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Dynamic solid phase microextraction sampling for reactive terpenes in the presence of ozone

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ABSTRACT

Dynamic gas sampling using solid phase microextraction (SPME) was evaluated for recovery of reactive terpenes and terpenoids in the presence of ozone. For limonene, α-terpineol and dihydromyrcenol in the 20–60 ppb range, this method achieves >80% recovery for ozone mixing ratios up to 100 ppb. Both the experimental results and a model analysis indicate that higher ozone concentrations and longer sampling times result in lower percent recovery. Typically greater than 90% recovery and ppb level method detection limits were achieved with a 5 min sample time. Increasing the flow rate from 100 to 400 sccm flow (5–20 cm s^{-1}) through the active sampler did not significantly affect sensitivity or recovery in most cases, probably due to negligible mass-transfer improvements. The recovery for each compound improves when sampling from a mixture of different species than that from a single compound sample. This may be due to competition for ozone amongst adsorbed species. Dynamic SPME sampling can improve detection and quantification of terpenes in reactive environments, especially for low vapor pressure (<5 mm Hg at 25 °C) compounds that can be adsorbed to ozone scrubbers used in other methods.

1. Introduction

Quantification of the concentration and emission rates of biogenic terpenes and terpenoids is important for both atmospheric and indoor air quality research. Biogenic terpenes such as isoprene and pinene contribute to the formation of photochemical oxidants and aerosols in the atmosphere [1,2]. In recent simulations, Curci et al. [3] estimated that biogenic VOCs contribute to, on average, 5% of ozone maxima over Europe, but 15% or greater in some urban areas. In buildings, ozone reactions with unsaturated terpenes can generate formaldehyde, aerosols and irritants [2,4–6]. Many terpenes are present at much higher concentrations indoors relative to outdoors, because they are widely used as fragrances and solvents in cleaning products, air fresheners, and personal care products [4,7–9]. Thus quantification of terpenes in either environment is crucial for understanding and predicting the concentrations of the products of this chemistry.

In both indoor and outdoor environments, ozone and other oxidants coexist with reactive terpenes, making measurement problematic. Although smog levels have improved, outdoor urban ozone concentrations can still rise over 100 ppb [10]. Indoor ozone concentrations tend to follow outdoor concentrations, and are between 10 and 70% of outdoor levels [11]. Even the lower indoor concentrations of ozone can interfere with the measurement of terpenes [12]. Analytical methods that collect and concentrate compounds on surfaces may be especially prone to recovery problems if ozone is not removed prior to collection. Unsaturated compounds attached or sorbed to surfaces tend to react rapidly with ozone. For example, Stokes et al. [13] showed that a surface bound unsaturated organic such as 1-pentene can react with ozone at rates nearly five orders of magnitude faster than it would in the gas phase. Surface conversion rates may be more related to the orientation and availability of double-bonds rather than to the gas-phase rates [14]. As surface coverage of the terpene increases, the rate of terpene–ozone reactions increase and recovery suffers. Relative to higher-volatility terpenes, reduced recovery would also be anticipated for lower volatility or polar terpenes with higher equilibrium surface coverage.

Evidence for this effect has been observed during the collection of terpenes on sorbent surfaces [15–17]. Tenax, Carbosorb and other sorbents are widely used to collect and concentrate gas-phase compounds for thermal desorption, separation and quantification by GC–MS or other methods [18]. At the inlet of a sorbent cartridge, analytes rapidly approach equilibrium surface coverage (maximum for those conditions) and are exposed to ambient concentrations of ozone during the entire duration of sampling. Surface conversion rates are thereby maximized in the inlet region. Several authors [15,19,20] have shown that when ozone is present, reactive terpenes degrade during sampling on Tenax, reducing

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Table 1
CAS #, purity, vapor pressure, and gas phase ozone reaction rates of terpenes.

Chemical name	CAS #	Purity (%)	Vapor pressure at 25 °C[a] (mm Hg)	Gas phase ozone reaction rate (cm^3 molecule^{-1} s^{-1})
Limonene	5989-27-5	97	1.45	6.40E−16[b]
Dihydromyrcenol	18479-58-8	99	0.124	<2.00E−18[c]
Tetrahydromyrcenol	18479-57-7	95	0.114	(anticipated ~ 0)
Terpineol	98-55-5	96	0.0196	3.00E−16[d]
Citronellal	106-23-0	93	0.254	2.40E−16[e]
Pinene	7785-70-8	98	4.54	8.20E−17[b]
Carene	13466-78-9	99	2.09	1.20E−16[b]
Linalyl acetate	115-95-7	97	0.131	4.30E−16[f]

[a] Vapor pressures are reported as the mean of estimated values by Antoine and Grain methods, except for terpineol, whose vapor pressure is estimated by modified Grain methods. All of the values are calculated by EPI Suite [38].

[b] Measured value [39].

[c] Measured value [40].

[d] Measured value [41].

[e] Measured value [36].

[f] Estimated value using AOPWIN module in EPI Suite [38].

recovery. Calogirou et al. [15] showed that recovery was reduced for lower-volatility compounds, polar oxygenates and compounds with multiple unsaturations. Several methods, such as adding an ozone trap before the sorption tube [21–28] or adding trans-2-butene to the sample gas as ozone scavenger [29], have been developed to overcome this problem. However, lower-volatility and polar terpenes tend to adsorb to traps, again reducing recovery [15]. The addition of scavenger gases increases the complexity and cost of sampling. Calogirou et al. also improved recovery by reducing the total sample time, thereby reducing the ozone–terpene contact time on the sorbent surface. However, even for very short sampling times, some terpenes still exhibited low recovery (<50%) due to their very high reaction rate with ozone on the surface of the sorbent.

