compound class or more generally applicable to a wide range of VOC within this volatility range. Furthermore, the C_{13} oxygenated hydrocarbon geranylacetone was included. Geranylacetone has a similar volatility and has previously raised interest because of its presence in ambient air and as an identified emission from vegetation [48–51].

For the estimation of SQT vapor pressures (P_s), first, vapor pressures of the *n*-alkanes *n*-dodecane to *n*-hexadecane were calculated by the Antoine equation using their published Antoine coefficients [52]. These calculations were done for the minimum temperature conditions in any compartment of the CDS (75 °C) and for the typical conditions of sample collection from the outlet of the CDS at 25 °C room temperature (Fig. 2). Next, exponential regression curves were calculated that describe the P_s as a function of the *n*-alkane retention index. This regression yielded the relationship of $P_s = 6.636 \times 10^{11} \times 0.9873^{RI}$ and $P_s = 2.473 \times 10^{11} \times 0.9911^{RI}$ for 25 and 75 °C, respectively. SQT vapor pressures were then calculated from these equations using their analytically determined RI. Table 2 lists the retention index data used and the P_s results of these calculations. The P_s and saturation mixing ratio data were subsequently used as guidance in the configuration and operation of the CDS.

A schematic of the CDS is illustrated in Fig. 3. The principal elements are a capillary diffusion compartment, a switching valve compartment, a dilution system, an on-line GC–FID instrument and a calibration reference standard.

2.1. Capillary diffusion compartment

The capillary diffusion compartment contains a total of 10 flow-controlled channels (for simplicity, only two channels are illustrated in Fig. 3) for liquid standard reservoirs that can be individually switched

Table 1
SQT and reference compounds used in this study

Compound	Molecular formula	Mol. weight (g/mol)	CAS number	Source	Purity (%)[a]
Diphenylmethane	$C_{13}H_{12}$	168.24	101-81-5	Aldrich	99
Geranylacetone	$C_{13}H_{22}O$	194.32	3796-70-1	Aldrich	96
Aromadendrene	$C_{15}H_{24}$	204.36	489-39-4	Fluka	>97.0
β-Caryophyllene	$C_{15}H_{24}$	204.36	87-44-5	Fluka	~99
α-Cedrene	$C_{15}H_{24}$	204.36	469-61-4	Fluka	>99.0
α-Copaene	$C_{15}H_{24}$	204.36	3856-25-5	Fluka	~95
α-Humulene[b]	$C_{15}H_{24}$	204.36	6753-98-6	Fluka	>98
Isocaryophyllene	$C_{15}H_{24}$	204.36	118-65-0	Aldrich	>98.0
Isolongifolene	$C_{15}H_{24}$	204.36	1135-66-6	Fluka	>98.0
1,3,5-Isopropylbenzene	$C_{15}H_{24}$	204.36	717-74-8	Aldrich	~97
Longifolene	$C_{15}H_{24}$	204.36	475-20-7	Aldrich	>98
α-Longipinene	$C_{15}H_{24}$	204.36	5989-08-2	Fluka	>99.0
δ-Neoclovene	$C_{15}H_{24}$	204.36	4545-680	Fluka	>98
Nonylbenzene	$C_{15}H_{24}$	204.36	1081-77-2	Fluka	p.a.
Isolongifolen-9-one	$C_{15}H_{22}O$	218.34	26839-52-1	Fluka	>99.5
Caryophyllene oxide	$C_{15}H_{24}O$	220.36	1139-30-6	Aldrich	99
Bisabolol	$C_{15}H_{26}O$	222.37	515-69-5	Fluka	~97
Cedrol	$C_{15}H_{26}O$	222.37	77-53-2	Fluka	>99
trans,trans-Farnesol	$C_{15}H_{26}O$	222.37	4602-84-0	Fluka	~97
Nerolidol[c]	$C_{15}H_{26}O$	222.37	7212-44-4	Aldrich	~98

[a] Purity as given by supplier's specification.
[b] Same as α-caryophyllene.
[c] Mixture of *cis*- and *trans*-Nerolidol.

and flow-controlled (Tylan 260 mass flow controllers, Coastal Instruments, Plano, TX, USA). The capillary diffusion vials (Fig. 4) were assembled from readily available materials (Swagelok stainless steel reducing union and PTFE ferrules). The analyte vials are made of borosilicate glass and are filled with ~200–300 μl of the liquid analyte. The Swagelok union is connected to a 0.32 cm Swagelok stainless steel tee via glass diffusion capillaries. Diffusion capillaries are made of ~0.32 cm O.D. borosilicate glass tubing. Length and inner diameter are selected depending on the analyte vapor pressure with ranges of 2.5–5 cm length and 0.08–0.3 cm inner diameter. The total weight of the capillary diffusion vials (including all fittings) is ~29 g. Analyte/capillary details are given in Table 3. The capillary diffusion oven is temperature controlled to 75±0.1 °C with a heater coil and a fan. Vials are sitting in a rack that was made of a piece of aluminum and has 2.5 cm wide, 1.25 cm deep holes to accommodate the capillary diffusion vials. The thermal mass of the aluminum block is expected to dampen temperature swings in the capillary diffusion oven in order to minimize the relatively large error inflicted from potential temperature variations (for instance 5–12% relative errors in the diffusion coefficient were reported for *n*-decane for 1 °C temperature fluctuations at different temperatures [34]). Pieces of uncoated, deactivated 0.25 mm I.D. 25 cm long fused-silica tubing are used to connect the Swagelok tees with manual 0.32 cm Swagelok three-port switching valves. These pieces of fused-silica tubing serve as flow restrictors and cause an overpressure of ~39 kPa in the capillary diffusion vials at a 10 ml min^{-1} flow of N_2. If desired, several capillary vials can be connected in series in one channel. In this manner, typically 15–25 different compounds have been in the CDS at a time. The non-SQT reference compounds occupy one of the channels. The three-port switching valves facilitate sampling of the individual flow from one channel or combining of several channels for mixture analysis. All tubing materials used were either uncoated, deactivated fused-silica capillary or 0.32 cm O.D. Silicosteel (Restek, Bellefonte, PA, USA).

Nitrogen was used as the dilution gas for the SQT

Table 2
Melting point, linear programmed retention index on DB-1, FID effective carbon number and saturation vapor pressure for *n*-alkanes, SQT and selected reference compounds

Compound	Melting point[a] (°C)	Boiling point[a] (°C)	Retention time (min)	DB-1 retention index	Effective carbon number	Saturation vapor pressure (kPa)[b]		Saturation mixing ratio (ppbv)[c]	
						25 °C	75 °C	25 °C	75 °C
n-Dodecane	−9.6	215	6.55	1200	12.0	1.51E−02	5.41E−01	180 000	4 390 000
n-Tridecane	−5.5	235	8.69	1300	13.0	4.43E−03	2.23E−01	52 600	1 810 000
1,3,5-Tri-isopropylbenzene		233	9.28	1322.6±0.2	15.0	3.26E−03	1.82E−01	38 800	1 470 000
Longipinene		236	9.41	1326.6±0.3	14.9	3.10E−03	1.75E−01	36 900	1 420 000
α-Copaene			10.14	1354.0±0.2	14.9	2.19E−03	1.37E−01	26 000	1 110 000
Isolongifolene		255	10.26	1357.9±0.1	14.9	2.08E−03	1.32E−01	24 700	1 080 000
Neoclovene			10.66	1370.9±0.3	14.9	1.76E−03	1.18E−01	21 000	958 000
Longifolene		254	10.69	1373.9±0.5	14.9	1.70E−03	1.15E−01	20 200	933 000
Diphenylmethane	23	264	10.93	1380.1±0.2	15.0	1.57E−03	1.09E−01	18 700	882 000
Isocaryophyllene		272	10.94	1380.6±0.2	14.9	1.56E−03	1.08E−01	18 500	878 000
α-Cedrene		261	11.05	1383.1±0.2	14.9	1.51E−03	1.06E−01	18 000	859 000
β-Caryophyllene		263	11.15	1391.8±0.2	14.8	1.35E−03	9.79E−02	16 100	795 000
n-Tetradecane	6	251	11.42	1400	14.0	1.24E−03	9.12E−02	14 800	741 000
Aromadendrene		262	11.72	1410.0±0.1	14.9	1.07E−03	8.32E−02	12 800	675 000
α-Humulene		267	12.19	1421.8±0.1	14.7	9.23E−04	7.48E−02	11 000	608 000
Geranylacetone			12.14	1423.0±0.1	12.0	9.09E−04	7.40E−02	10 800	601 000
n-Pentadecane	9	269	14.58	1500	15.0	3.43E−04	3.72E−02	4070	302 000
cis-Nerolidol			14.91	1510.4±0.1	14.1	2.99E−04	3.39E−02	3550	275 000
Caryophyllene oxide	62		15.63	1534.1±0.1	13.8	2.21E−04	2.74E−02	2630	223 000
trans-Nerolidol			15.84	1538.5±0.1	14.1	2.09E−04	2.64E−02	2490	214 000
Nonylbenzene			16.07	1542.8±0.1	15.0	2.21E−04	2.74E−02	2630	223 000
Cedrol	82		16.16	1548.1±0.3	14.4	1.85E−04	2.42E−02	2200	197 000
n-Hexadecane	18	287	17.96	1600	16.0	9.40E−05	1.52E−02	1120	123 000
Isolongifolen-9-one	34		18.86	1627.9±0.1	14.1	6.71E−05	1.19E−02	797	96 300
Bisabolol (isomer A)			19.61	1646.4±0.3	14.2	5.30E−05	1.01E−02	630	81 600
Bisabolol (isomer B)			19.66	1649.0±0.2	14.2	5.30E−05	1.01E−02	630	81 600
trans, trans-Farnesol			25.12	1775.9±0.2	14.3	1.02E−05	3.16E−03	121	25 700H8

[a] Approximate values from the supplier's information; boiling point at atmospheric pressure.
[b] Saturation vapor pressures were calculated from the Antoine equation (*n*-alkanes) and from an exponential regression curve that was calculated from the *n*-alkane $P_s = f(\mathrm{RI})$ relationship (Fig. 2).
[c] Saturation mixing ratios were calculated for an ambient pressure of 84.1 kPa.

standard (ultra high purity grade containing less than 1 ppm oxygen; Airgas, Boulder, CO, USA). In order to minimize potential SQT oxidation reactions in the CDS, special emphasis was given to reduce residual oxygen to minimum levels. Therefore, the nitrogen gas from the compressed gas cylinder was further purified with a total of three oxygen traps in series (Big Oxygen trap, Alltech, Deerfield, IL, USA, specified to 50 ppb residual O_2; large Oxytrap, Alltech, specified to 1 ppb residual O_2; and Indicating Oxytrap, Alltech, specified to 1 ppb residual O_2).

2.2. Valve switching compartment

The output from the capillary vial oven is directed into a valve compartment that contains two two-position switching valves. A 0.32 cm four-port valve (Valco Instruments, Houston, TX, USA) allows the selection of either SQT mixtures or a hydrocarbon reference standard for analysis. For sample injection into the GC–FID, a 0.32 cm six-port valve with a ~1-ml glass sample loop (0.32 cm O.D.) is used. Both valves are heated with valve heaters. In addition, the air space in the valve compartment is heated and circulated with a fan. The pressure in the sample loop is monitored with a pressure gauge that is teed into the flow path between the sample loop and a flow restrictor.

2.3. Gas chromatography

A heated transfer line (uncoated, deactivated

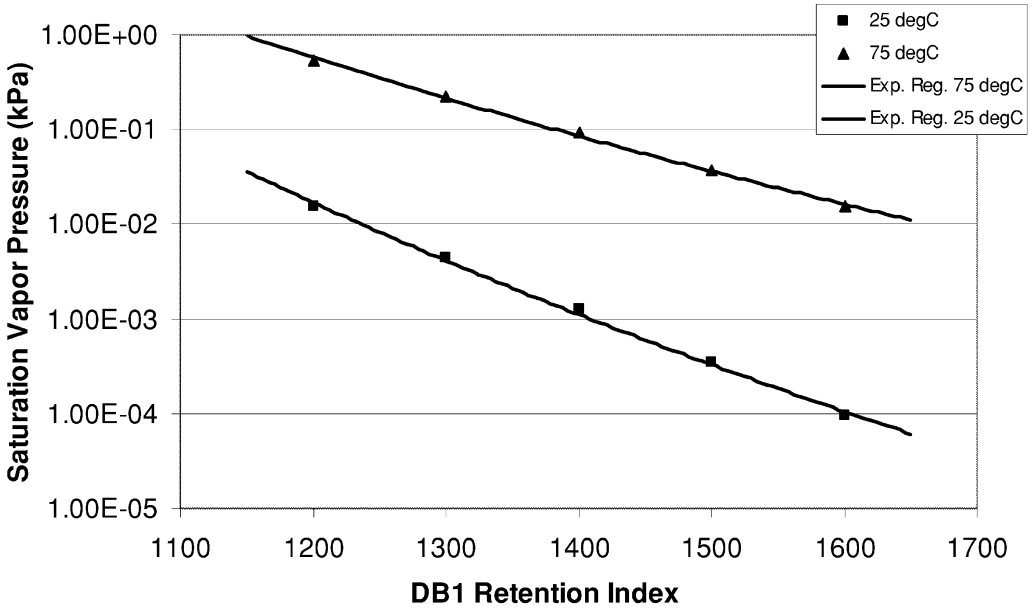

Fig. 2. Saturation vapor pressures as a function of retention index at 25 and 75 °C. This relationship was developed using *n*-alkane thermodynamic data (dodecane through hexadecane). Subsequently, exponential regression curves were determined through the *n*-alkane data. Saturation vapor pressures of SQT were then estimated from this relationship using their experimentally determined DB-1 retention indices.

fused-silica tubing kept at 150 °C) connects the injection valve with the GC column. The standard GC injection time is 1 min. The GC column is a 0.32 mm I.D.×30 m, 0.1 μm film DB-1 capillary column (J&W Scientific, Folsom, CA, USA). The GC (Hewlett-Packard 5890) oven program was as follows: 40 °C for 2 min, 20 °C min^{-1} to 80 °C, 3 °C min^{-1} to 145 °C, 45 °C min^{-1} to 225 °C, 225 °C for 3 min. Under these conditions, SQT are focused onto the column head during the sample loop injection. The GC carrier gas was He (ultra-high purity, Airgas) 4.9 ml min^{-1} at 40 °C. A sample chromatogram obtained under these conditions is illustrated in Fig. 5.

2.4. Dilution system

At the output of the CDS, the proper selection of flow resistances with a needle valve and a capillary resistor (0.53 mm I.D.×8 cm uncoated deactivated fused-silica) facilitate the splitting of a portion of the standard flow for subsequent dilution. The overall dilution gas flow is adjustable to a maximum flow of 5 l min^{-1} and can be controlled for humidity and ozone (UVP model OG-2, Upland, CA, USA).

2.5. Hydrocarbon reference standard

A hydrocarbon reference standard was prepared gravimetrically at the Climate Monitoring Diagnostics Laboratory of the National Oceanic and Atmospheric Administration (Boulder, CO, USA). A wide range of volatilities was selected for this standard in order to study the GC–FID response over a volatility range similar to that of the SQT analytes. Another purpose of this standard was to monitor the recovery of semi-volatile hydrocarbons from a pressurized gas cylinder by comparison with the storage of lighter compounds. Components and mixing ratios of this hydrocarbon standard were isoprene 546 ppbv, isooctane 262 ppbv, dodecane 351 ppbv, tridecane 342 ppbv, tetradecane 206 ppbv, pentadecane 272 ppbv, and hexadecane 309 ppbv. Details on the preparation and stability testing of this standard will be presented elsewhere (unpublished research). The reference standard cylinder and the transfer line to the CDS