Solid phase micro extraction (SPME) is widely used in analysis of organic compounds in both air and water [30–33]. By concentrating sorbates into a thin layer of sorbent material, SPME combines sampling, extraction, and concentration, and does not require a solvent for sample introduction and analysis [34]. While it is common to use SPME as an equilibrium sampler, a potential advantage of this method is that it can be applied such that the sorbent material surface does not reach equilibrium with the gas. The surface coverage of the analyte is minimized, reducing the average rate of ozone–terpene collisions. Researchers have studied SPME sampling of low-reactivity aromatic compounds in the presence of ozone [35] and also verified that the SPME fiber will not be affected or damaged when the ozone mixing ratio is as high as 1000 ppb. Several ozone–terpene kinetics studies have used SPME in the presence of ozone to detect terpenes [36,37]. Harrison et al. [36] measured ozone–citronellal kinetics using a polydimethylsiloxane divinylbenzene (PDMS/DVB) coated SPME fiber in the presence of 0.3–0.5 ppm citronellal and 0.05–0.15 ppm ozone. No explicit determination of how ozone would affect recovery was reported, but kinetic results with reference terpene compounds suggested that ozone did not significantly impact recovery.

In an effort to improve terpene measurements in reactive environments and eliminate the need to trap ozone or introduce other species into the collecting media, we have evaluated the impact of ozone on terpene and terpenoid recovery in a dynamic SPME sampling system. Our objective was to identify conditions, such as the sampling time, that result in good recovery and sensitivity.

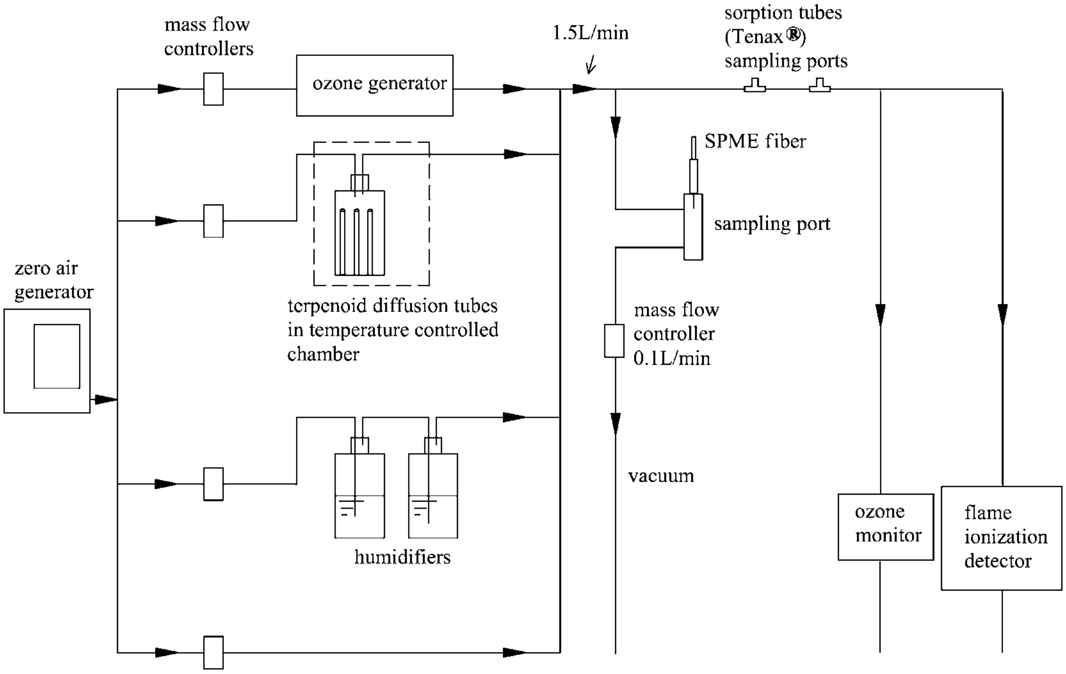

Fig. 1. Apparatus used for gas standard generation and experimental determination of recovery.

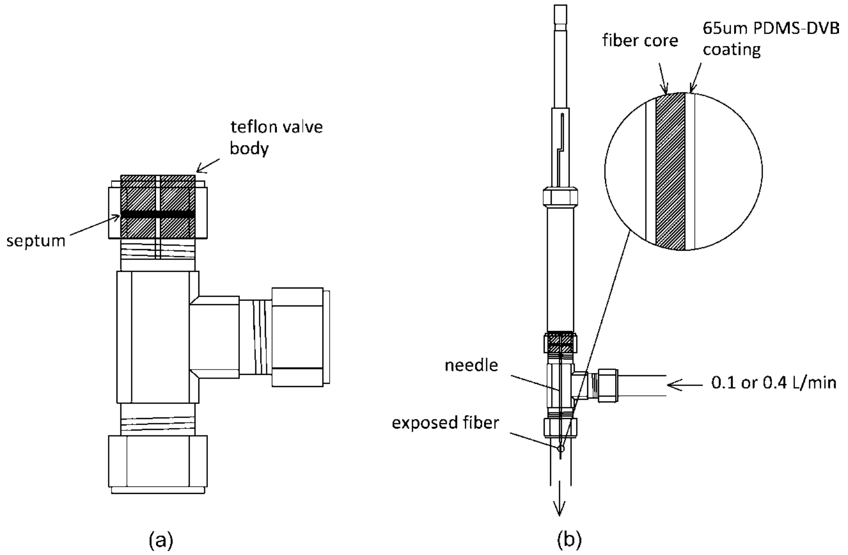

Fig. 2. (a) Schematic of the dynamic sampler. (b) The dynamic sampler coupled with a SPME fiber assembly.