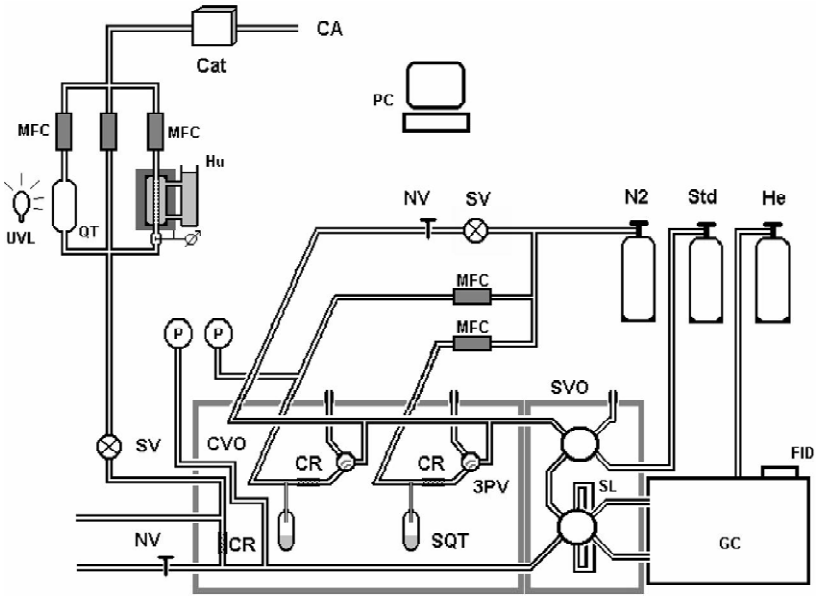

Fig. 3. Capillary diffusion calibration system. This figure illustrates two of the 10 channels with SQT capillary diffusion vials. Abbreviated components are (in alphabetical order): CA: compressed air; CAT: heated [350 °C] PtO/Alumina bed for scrubbing of house compressed air, CR: capillary resistance, CVO: capillary vial oven (at 75 °C), FID: flame ionization detector, GC: gas chromatograph, Hu: humidifier, MFC: mass flow controller, NV: needle valve, P: pressure gauge, PC: personnel computer, QT: quartz tube, SL: sample loop, SQT: vial with SQT liquid and glass capillary, Std: hydrocarbon reference standard (isoprene, isooctane, *n*-dodecane to *n*-hexadecane from a heated cylinder is used for calibrating FID response), SV: shut-off valve, SVO switching valve oven (at 170 °C), UVL: UV lamp for ozone generation, 3PV: manually switched 0.32 cm Swagelok three-port valve.

were insulated and heated to 75 and 125 °C, respectively.

2.6. Computer control

Most components of the CDS are controlled via digital input/output and analog multiplexer computer boards. Computer control includes all heated zones, flow rates and switching valves. The control software is HP VEE 4.0 (Hewlett-Packard, Loveland, CO, USA). Many analytical experiments described in this study were conducted by automated sequences developed in this software.

3. Results

3.1. Diffusion rate determination

SQT diffusion rates have been monitored gravimetrically over 1.5 years by regular weighing of the capillary diffusion vials and by regularly monitoring the SQT mixing ratio with the calibrated, on-line GC. The gravimetric monitoring posed a procedural challenge because of the relatively small weight loss of the capillary diffusion vials in relation to their total weight. Typically, vials were weighed weekly. Weekly weight losses were on the order of 100–1200 μg. With a total capillary diffusion vial weight of ~29 g, a resolution of $\sim 3 \times 10^{7}$ is needed in order to achieve a 10% accuracy/precision on the weighing procedure. Weighings were carried out on a Sartorius R 200D balance (Goettingen, Germany), which has a 10^{-5} g resolution. In practice, it was found that this accuracy and precision were impossible to achieve. Balance drifts over the 1-week intervals due to changes in environmental conditions typically were on the order of ~50–300 μg and compromised the results for the gravimetric diffusion rates. A significant improvement was achieved using an empty capillary diffusion vial as a reference weight. This reference was placed in the capillary

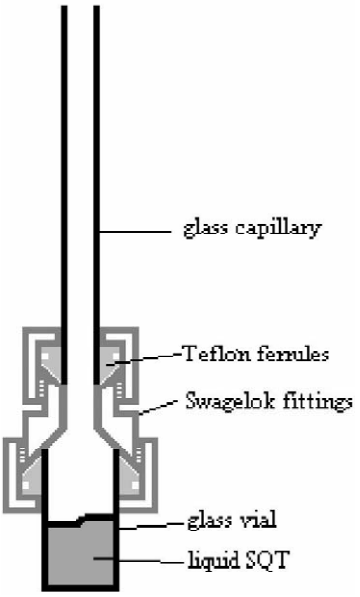

Fig. 4. Capillary diffusion vessel containing a small glass vial with SQT standards. The vial itself is made from a 1 cm long piece of 0.64 cm O.D., 0.4 cm I.D. glass tubing that was fused over a torch at one end to form a cup. Diffusion capillaries are made of ~0.32 cm O.D. pieces of glass tubing in various lengths and inner diameters (Table 3). Glass vials and diffusion tubes are connected by a 0.64 to 0.32 cm stainless steel Swagelok reducing union and sealed with two-piece 0.64 and 0.32 cm PTFE ferrules, respectively.

vial oven and treated in the same manner as SQT diffusion vials. Another important procedural detail was to allow sufficient time (~2 h) for the SQT diffusion vials to cool down to room temperature and equilibrate with the relative humidity of room air. Each SQT weighing was bracketed by a reference standard measurement taken directly before and after, and the mean of the reference measurements was then subtracted from the SQT weight. In this manner, an estimated ~50 μg precision and accuracy were achieved in the weekly weighing data. An anonymous reviewer suggested that static charge build-up may be a source of the observed variation and that anti-static pads (alpha particle emitters) may yield an improvement. The weighing results were statistically improved upon by monitoring the weight loss over extended periods of time and averaging of the weekly data. Frequently, somewhat higher (~20–60%) diffusion rates were observed during the first couple of weeks after the vials were filled with new liquid standard, which probably resulted from the initial evaporative loss of volatile solvent impurities.

Diffusion rates were also determined by quantitative analysis with the on-line GD/FID. The FID carbon response factor was determined from analysis of the hydrocarbon reference standard. SQT mixing ratios were then determined by two methods: injection of single channel standards (individual) and injection of SQT mixtures from combining all 10 channel standard flows (Fig. 5). The former method was the mandatory choice in cases where co-elution of SQT or/and reference compounds occurred. The sample pressure in the sample loop was monitored and used to correct differences in sample pressures between reference standard, individual SQT and SQT mixtures. For quantification of SQT, their effective carbon numbers were estimated using literature data on FID response from molecular structures [53,54]. Correction factors used where −0.05 for olefinic carbon atoms, −0.42 for primary alcohol carbon atoms, −0.58 for secondary alcohol carbon atoms and −0.80 for carbonyl carbon atoms. The resulting SQT effective carbon numbers are given in Table 2. Data for 10 successive weekly gravimetric and on-line GC determined diffusion rates are given in Table 3 and in Fig. 6. Also included are results from a third, independent quantification approach: The output of nine channels was diluted with zero air to sub-ppb levels and 2.5 l samples were collected over 10 min on five different adsorbents (Tenax TA, Tenax GR, Carbotrap, Carbotrap C, Unibeads). Adsorbent cartridges were then analyzed by thermal desorption with GC–FID quantification. A more detailed description of these experiments will be presented elsewhere (unpublished research). The gravimetric data had a number of very unusual high or low outliers, which were assumed to be a result from artificial weight loss or gain of the capillary diffusion cells (e.g. by collection of dust or loss [from breakage] of small pieces of the glass capillaries). Therefore, results that deviated more than 50% of the overall mean were excluded from the gravimetric data set.

3.2. Sample loop experiments

Materials and temperatures for the injection loop

Table 3
Diffusion capillary dimensions, diffusion rates determined over 10 weeks by gravimetry (with the on-line GC as individual compound and as mixture injection), and by collection of 2.5 l diluted samples (as mixture) onto five types of solid adsorbents with subsequent thermodesorption GC/FID analysis. Diffusion coefficients were calculated from the on-line GC diffusion rate data

Compound	Diffusion capillary (mm)		Diffusion rate[a] (ng s^{-1})				Diffusion coefficient[b] (cm^2 s^{-1})	
	Length	I.D.[b]	Gravimetry	GC		Adsorbent results	75 °C, 126 kPa	25 °C, 101 kPa
				Online individual	Online mixture			
1,3,5-Tri-isopropylbenzene	50	0.84	2.20±0.26 (8)	1.24±0.05 (10)	1.23±0.03 (10)	1.22±0.07 (27)	0.087	0.080
Longipinene	50	0.98	1.40±0.16 (10)	1.71±0.09 (10)	1.73±0.04 (10)	1.52±0.12 (27)	0.091	0.084
α-Copaene	50	0.85	0.84±0.17 (10)	0.91±0.09 (10)	0.91±0.02 (10)	0.86±0.07 (27)	0.082	0.075
Isolongifolene	50	0.95	1.22±0.19 (10)	1.39±0.02 (10)	1.46±0.03 (10)	1.26±0.07 (27)	0.105	0.096
Neoclovene	50	0.91	0.98±0.09 (9)	1.08±0.04 (10)	1.04±0.02 (10)		0.100	0.092
Longifolene	50	0.86	0.72±0.26 (8)	1.09±0.06 (10)	1.12±0.07 (10)		0.116	0.106
α-Cedrene	50	0.86	0.79±0.11 (10)	0.91±0.04 (10)	1.00±0.07 (10)	0.94±0.08 (27)	0.105	0.096
Diphenylmethane	50	1.00	0.55±0.15 (9)	0.59±0.03 (10)	1.56±0.05 (9)[c]	0.56±0.06 (27)	0.080	0.074
Isocaryophyllene	50	0.95	0.99±0.16 (8)	1.16±0.05 (10)			0.107	0.098
β-Caryophyllene	50	1.80	2.42±0.13 (10)	2.74±0.07 (10)	2.77±0.08 (10)	2.83±0.25 (27)	0.078	0.071
Aromadendrene	50	0.97	0.77±0.14 (9)	0.91±0.02 (9)	0.86±0.01 (10)		0.105	0.096
Geranylacetone	50	1.82	1.26±0.17 (9)	1.52±0.08 (10)	1.97±0.12 (8)[d]	1.30±0.14 (27)	0.059	0.054
α-Humulene	50	0.89	0.56±0.14 (9)	0.71±0.12 (10)		0.64±0.06 (27)	0.108	0.099
cis-Nerolidol			0.64±0.11 (8)[e]	0.29±0.03 (10)	0.17±0.05 (10)	0.24±0.03 (27)	0.008	0.007
trans-Nerolidol	25	2.07		0.31±0.04 (10)	0.11±0.02 (8)	0.39±0.05 (27)	0.011	0.010
Caryophyllene oxide	25	1.80	0.78±0.12 (10)	0.51±0.07 (10)	0.49±0.06 (9)	1.17±0.11 (27)[f]	0.024	0.022
Nonylbenzene	50	2.02	0.65±0.18 (8)	0.77±0.02 (10)	0.76±0.04 (10)		0.067	0.061
Cedrol	25	1.83	0.58±0.17 (9)	0.43±0.09 (10)	0.53±0.05 (10)	0.41±0.08 (27)	0.022	0.020
Isolongifolene-9-one	25	1.81	0.45±0.11 (7)	0.74±0.09 (10)	0.93±0.10 (8)	0.38±0.04 (27)	0.080	0.073
Bisabolol	25	3.01	0.26±0.19 (6)	0.13±0.04 (9)	0.14±0.02 (9)	0.70±0.18 (27)	0.024	0.022
trans,trans-Farnesol	25	2.99	0.31±0.19 (4)	0.02±0.01 (9)	0.13±0.03 (9)		0.074	0.067

[a] Data given are mean values with SD. The number of used data is given in parentheses. For the adsorbent data, the standard deviation represents the deviations of the means from five different adsorbent materials, the number of repeats is the total number of samples analyzed.
[b] Mean of six measurements (three at each end), except for bisabolol and farnesol.
[c] Total value for diphenylmethane and isocaryophyllene (co-eluting peaks).
[d] Total value for geranylacetone and α-humulene (co-eluting peaks).
[e] Gravimetric diffusion rate for nerolidol is the sum of both isomers in the standard mixture.
[f] Total value for caryophyllene oxide and nonylbenzene (co-eluting peaks).

of the on-line GC (Fig. 2) were tested extensively. The goal of these experiments was to determine the conditions for quantitative injection onto the GC column. Additionally, these experiments were expected to reveal valuable information for the selection of materials and analytical conditions in the handling of SQT gas-phase samples.

Critical requirements for the on-line GC injection system are the complete transfer of the injection loop volume onto the GC column, no analyte retention on the sample loop walls, and no losses of SQT from possible decomposition or re-arrangement reactions. Sample loop materials investigated included stainless steel, Silicosteel, PTFE, nickel, borosilicate glass, and uncoated, deactivated fused-silica tubing. Except for the fused silica tubing, sample loops were made of ~25 to 50 cm length, 0.32 cm O.D. tubing and loop volumes were in the range of 0.6–1.0 ml. The surface-to-volume ratio of the different sample loops tested ranged from 2140 to 2900 m^{-1}. Accurate volumes were determined by measuring internal diameter and length of the tubing material as well as gravimetrically after filling the loops with water. Subsequently, the sample loops were rinsed with methanol and dried under nitrogen purge. For comparison purposes, results of different materials were normalized to the particular sample loop volume. Experiments included variation of both temperature

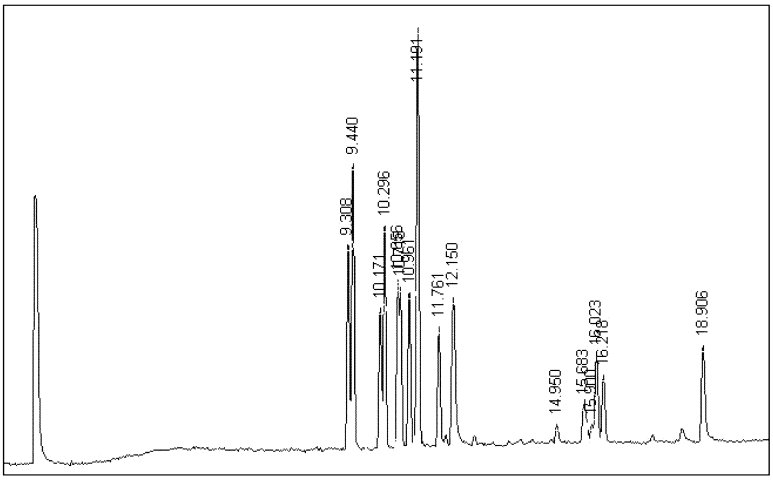

Fig. 5. Chromatogram of SQT standard mixture analyzed by loop injection with the on-line GC–FID. Peaks in this chromatogram (with retention times) are from 1,3,5-tri-isopropylbenzene (9.308 min), longipinene (9.440), α-copaene (10.171), isolongifolene (10.296), neoclovene (10.656), longifolene (10.718), α-cedrene (10.961), β-caryophyllene (11.191), aromadendrene (11.761), gernaylacetone and α-humulene (co-eluting at 12.150), *cis*-nerolidol (14.950), caryophyllene oxide (15.683), *trans*-nerolidol (15.900), nonylbenzene (16.023), cedrol (16.218) and isolongifolen-9-one (18.906).

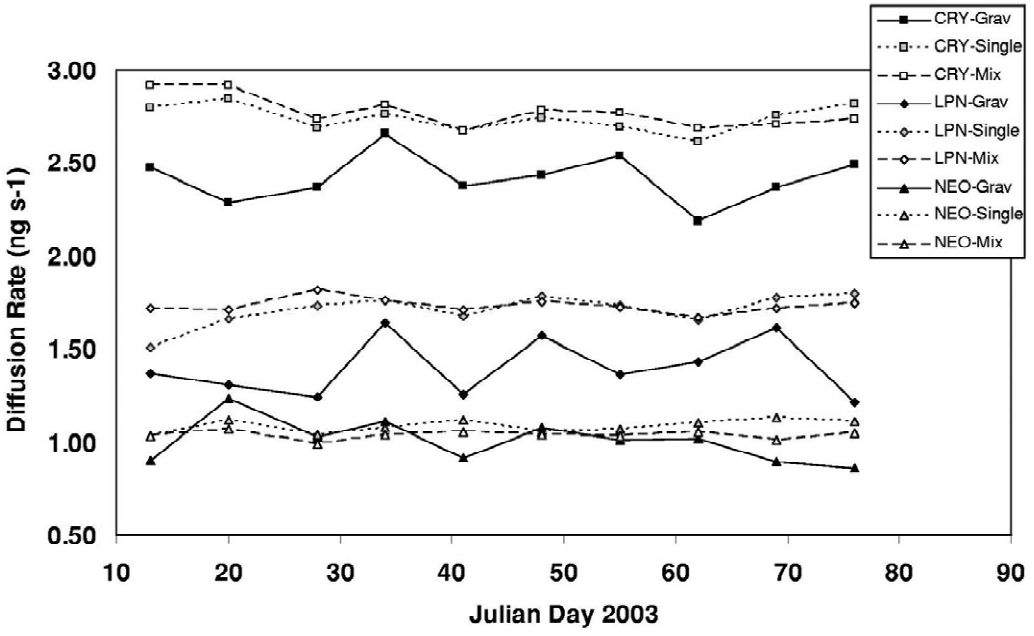

Fig. 6. Example of diffusion rates (ng s^{-1}) determined by weekly, gravimetric monitoring of the weight loss of the capillary diffusion vial (solid line) and by on-line GC determination as individual channels (dotted line) and as a mixture of all channels (staggered line). Illustrated compounds are β-caryophyllene (CRY, square symbols), longipinene (LPN, diamond symbols), and δ-neoclovene (NEO, triangle symbols). The weighing and GC analysis dates are given by the Julian day in 2003.

and injection time. For injection times longer than 2 min, the initial oven program temperature was extended accordingly. Sample loop temperatures were modified by setting the temperatures of both switching valve heaters (Fig. 2) and the valve oven compartment heaters to the same values. The theoretically required injection time was calculated from the GC column flow-rate (4.9 STP ml min^{-1} He) at the GC oven injection temperature (40 °C). Under ideal (turbulent) flow, these conditions would result in a ~12 s sample transfer time. However, since the carrier gas flow in the sample loop was calculated to be laminar in this situation, somewhat longer injection times are expected in practice.