2. Experimental

2.1. Reagents and supplies

(R)-(+)-Limonene, dihydromyrcenol (DHM), tetrahydromyrcenol (THM), α-terpineol, citronellal, (1R)-(+)-α-pinene, (1S)-(+)-3-carene, and linalyl acetate were obtained from Sigma–Aldrich (St. Louis, MO) at the highest purity available. They were chosen to represent volatile and semi-volatile terpenes and terpenoids with high and low reactivity. The vapor pressure and gas phase ozone reaction rates are listed in Table 1. THM is fully saturated and not expected to react with ozone. It is used as a control and an internal standard for sampling in the presence of ozone. Supelco StableFlex^{TM} SPME fibers (65 μm PDMS–DVB coating; manual holder) were obtained from Sigma–Aldrich (St. Louis, MO).

2.2. Experimental apparatus

A sketch of the apparatus used to produce the gas mixture is shown in Fig. 1. A Parker Balston (Haverhill, MA) zero air generator was used to deliver clean air to the system, and MKS (Crewe, UK) flow controllers were used to control the flow at desired rates. In this study, the relative humidity of the gas mixture was 50% for all experiments. Ozone was generated and monitored by a Dasibi (Glendale, CA) ozone generator and monitor. The ozone concentration in the gas standard was controlled by adjusting the voltage to the UV lamp in the ozone generator. To minimize the extent of analyte–ozone reactions in the gas phase, ozone was introduced through a port 10 cm upstream of the sampling port, for a residence time of 0.1 s prior to reaching the SPME fiber. Terpenes were generated using a temperature controlled flow-through system consisting of diffusion tubes in a glass reservoir. A range of diffusion tube sizes (diameter and length) was used to adjust the concentration of terpenes. The temperature was maintained at $25.0 \pm 0.5\,^{\circ}\mathrm{C}$ for all experiments. The concentrations of terpenes were measured in the absence of ozone using thermal desorption tubes (Markes International Ltd., Llantrisant, UK). To verify that the concentration of the gas standard was stable during experiments, a standalone SRI (Torrance, CA) flame ionization detector (model 110) was used to draw a sample from the exhaust at 80 sccm and its signal was recorded.

2.3. Dynamic sampler

A 3/8 inch (95 mm) stainless steel compression tee (Swagelok, Solon, OH) was used as the main body of the SPME sampling device (Fig. 2a). A modified Teflon Mininert valve body (Supelco, Bellefonte, PA) with a septum seal was inserted into the tee to center and stabilize the SPME needle. The two other ports of the tee were used as the gas inlet and outlet. The flow rate through the dynamic sampler was controlled at 100 or 400 sccm, by a flow controller attached to vacuum. To sample, the SPME fiber was inserted through the valve and exposed (parallel) to the flowing gas mixture (Fig. 2b). Exposing the fiber to a flowing stream reduces the sampling time by decreasing the boundary layer resistance to mass transfer [42]. The dynamic sampling device was placed in a temperature controlled cabinet maintained at $25 \pm 0.5\,^{\circ}\mathrm{C}$.

2.4. SPME/GC/FID

Each SPME sample was analyzed immediately after sample collection. An Agilent 6890 gas chromatograph with a flame ionization detector (GC/FID) was used in this study. For SPME fibers, a liner with a 0.75 mm inner diameter was used in the injection port. The injection port was maintained at 250 °C for fast desorption in splitless mode. The SPME fiber was retained in the injection port for 5 min. A single fiber was used repeatedly for all experiments. A HP-5 capillary column (30.0 m × 320 μm; 0.25 μm film thickness) was used under 8 psi constant pressure. The oven temperature ramp was 50–250 °C at a rate of $20\,^{\circ}\mathrm{C\,min^{-1}}$. FID detector temperature was set to 250 °C. The total run time was 10 min.

2.5. Calibration of thermal desorption tubes

The concentrations of terpenes were measured in the absence of ozone using thermal desorption tubes filled with Tenax-TA (Markes, Llantrisant, UK), thermal desorber (Markes, Llantrisant, UK), and Agilent 6890 GC/FID system [18]. The standard solution was prepared by dissolving a small amount of each terpene into methanol. The solution concentration of the 9 terpenes ranged from 20.6 to $23.3\,\mathrm{ng\,\mu L^{-1}}$. To develop a gravimetric calibration curve for TD tubes, different volumes of the standard solution (10, 20, 40, 80 μL) were injected into 5 different TD tubes, purged with high purity nitrogen to drive off methanol, and injected and analyzed on the GC/FID system. To verify the terpene concentration in the

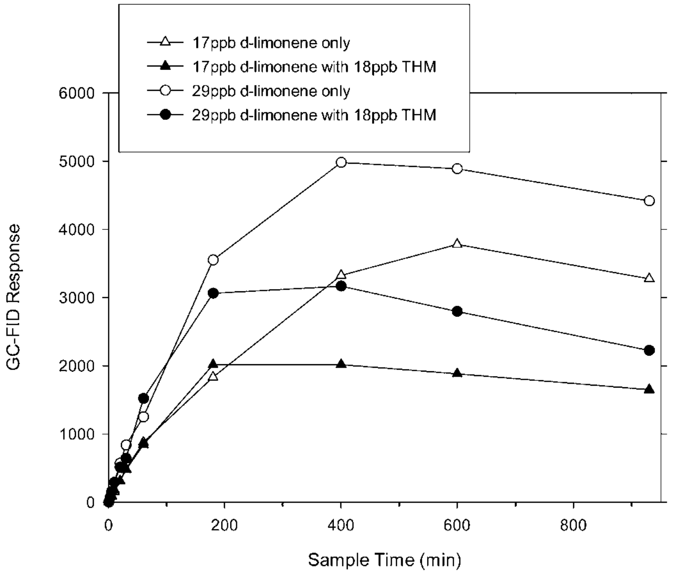

Fig. 3. The effect of 18 ppb THM on the mass collected (FID signal) of 17 ppb limonene.

dynamic sampler, gas (without ozone) was drawn through a TD tube at 100 sccm for 10 min. Triplicates were used to ensure the accuracy of the sampling. Resulting FID peak areas were compared against the gravimetric calibration.

3. Procedures

3.1. Internal standard

THM was chosen as an internal standard since it is saturated and not expected to react readily with ozone. To ensure that THM itself does not react with ozone, the peak areas were compared for THM at 80 ppb, with and without ozone at 580 ppb (an arbitrarily large value). Five replicates were collected at each condition using two sampling times (5 and 30 min). During all other experiments, THM was maintained at 18 ppb as an internal standard.

3.2. Competitive adsorption with internal standard and reaction products

It has been reported that analytes compete with each other for adsorption sites on SPME fibers that contain divinylbenzene [42]. Ozone–terpenoid reaction products may also compete with the reagents. The effect of potential competitive adsorption between the analytes, internal standard, and ozone reaction products was tested using gas mixtures containing limonene only, limonene with 18 ppb THM, and limonene with 18 ppb THM and 100 ppb ozone. Sampling time ranged from 2 to 930 min. Two limonene concentrations were used for each condition (17 and 29 ppb). Here and throughout, terpene concentrations were chosen to reflect the low-ppb range (<100 ppb) that may be observed in buildings [43].

3.3. Effect of ozone concentration, sampling time and flow rate on recovery of individual analytes

For this recovery assessment, the gas mixture contained a single compound (d-limonene, α-terpineol or DHM), the internal standard and/or ozone. The sample was collected for sampling times ranging from 2 to 30 min at 0, 30, and 100 ppb ozone, at a high and low terpenoid mixing ratio, and at a 100 and 400 sccm sample flow rate (equivalent to mean velocity in the sampler equal to 5 and 20 cm s^{-1}, respectively). The high and low mixing ratios (ppb) for each terpenoid were as follows: d-limonene (17, 29), α-terpineol (15, 48), DHM (18, 45). The SPME fiber was also exposed to clean air and ozone to test for any coating specific reaction products.

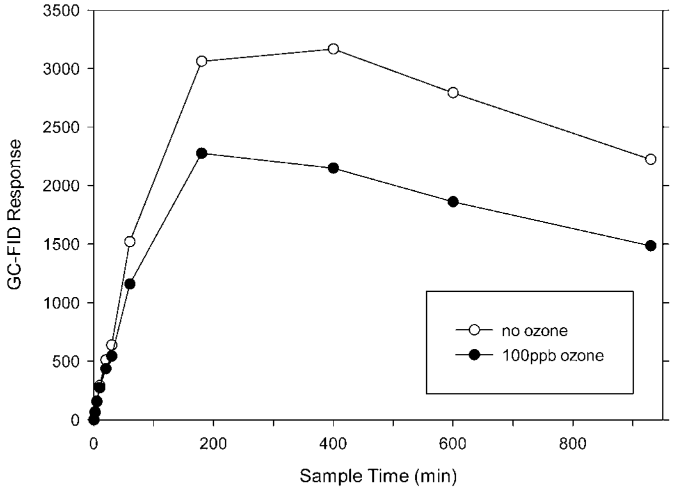

Fig. 4. The effect of 100 ppb ozone on the mass collected (FID signal) of 17 ppb limonene, with 18 ppb THM.

3.4. Effect of ozone concentration and sampling time on recovery of multiple analytes

The following gas mixture was generated and the SPME recovery evaluated with 0, 30, and 100 ppb ppb ozone: 51 ppb pinene, 60 ppb carene, 16 ppb limonene, 39 ppb DHM, 39 ppb THM, 35 ppb citronellal, 17 ppb terpineol, and 14 ppb linalyl acetate. The flow rate was 100 sccm and samples were collected for times ranging from 2 to 30 min.