Best results were found for a glass sample loop and the observations for the glass sample loop will be described in detail in the following. Many of the results for glass are similar to other materials tested. Specific results for those materials will be enumerated subsequently.

Dependencies of SQT recoveries as a function of sample loop temperature are shown in Fig. 7. For this experiment, the sample loop was purged with the SQT standard continuously between GC runs and the sample loop was then injected for 1 min. The expected change in the injected sample volume from the expansion of an ideal gas with increasing temperature is included in this figure for comparison purposes. Clearly, these results illustrate strong temperature dependencies that cannot be explained by the thermal gas expansion effects. Firstly, SQT compounds show substantial losses at temperatures below ~90 °C. Above 90 °C, data show much smaller dependencies with increasing temperature, and the gradual decline agrees reasonably well with the expected response from the ideal gas expansion. A

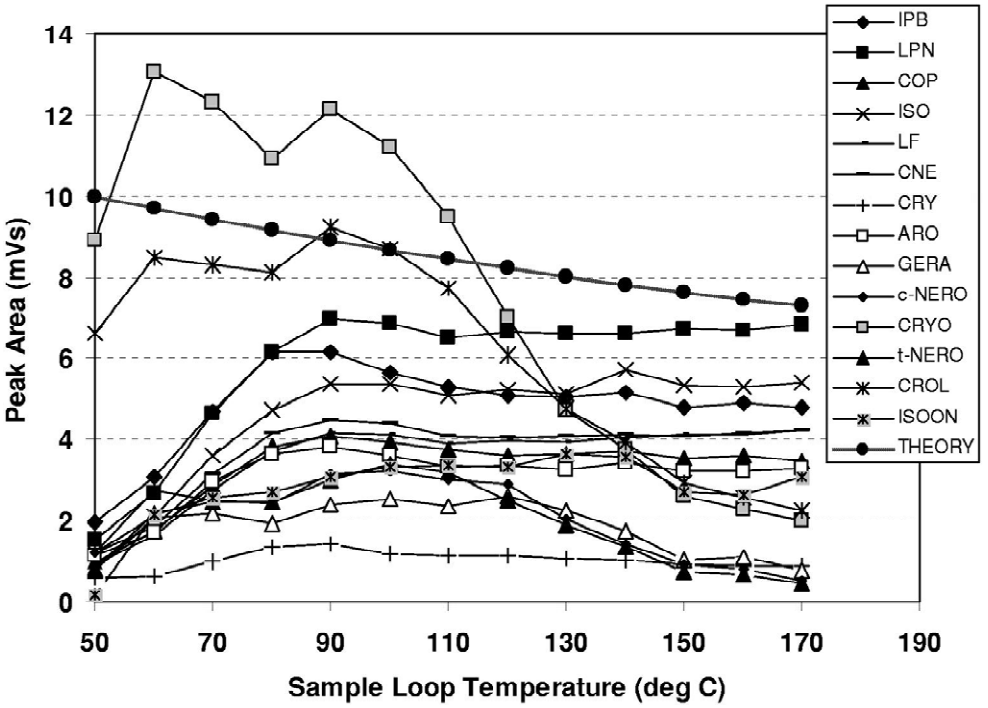

Fig. 7. Abundance of analytes as a function of sample loop (glass) temperature with 1 min injection time. The theoretically expected decline of the sample volume from the gas expansion with increasing temperature is shown for comparison. Compound abbreviations used are IPB = 1,3,5-tri-isopropylbenzene; LPN = longipinene; COP = copaene; ISO = isolongifolene; LF = longifolene; CNE = cedrene; CRY = β-caryophyllene; ARO = aromadendrene; GERA = geranylacetone; c-Nero = *cis*-nerolidol; CRYO = caryophyllene oxide; t-NERO = *trans*-nerolidol; CROL = cedrol; ISOON = isolongifolen-9-one.

remarkably different behavior is observed for the oxygenated SQT cedrol, caryophyllene oxide, isolongifolen-9-one and nerolidol. Here, recovery rates increase significantly to a maximum at temperatures of ~60 to 100 °C before they drop rather steeply towards higher temperatures. Calculated mixing ratios of these compounds in the 60–100 °C temperature range were much higher (~2–5 times) than expected from their gravimetric diffusion rates. Consequently, it was concluded that these enhanced recoveries resulted from an artificial enrichment of these analytes on the sample loop walls during the sample loop purge time and a subsequent release into the gas-phase of the GC carrier gas flow during the 1-min injection period.

In order to further study this assumption, SQT recoveries were measured at increasing loop injection times at 75 and 175 °C. Results from these experiments are shown in Fig. 8. At 75 °C, SQT abundances increase well beyond the theoretically calculated injection time. However, while the non-oxygenated SQT show little change beyond ~30 s, oxygenated SQT continue to rise until about 500 s injection time. In contrast, the data from the same experiment at 175 °C injection temperature show that all non-oxygenated SQT compounds as well as the oxygenated SQT cedrol, nerolidol and caryophyllene oxide undergo quantitative injection within ~20 s time. However, the least volatile SQT isolongifolen-9-one still shows behavior that deviates from the ideal gas-phase conditions. It is striking that at 175 °C, mixing ratio results for most of the oxygenated SQT are significantly lower than at 75 °C and in much better agreement with their expected mixing ratios from the gravimetrically determined diffusion rates.

The conclusion from these experiments is that for glass loops, temperatures in excess of ~90 and ~150 °C are required for SQT and the oxygenated SQT, respectively, in order to avoid analyte adsorption to the walls of the sample loop. Below these threshold temperatures, enrichment, respectively a ‘‘coating’’ of the sample loop wall occurs during the purging stage. During the GC injection phase, the analytes are then volatilized and the amount of SQT injected onto the GC column is well in excess of the expected gas-phase standard concentration. For isolongifon-9-one, the least volatile SQT included in these experiments, even 175 °C was too cold to prevent wall adsorption.

Next, single compound measurements were carried out in order to investigate potential losses, e.g. from decomposition or rearrangement reactions under these required, unexpectedly high temperatures for GC injection. All materials were tested at 170 °C with 15 min sample loop purging time prior to 1 min injection. An example with the results of one of the SQT tested (isolongifolene) is shown in Fig. 9. In a number of cases, these experiments revealed analyte losses. In cases where SQT losses were observed, new peaks were found in the chromatograms. It was not possible to provide identification of these peaks with the FID detector; however, the unequivocal occurrence of the same peaks in the material experiments was a strong indication that these signals were products of parent SQT compounds. Detailed results for the sample loop materials are summarized in the following.

3.2.1. Glass

Consistent results were obtained for two borosilicate glass (Friedrich & Dimmock, Millville, NJ, USA) sample loops that were investigated. None of the test compounds showed any decomposition losses within the experimental temperature range. As already detailed above, temperatures in excess of ~90 and ~150 °C are required for SQT and most oxygenated SQT in order to prevent wall effects. Glass was found to be the favorite of all materials tested.

3.2.2. Stainless steel

Stainless steel tubing (Alltech) was found to be the least suitable material as it induced losses/rearrangement reactions for several of the tested compounds (caryophyllene oxide, farnesol, cedrol, bisabolol). Farnesol was completely lost on stainless steel. For all of these compounds, unidentified product peaks were observed in the chromatograms. Furthermore, the sample loop temperature needed to prevent SQT adsorption inside the sample loop was approximately 20–30 °C higher than for glass.

3.2.3. PTFE

A problem with the sample loop made of PTFE tubing (Teflon, Cole Parmer, Vernon Hills, IL, USA)

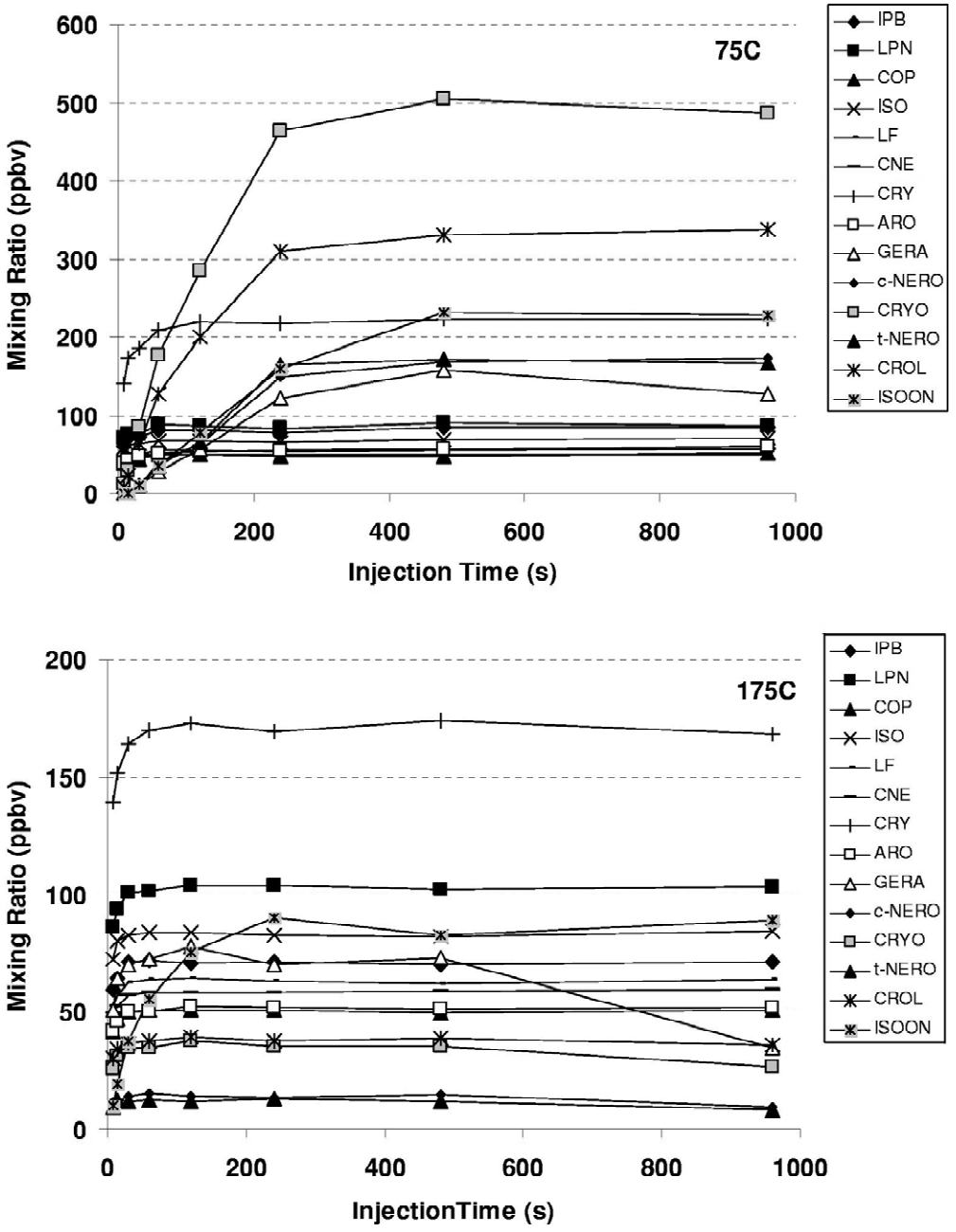

Fig. 8. Experiments with increasing injection time at 75 °C (top) and 175 °C (bottom). The theoretically calculated time required to transfer the gas-phase analytes onto the GC column was calculated as ~12 s. The data obtained at 175 °C loop temperature reflect this expected behavior. In contrast, at 75 °C loop temperature, some of the analytes show a steady increase up to ~8 min injection time due to continuous evaporation of analytes from the wall of the sample loop. Compound abbreviations used are the same as in Fig. 7. The ~50% drop in geranylacetone at 960 s injection time deviated from other observations and this data point is assumed to be an outlier.

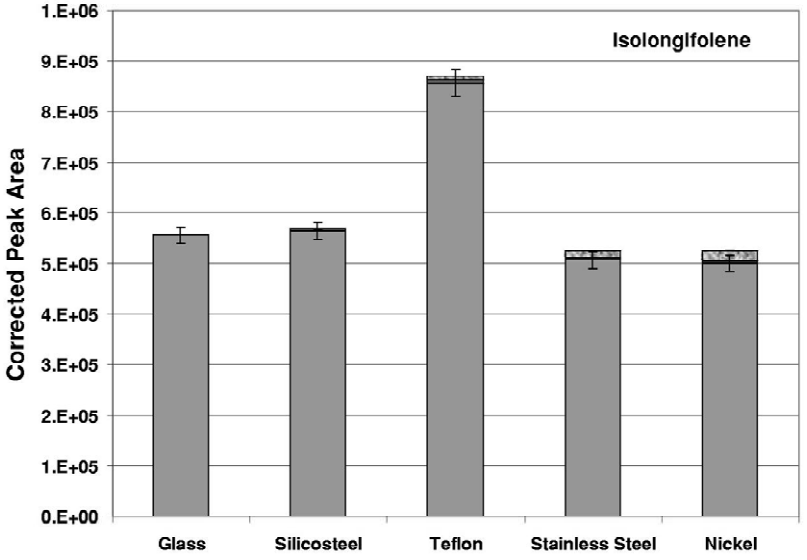

Fig. 9. Recovery of isolongifolene from different sample loop materials at 170 °C. Data are mean values from three repeats with standard deviation error bars. Identified products are added in peak area counts on top of the isolongifolene peak area. The increased results for PTFE are suspected to be from the permeation of the analyte into the tubing material and subsequent release during the injection period.

was that contamination peaks were consistently observed unless the sample loop was purged continuously for at least 30 min prior to injection. These contaminant peaks would reappear after intermittent interruption of the purge flow. First, SQT recovery rates for all tested compounds appeared to be high (Fig. 9), however closer examination, e.g. experiments with increasing injection time (at 170 °C), revealed increasing peak areas past 60 s injection times. Consequently it was concluded that the calculated recovery rates were artificially enhanced from reversible uptake into the PTFE material. Obviously, a similar effect, as observed for glass at lower temperatures, was still prevalent for PTFE at 170 °C. Conclusively these experiments indicated that under the tested conditions, SQT and contaminants readily permeate in and out of PTFE, making this material unsuitable for sample loop use or related applications where wall uptake/saturation and possible subsequent release is not permissible.

3.2.4. Fused silica tubing

The testing of uncoated, deactivated fused-silica tubing posed technical problems. More than 5 m length of 0.53 mm I.D. was needed in order to achieve the desired injection volume. The flow resistance of this length of tubing was substantial and caused significant back pressure and flow-rate fluctuations when the injection valve was switched. Also, several tubing materials tested proved too fragile and frequent breakage occurred when the valve compartment temperature was changed or from switching of the injection valve.

3.2.5. Silicosteel

Recovery rates on Silicosteel (Restek) were similar to glass, except for isolongifolen-9-one, which showed ~30% loss on Silicosteel. The silico treatment appeared to overcome most of the rearrangement/decomposition losses observed on stainless steel. Temperatures required for prevention of wall losses were higher for Silicosteel than for glass, stainless steel and nickel. Most likely, this effect stems from an increase in the surface area from the silico treatment.

3.2.6. Nickel

Electroformed nickel tubing (Valco) gave similar results as for glass for SQT and non-SQT reference compounds, however, somewhat lower recovery rates were found for some of the oxygenated SQT, e.g. farnesol (~40% of glass), caryophyllene oxide

(~70%), bisabolol (~70%). Unidentified peaks (suspected rearrangement products) were observed for caryophyllene oxide and farnesol.