3.5. Qualitative sorption-reaction model

A model was developed to evaluate the qualitative dynamics of sampling in a reactive environment. During the early period of sampling, the concentration near the surface of the SPME film is very small relative to the mean gas concentration [42]. The concentration at the surface is at equilibrium with this near-surface concentration, but the inner pores of the DVB may not be at equilibrium. At the concentrations of terpenes used in this study, the surface density of terpenes is low and the ozone–terpene reaction rate at the surface is negligible. We also apply the reasonable assumption that ozone does not react readily with PDMS or DVB. Therefore, the ozone concentration adsorbed to the surface is constant and proportional to the measured gas-phase concentration. Finally, the reaction of ozone with the surface bound terpene is first order in each of the reactants. By applying a mass balance, the rate of mass adsorbed per unit area of fiber surface (m_A) equals the adsorption rate minus the desorption rate and the loss rate due to reaction. The model is expressed in Eq. (1).

$$\frac{dm_A}{dt} = \vartheta_t C_A - \left(\frac{\vartheta_t}{K_A^E} + K_2 K_A^E K_{O_3}^E C_{O_3}^E\right) m_A \qquad (1)$$

where ϑ_t is the transport limited deposition velocity (expressed in terms of boundary layer thickness and diffusion coefficient by Koziel et al. [42]), C_A and C_{O_3} are the concentration of analyte and ozone in the gas sample, respectively, K_A^E and $K_{O_3}^E$ are adsorption equilibrium constants for the analyte and ozone, respectively and K_2 is the rate constant for the ozone–analyte reaction on the fiber surface. The adsorption equilibrium constant is defined as the gas phase concentration divided by the equilibrium value of m_A. The following expressions are constant:

$$A = \vartheta_t C_A \tag{2}$$

$$B = \frac{\vartheta_t}{K_A^E} + K_2 K_A^E K_{O_3}^E C_{O_3} \tag{3}$$

For an initial adsorbed mass equal to zero, Eq. (1) can be solved and simplified:

$$m_A = \frac{A}{B}(1 - e^{-Bt}) \tag{4}$$

This qualitative model predicts that as sampling time increases, analyte percent recovery is expected to diminish. Also, as ϑ_t increases the mass on the fiber reaches equilibrium more rapidly, but the equilibrium mass is larger and recovery will be higher. Therefore, a flowing sampler operated for short sampling time periods (time-weighted sampling) may be more advantageous for sampling in reactive media than a static sampler operated for long time periods. Equilibrium sampling results in the lowest possible recovery.

4. Results and discussion

4.1. Internal standard

THM recovery averaged 100 ± 7% in the presence of ozone under all conditions and was therefore considered to be a suitably non-reactive internal standard for this study. No products of a reaction with THM were observed.

4.2. Calibration of Tenax sorption tubes and SPME

The Tenax sorption tubes calibration curves exhibited good linearity (R^2 varied from 0.9942 to 1 for different compounds) in the range of 0 to ~2500 ng. The instrumental detection limits varied from 15 to 25 ng. The detection limits for dynamic SPME sampling and GC/FID analysis depended on the SPME sampling time. For a 5 min sampling time, the detection limits varied from 1.6 to 5.8 ppb for different compounds. Reproducibility for all compounds evaluated was 5% or better.

4.3. Competitive adsorption with internal standard and reaction products

In Fig. 3 are shown the results of competitive adsorption experiments with limonene, THM and (potentially) ozone reaction products. For very long sampling times, THM significantly reduces the mass of limonene collected on the SPME fiber. Competitive adsorption was not significant for sampling times less than 10 min. For lower-volatility compounds (terpineol and DHM), we observed no significant competition up to 30 min. Therefore, up to 10 min, any observed reduction in the recovery of limonene and species with similar or lower vapor pressures, is likely due to reactions and/or competition with reaction products. A reduced recovery of limonene was observed in the presence of 100 ppb ozone and the reduction increased with increasing sample time (Fig. 4). This corresponds qualitatively with anticipated mass reduction due to a combination of ozone reactions reducing limonene concentration on the surface and reaction products competing with limonene adsorption. Since the contact time of limonene and ozone in gas phase is less than 0.1 second, reaction products generated by gas-phase reactions are not likely to influence recovery. No reaction products were observed for the reaction of ozone in clean air with the coating on the fiber.

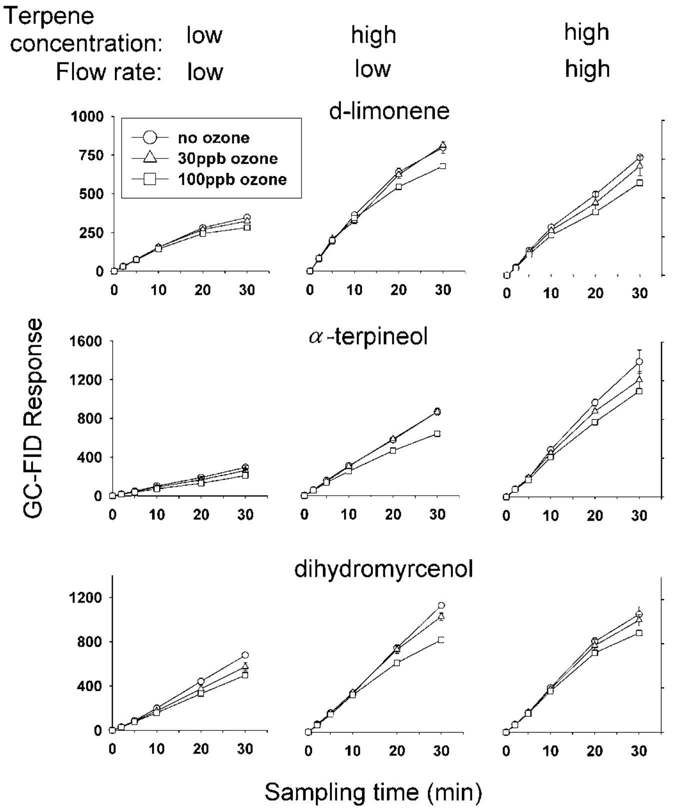

Fig. 5. Single compound responses for different concentrations, flow rates and ozone levels.