3.3. Diffusion coefficients

SQT diffusion coefficients can be calculated from Eq. (1) using the diffusion rates determined by the gravimetric and/or the on-line GC method. Results of these calculations are included in Table 3. These values are valid for the experimental conditions in the capillary diffusion vials, e.g. 75 °C and 126 kPa pressure in nitrogen. The diffusion coefficients were normalized to 25 °C and 101 kPa using the kinetic theory expression:

$$D_{298} = D_T\,(298\,K \times T^{-1})^n\,(P \times (101\,\text{kPa})^{-1}) \qquad (2)$$

where $n = 2$ was used for these calculations [39]. The normalized data are also included in Table 3.

4. Discussion

Generally, the diffusion rates determined by gravimetry and on-line GC monitoring showed a reasonable agreement within the margins of errors for each of the methods. Diffusion rates calculated from these two different approaches typically agreed to within 10% (Table 3). The on-line GC procedure was the more precise method. The median relative standard deviation of the data presented in Table 3 was 18.0% for gravimetry, 5.0% for the on-line individual procedure, 6.1% for the on-line mixture method and 9.7% between the five different adsorbents. Precision and accuracy of diffusion rate determinations improve with increasing compound vapor pressure and diffusion rate (dependent on capillary dimensions). Similar observations have been reported in other studies of lighter VOC, monoterpenes and four SQT [27,37]. Even though the gravimetric procedure yielded a poorer precision than the GC method, in general the achieved precision was better than the results of Komenda et al. [27] who report 11.8–42.2% precision for four SQT and geranylacetone. The comparison of the four different quantification methods allowed to identify selected cases where the gravimetric method yielded erroneous data, such as for 1,3,5-tri-isopropylbenzene, where for an unknown reason the gravimetric data appears to be ~75% too high.

The CDS has been operated for 1.5 years, and it has been found that continuous monitoring by gravimetry and on-line GC are important, complementary methods for tracking the CDS output concentrations. Only in this manner, analytical errors such as from solvent losses, surface effects, and possible SQT rearrangement or polymerization reactions can be identified and addressed. The on-line GC allowed identification and differentiation of two racemic bisabolol isomers, and of the *cis* and *trans* isomers of nerolidol. GC analysis of the cedrol standard alone revealed impurities (or possibly degradation products) of α-cedrene and β-caryophyllene. These two peaks gradually increased over time indicating a slow rearrangement of cedrol into these two product compounds. This observation also explains why the gravimetric diffusion rate data for cedrol is higher than the GC determinations and why the mixture on-line GC data for α-cedrene and β-caryophyllene are higher (contribution from the cedrol channel). Similarly, the GC analysis revealed that farnesol decomposed into four unidentified products, the sum of which (quantified by GC) accounted for the gravimetric diffusion rate.

Overall, it proved highly valuable to operate this system continuously, with little interruption, in order to establish long-time records of diffusion rates. New liquid standards may require substantial purging times (in our case up to 2 weeks) before stable output rates are achieved.

Proper choices of tubing materials, temperature control and allowance of sufficient equilibration times are important. The sample injection loop turned out to be the most critical component for the on-line GC monitoring. Use of borosilicate glass and sample loop and switching valve temperatures at ~170 °C are needed to prevent adsorptive losses to walls and to achieve true gas-phase behavior for SQT and oxygenated SQT compounds. It is remarkable that these wall losses occur even though the SQT gas-phase mixing ratios were several orders of magnitude below the physical condensation point of the analytes. For instance, for longipinene in the glass sample loop experiment, a temperature of ~90 °C was necessary to prevent sticking to the wall

of the sample loop. The gas-phase longipinene mixing ratio in the SQT challenge mixture in this experiment was ~100 ppbv. From the retention index–vapor pressure relationship developed in the Experimental section, it was calculated that the longipinene gas-phase saturation mixing ratio at this temperature is ~4000 ppm. Consequently, SQT uptake to the walls occurs even though the gas phase mixing ratio is a factor of $>10^4$ below the physical saturation mixing ratio. The condensation temperatures for a 100 ppbv mixing ratio of *n*-tridecane and *n*-tetradecane were estimated from the Antoine equation to be ~251 and 262 K, respectively. The condensation temperature of a 100 ppbv mixing ratio of longipinene (RI = 1327) is estimated to lie between these two values. Therefore, it can be concluded that temperatures must be approximately 110 °C above the SQT condensation temperature in order to avoid wall adsorption effects.

At these required high temperatures, metal surfaces induce catalytic decomposition/rearrangement reactions for certain SQT. These observations compare with results from solid adsorbent testing, where it was shown that β-pinene, an unsaturated, biogenic C_{10} monoterpene hydrocarbon undergoes rearrangement at the required temperature for thermal desorption from carbon-type adsorbents [55,56].

SQT diffusion coefficient data have not been published, but the data obtained here can be qualitatively compared with other VOC. Generally, diffusion coefficients decrease with the size of the molecule. Data for C_6–C_{10} hydrocarbons at standard conditions lie in the range of 0.04–0.11 cm s^{-1} [34,37,39]. Most of the calculated SQT diffusion coefficients fall within this range with the exception of the heavier, oxygenated SQT.

The diffusion coefficient data included in Table 3 should be considered as approximate since a number of assumptions and simplifications were used in these calculations. These data rely on the analytically determined diffusion rates (Table 3), the estimated SQT vapor pressure data (Table 2), capillary dimensions and the pressure in the capillary diffusion vial (which is only monitored in one channel and assumed to be the same in all others). Only the length and diameter of the glass capillary tubing pieces were considered in the calculation of the overall diffusion resistance. This calculation omits the diffusion path from the surface of the liquid to the bottom end of the capillary tubing. The most significant resistance here is the bore of the Swagelok reducing union with an internal diameter of ~2.4 and ~5 mm length. This diffusion distance is comparatively insignificant for the narrow, 50 mm capillaries, but becomes more important for the shorter and larger I.D. capillaries (Table 3). Another uncertainty factor is introduced in the pressure/temperature correction. The factors of *n* in Eq. (2) may lie between 1.5 and 2 [34,35,39]; a value of $n = 2$ was used in this study for calculating the data in Table 3.

Diffusion coefficients for heavier alcohols are expected to be somewhat lower than for hydrocarbons [34], however the data for bisabolol and farnesol are ~2–3 times lower than expected. This discrepancy may be due to the relatively higher effect of the flow restriction from the Swagelok union (see above) or possibly from low evaporation rates in relation to the diffusion rate (see discussion in Ref. [37]). Conclusively, the overall accuracy of the diffusion coefficient data is estimated to be better than ±50% for the SQT and somewhat less accurate for the oxygenated compounds. Therefore, overall the diffusion coefficients in Table 3 are useful for considerations in the design of SQT capillary diffusion instruments.

5. Conclusions

The capillary diffusion system was shown to deliver a reproducible output of SQT standard atmospheres. After careful consideration of analytical details and parameters, quantification of the system output by gravimetry and by direct loop injection onto an on-line GC gave consistent results. However, on-line GC monitoring is the preferable technique because of improved accuracy, improved precision, and because GC monitoring allows identification of potential changes in diffusion rates from chemical changes of the SQT liquid or residual solvent evaporation.

Gas-phase SQT atmospheres undergo equilibration with the surface of materials in contact and significant amounts of SQT adhere (or ‘‘stick’’) to the surfaces. This process can result in substantial analytical errors from losses of gas-phase SQT prior to

equilibrium and gains in gas-phase SQT when a previously equilibrated system is purged with a clean, SQT-free gas. These errors can be minimized and avoided by allowing sufficient purge and equilibration times and by keeping all tubing and valve materials at elevated temperatures.

Comparison of SQT with similar volatility organic hydrocarbon reference compounds revealed that the SQT results are applicable to vapors of VOC in the same volatility range. Hence, these analytical properties are mostly determined by the chemical physical behavior rather than by SQT characteristic chemical properties.

The SQT standards generated by the CDS are currently being used in the investigation of Tenax TA, Tenax GR, Carbotrap, Carbotrap C, Unibeads and Glass Beads solid adsorbents materials for enrichment of SQT in samples collected from enclosure experiments and in ambient air. Other experiments include the effects of varying humidity and ozone in sample air. Results from this research will be presented in a later publication (unpublished research).

Considering the substantial losses observed for SQT on unheated and unequilibrated tubing materials, it appears likely that previous studies on BVOC emissions from vegetation, where such effects were not adequately addressed, may have suffered from significant analytical losses of SQT. Consequently, SQT may have eluded detection during previous investigations or only have been partially identified. Therefore, current emission rate and landscape flux estimates, which rely on these data, may be low and warrant more carefully designed experimental investigations.

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References

[1] R.G. Buttery, C. Xu, L.C. Ling, J. Agric. Food Chem. 33 (1985) 115.
[2] C. Bicchi, A. D'Amato, F. David, P. Sandra, J. High Resolut. Chromatogr. 12 (1989) 316.
[3] A. Omata, S. Nakamura, K. Yomogida, K. Moriai, Y. Ichikawa, I. Watanabe, Agric. Biol. Chem. 54 (1990) 1029.
[4] A. Winer, J. Arey, R. Atkinson, S. Aschman, W. Long, L. Morrison, D. Olszyk, Atmos. Environ. 26A (1992) 2647.
[5] G. Konig, M. Brunda, H. Puxbaum, C.N. Hewitt, S.C. Duckham, Atmos. Environ. 29 (8) (1995) 861.
[6] J. Rudolph, A. Wedel, G. Schuh, A. Heiden, J. Wildt. Emissions of volatile organic compounds from agriculturally used vegetation: Ambient measurements, field studies of emissions and laboratory investigations. Workshop on Biogenic Hydrocarbons in the Atmospheric Boundary Layer, University of Virginia, 1997, pp. 22–25.
[7] J. Llusia, J. Penuelas, Can. J. Bot. 76 (1998) 1366.
[8] Q.H. Zhang, G. Birgersson, J.W. Zhu, C. Lofstedt, J. Lofqvist, F. Schlyter, J. Chem. Ecol. 25 (1999) 1923.
[9] H.J. Kim, K. Kim, N.S. Kim, D.S. Lee, J. Chromatogr. A 902 (2000) 389.
[10] H. Hakola, T. Laurila, V. Lindfors, H. Hellen, A. Gaman, J. Rinne, Boreal Environ. Res. 6 (2001) 237.
[11] G. Schuh, A.C. Heiden, T. Hoffmann, J. Kahl, P. Rockel, J. Rudolph, J. Wildt, J. Atmos. Chem. 27 (1997) 291.
[12] U. Hansen, G. Seufert, Phys. Chem. Earth B 26 (1999) 681.
[13] P. Ciccioli, E. Brancaleoni, M. Frattoni, V. Di Palo, R. Valentini, G. Tirone, G. Seufert, N. Bertin, U. Hansen, O. Csiky, R. Lenz, M. Sharma, J. Geophys. Res. 104 (1999) 8077.
[14] R.J. Bartelt, D.T. Wicklow, J. Agric. Food Chem. 47 (1999) 2447.
[15] N.G. Agelopoulos, K. Chamberlain, J.A. Pickett, J. Chem. Ecol. 26 (2000) 497.
[16] D. Helmig, L.F. Klinger, A. Guenther, L. Vierling, P. Zimmerman, Ch. Geron, Chemosphere 38 (1999) 2163.
[17] N.G. Agelopoulos, A.M. Hooper, S.P. Maniar, J.A. Pickett, L.J. Wadhams, J. Chem. Ecol. 25 (1999) 1411.
[18] D. Helmig, L.F. Klinger, A. Guenther, L. Vierling, P. Zimmerman, C. Geron, Chemosphere 38 (1999) 2189.
[19] P.W. Pare, J.H. Tumlinson, Nature 385 (1997) 30.
[20] P.W. Pare, J.H. Tumlinson, Plant Physiol. 114 (1997) 1161.
[21] P.W. Pare, J.H. Tumlinson, Plant Physiol. 121 (1999) 325.
[22] J. Degenhardt, J. Gershenzon, Planta 210 (2000) 815.
[23] E. Pichersky, J. Gershenzon, Curr. Opin. Plant Biol. 5 (2002) 237.
[24] D. Grosjean, E.L. Williams, E. Grosjean, J.M. Andino, J.H. Seinfeld, Environ. Sci. Technol. 27 (1993) 2754.

[25] Y. Shu, R. Atkinson, Int. J. Chem. Kin. 26 (1994) 1193.
[26] T. Hoffmann, J.R. Odum, F. Bowman, D. Collins, D. Klockow, R.C. Flagan, J.H. Seinfeld, J. Atmos. Chem. 26 (1997) 189.
[27] M. Komenda, E. Parusel, A. Wedel, R. Koppmann, Atmos. Environ. 35 (2001) 2069.
[28] D. Helmig, Atmos. Environ. 31 (1997) 3635.
[29] B. Pate, R.K.M. Jayanty, G.F. Evans, J. Air Waste Manage. Assoc. 42 (1992) 460.
[30] M. G. Miguel, A comparison study to determine the effects of pressure, relative humidity, and canister residence time on NMHC recovery rates from stainless steel canisters. In: Measurement of Toxic and Related Air Pollutants, Air & Waste Management Association, Research Triangle Park, NC, 1995, pp. 119–125.
[31] R.K.M. Jayanty, J.R. Albritton, Y.H. Straley, D.J. von Lehmden, J. Air Waste Manage. Assoc. 42 (1992) 1198.
[32] E.C. Apel, J.G. Calvert, F.C. Fehsenfeld, J. Geophys. Res. 99 (D8) (1994) 16651.
[33] E.C. Apel, J.G. Calvert, J.P. Greenberg, D. Riemer, R. Zika, T.E. Kleindienst, W.A. Lonneman, K. Fung, E. Fujita, J. Geophys. Res. 103 (1998) 22281.
[34] A.P. Altshuller, I.R. Cohen, Anal. Chem. 32 (1960) 802.
[35] K. Schoene, J. Steinhanses, Fresenius Z. Anal. Chem. 335 (1989) 557.
[36] M. Staudt, G. Seufert, D. Kotzias, B. Frenzel, Fresenius Environ. Bull. 4 (1995) 743.
[37] M. Gautrois, R. Koppmann, J. Chromatogr. A 848 (1999) 239.
[38] M. Possanzini, V. Di Palo, E. Brancaleoni, M. Frattoni, P. Ciccioli, J. Chromatogr. A 883 (2000) 171.
[39] G.A. Lugg, Anal. Chem. 40 (1968) 1072.
[40] G.O. Nelson, Controlled Gas Atmospheres, Ann Arbor Science, MI, 1971.
[41] Pannwitz, K.H., 1984. Diffusion coefficients. Drager Review 52.
[42] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, McGraw-Hill, New York, 1986.
[43] H. Van den Dool, P.D. Kratz, J. Chromatogr. 11 (1963) 463.
[44] F. Saura-Calixto, A. Gracia-Raso, P.M. Deya, J. Chromatogr. Sci. 20 (1982) 7.
[45] T.C. Gerbino, G. Castello, J. Chromatogr. 537 (1991) 305.
[46] R.C. Fischer, R. Wittlinger, K. Ballschmiter, Fresenius J. Anal. Chem. 342 (1992) 421.
[47] W. Spieksma, R. Luijk, A.J. Govers, J. Chromatogr. A 672 (1994) 141.
[48] D. Helmig, W. Pollock, J. Greenberg, P.R. Zimmerman, J. Geophys. Res. 101 (1996) 14697.
[49] P. Fruekilde, J. Hjorth, N.R. Jensen, D. Kotzias, B. Larsen, Atmos. Environ. 342 (1998) 1893.
[50] J.H. Sartin, C. Halsall, B. Davison, S. Owen, C.N. Hewitt, Anal. Chim. Acta 428 (2001) 61.
[51] R.A. Malizia, D.A. Cardell, J.S. Molli, R.J. Grau, J. Essent. Oil Res. 14 (2002) 132.
[52] NIST Standard Reference Database Number 69—July 2001 Release, http://webbook.nist.gov/chemistry/
[53] J.T. Scanion, D.E. Willis, J. Chromatogr. Sci. 23 (1985) 333.
[54] A.D. Jorgensen, K.C. Picel, V.C. Stamoudis, Anal. Chem. 62 (1990) 683.
[55] X.-L. Cao, C.N. Hewitt, Chemosphere 27 (1993) 695.
[56] R.R. Arnts, D.F. Smith, T.E. Kleindienst, Development of multi-bed adsorbent method for sampling and analysis of polar and non-polar biogenic volatile organics, in: Measurement of Toxic and Related Air Pollutants, May 16–18, Research Triangle Park, NC, 1995.