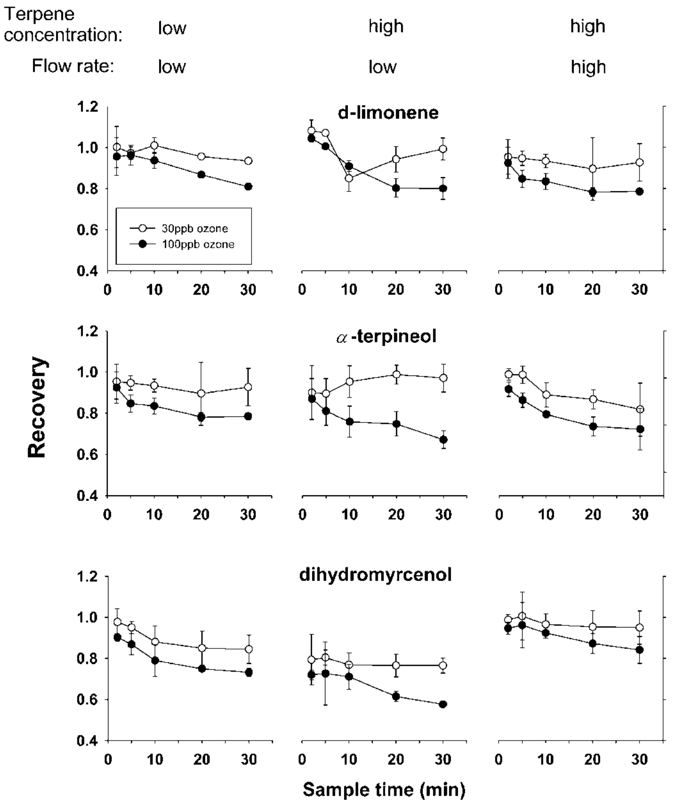

Fig. 6. Single compound recovery for different concentrations, flow rates, and ozone mixing ratios.

4.4. Recovery of a single compound

Shown in Fig. 5 are normalized FID responses for each set of conditions (low concentration low flow, high concentration low flow, and high concentration high flow) for d-limonene, α-terpineol, and DHM. The curves qualitatively match model predictions: (1) under the same conditions (terpene concentration, flow rate, and ozone concentration), longer sampling times results in lower recovery, and (2) higher ozone concentrations result in lower analyte mass accumulated on the fiber if other conditions (terpene concentration, flow rate, and sampling time) are the same.

Recoveries are shown in Fig. 6. Overall, the recovery ranges from 65 to 115%. For 10 min sampling at 100 ppb ozone, recoveries were ~80% or better. For 5 min sampling at 30 ppb, recovery was generally not significantly lower than 100%. Thus, this method is sufficient for quantification of reactive semi-volatile compounds, even in the presence of ambient ozone levels. Interestingly, although limonene has a gas-phase reactivity that is 300 times greater than that of dihydromyrcenol, the recovery of limonene is very similar to the recovery of DHM for the same sampling conditions. Thus, the method appears to be fairly robust for a both low and high reactivity terpenoids. Recovery is reduced as

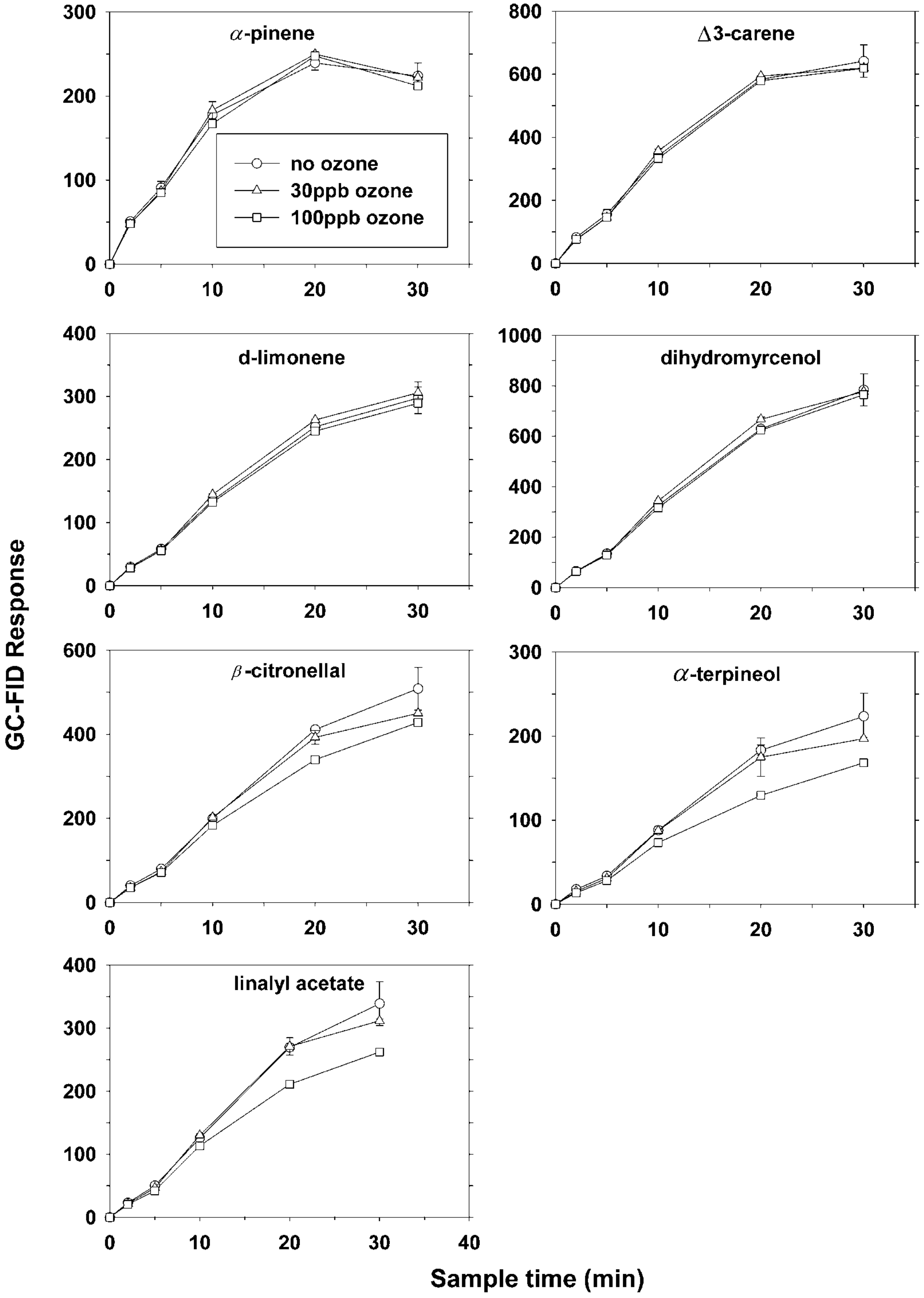

Fig. 7. Normalized FID responses as a function of sampling time for individual terpenes in a gas mixture with ozone.

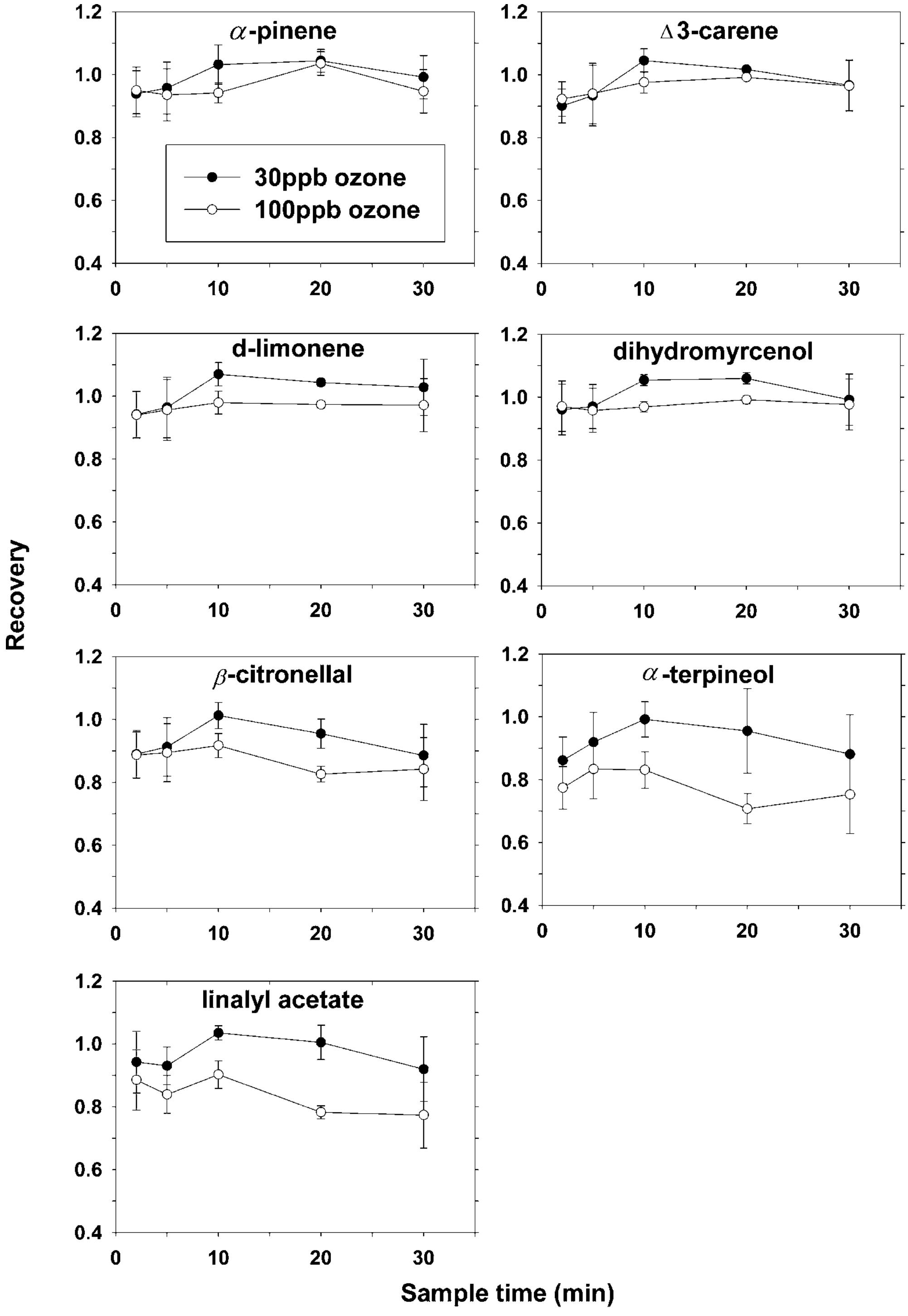

Fig. 8. The recovery as a function of sampling time of individual terpenes in a gas mixture with ozone.

the ozone concentration increases and (usually) as sampling time increases.

We observed higher velocity does not significantly increase mass accumulated on the fiber, except in the case of terpineol (Fig. 5). Therefore, the mass transfer coefficient did not significantly increase over this range. This was observed by Koziel et al. [42], but for a somewhat higher velocity system and for perpendicular flow. The apparent difference in terpineol uptake with increased velocity was reproducible but a satisfactory explanation is not apparent. The difference in mass-transfer characteristic due to slight differences in diffusivity is not likely to have a significant impact on ϑ_t.

Increasing the flow rate from 100 to 400 sccm does not significantly increase the recovery except, perhaps, in the case of DHM. If DHM had a significantly larger adsorption equilibrium constant, K_{A}^{E}, ϑ_t would more strongly influence recovery (Eq. (4)). However, this does not appear to be the case as equilibrium mass uptake on the fiber is similar for terpineol and for DHM. As the present conditions result in adequate recovery, we did not operate the system at a lower flow rate. However, we anticipate that recovery would be somewhat reduced for a much lower flow rate, as predicted by Eq. (4).

4.5. Multiple compounds in the presence of ozone

Shown in Fig. 7 are normalized FID responses for individual compounds in the multiple compound mixture. For the higher-volatility compounds (pinene, carene, and limonene), the adsorption profile is not linear for sampling times greater than 20 min. This is likely due to the competition for the adsorption sites with the other, lower volatility, compounds.

Recoveries for individual compounds in the multiple compound mixture are shown in Fig. 8. In the presence of ozone, the recoveries of limonene, dihydromyrcenol, and terpineol in the mixture are higher than their recoveries in the single compound samples. At a high adsorbed surface density, reactive compounds can compete with each other for ozone and, potentially, improve recovery for individual compounds by spreading out reactive losses across all adsorbed species. All else being equal, more of the lower-volatility species (smaller adsorption constant) will be present on the fiber and out-compete the higher-volatility species for ozone. Amongst the lower-volatility species, gas-phase reactivity appears to correlate roughly with recovery. At 100 ppb ozone, DHM, exhibits significantly higher recoveries than terpineol, citronellal or linalyl acetate which have gas-phase reactivity approximately 100 times greater than DHM. This competition and improved recovery is not anticipated to occur for very low gas-phase terpene concentrations (a few ppb). Low adsorbed surface density on the SPME fiber would reduce ozone uptake, resulting in higher near-surface ozone concentrations and higher relative rates of terpene oxidation on the SPME fiber. The recovery of pinene and carene (Fig. 8) was not affected by the displacement phenomenon shown in Fig. 7.

4.6. Sensitivity and detection limit in the presence of ozone

Because of the improved mass transfer conditions, dynamic sampling is more sensitive than static sampling for the same time-weighted averaging period [44]. The method detection limit was estimated based on twice the standard deviation of the peak areas of the lowest mass injection by SPME. For the eight compounds studied in the presence of ozone, the MDL ranged from 1.6 to 5.8 ppb for a 5 min sampling time, and the presence of 30 or 100 ppb ozone does not affect the MDL significantly.

4.7. Effect of relative humidity

The effect of humidity was not evaluated in this research. Equilibrium mass collected by SPME can be influenced by relative humidity [45]. SPME sampling of BTEX was not affected by the relative humidity when the humidity was lower than 45% [46]. For time-weighted sampling, and short sample times, uptake on the fiber is transport limited and relative humidity is not anticipated to significantly alter the results. However, polar terpenoids such as terpineol and DHM are alcohols and strong interactions with water may influence equilibrium partitioning (K_A^E in Eq. (1)). The quantity of water on the fiber may also influence the rate of the reaction with ozone and distribution of products generated.

The application of SPME for rapidly quantifying gas-phase concentrations of reactive terpenoids in the presence of ozone was demonstrated. We observed good recovery for environmentally relevant concentrations, even in the presence of 100 ppb ozone. Properly applied, this method improves upon recovery using flow-through sorbent samplers and eliminates the need for ozone traps or scavenger gases. However, if sampling conditions are favorable for surface reactions, ozone and other oxidants can consume reactive terpenes adsorbed onto the SPME fiber resulting in poor recovery. Interference may also result from accumulation of reaction products on adsorption sites in the SPME coating.

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