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SPME-based mobile field device for active sampling of volatiles

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Abstract

Monitoring plant volatile organic compound (VOC) profiles can reveal information regarding the health state of the plant, such as whether it is nutrient stressed or diseased. Typically, plant VOC sampling uses sampling enclosures. Enclosures require time and equipment which are not easily adapted to high throughput sampling in field environments. We have developed a new, easily assembled active sampling device using solid phase microextraction (SPME) that uses a commercial off the shelf (COTS) hand vacuum base to provide rapid and easy mobile plant VOC collection. Calibration curves for three representative plant VOCs (α-pinene, limonene, and ocimene) were developed to verify device functionality and enable the quantification of field-samples from a Meyer lemon tree. We saw that the active sampling allowed us to measure and quantify this chemical in an orchard setting. This device has the potential to be used for VOC sampling as a preliminary diagnostic in precision agriculture applications due to its ease of manufacturing, availability, and low cost of the COTS hand vacuum module.

Keywords

volatile organic compounds (VOCs); solid phase microextraction (SPME); gas chromatography mass spectrometry (GC/MS); active sampling; plant volatiles

1. Introduction

The monitoring of volatile organic compounds (VOCs) is important for a variety of applications such as pollution assessment [1, 2] and industrial process monitoring [3, 4].

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Conflicts of interest

There are no conflicts to declare.

Software and device design information

The software code and PCB design specifications for our active sampler device are available on GitHub. Please refer to Professor Cristina Davis' webpage for more information. This material is available as open source for research and personal use under a modified BSD license. Commercial licensing may be available, and a license fee may be required. The Regents of the University of California own the copyrights to the software and PCB designs. Future published scientific manuscripts or reports using this software and/or hardware designs must cite this original publication.

Volatiles emitted by plants can provide information regarding the health state of the plant such as nutrient deficiency [5], disease affliction [6-8], or pest infestation [9, 10]. Therefore, profiling of volatile metabolites has been suggested as a plant disease diagnostic tool that may have great practical implications [6].

Given the relatively low concentration of plant volatiles, it is typical to collect VOCs non-invasively either using an enclosure and/or sorbent [10]. While plant enclosures offer many benefits, high throughput sampling with enclosures is challenging as each plant requires its own enclosure and related equipment. Also, a large capacity air pump (or pumps) would be required to generate circulation air for numerous plants. Supplies and the corresponding costs can accumulate quickly. Furthermore, enclosures increase analysis time as once each plant has been set up inside an enclosure, it is typical to wait at least 24 hours before sampling as the plant needs to adapt/equilibrate and recover from any installation damage or disturbance to the plant equilibrium [11, 12]. Developing methods that do not require enclosures will increase throughput while minimizing costs to the necessary level to make VOC diagnostics practical.

Sorbents such as solid phase micro-extraction (SPME) fiber also provide a means for collecting and concentrating plant VOCs [13]. An important advantage of SPME is direct compatibility with injectors of most of commercial gas chromatographs (GC), which allows for analysis of the collected sample without an additional sample transfer step or costly custom setup. SPMEs are typically used for passive sampling, such as leaving the SPME undisturbed in a plant enclosure to preconcentrate volatiles [14, 15]. However, passive SPME sampling has a number of limitations for field sampling such as the SPME fiber needs to be shielded from items that might damage it such as leaves, branches, and animals and it must be placed carefully so as to not disturb the plant and generate an artificially high signal.

In some environmental applications, SPME are used in active sampling [16-18]. Active sampling allows for a continuous flow of air to pass over the SPME fiber at a specified flow rate. This is particularly important in field sampling to ensure reproducible results, as a slight change in air velocity could potentially affect the amount of analyte adsorbed onto the fiber [17]. Compared with passive sampling, active sampling virtually eliminates the wall effects of the sampling vessel and provides a continuous flow of air containing a near constant concentration of analytes to the SPME [19]. Furthermore, this system enhances sensitivity of SPME for air sampling due to an increase in the amount of analytes extracted [20]. A common method of active SPME sampling typically uses a SPME fiber holder to introduce the sorbent tip into an airflow containing the VOCs of interest either through a septum in a compression fitting tee or through a custom holder block, while the active flow is generated by a sampling pump [18, 21-24]. These sampling devices typically have limited mobility as they are designed to attach to enclosures and often use expensive sampling pumps to generate the active flow.

In this paper, we describe and benchmark a hand-held, portable sampling device designed specifically for conventional SPME fibers to actively collect plant volatiles for subsequent gas chromatography/mass spectrometry (GC/MS) analysis without the need of an enclosure.

The developed device is inexpensive to manufacture and is based on easily available commercial-off-the-shelf (COTS) parts and modules, with a hand vacuum as the flow source. The device protects the SPME while also allowing for sampling from areas that could not typically be reached without otherwise disturbing the plant. This could potentially allow for wide acceptance of the sampling method which, in turn, would allow for immediate comparison of data among users. To assess device performance, calibration curves were developed using chemical standards α-pinene, limonene, and ocimene as representative plant volatiles. The device was then used for field sampling of a Meyer lemon citrus tree and components of the orchard trees VOC output were measured.

2. Experimental

2.1 GC/MS Analysis Protocol

Five commercial 75 μm carboxen/polydimethylsiloxane (CAR/PDMS) solid phase microextraction (SPME) fibers (Restek, Bellefonte, PA) were used as the sampling sorbent for the active sampler. This type of sorbent has been chosen due to its suitability for trace level volatiles analysis of low molecular weight compounds (MW 30-225). Prior to sample collection, the fibers were conditioned at 280 °C for 1 h in a flow of inert gas to remove any background chemicals retained on the sorbent, per the manufacturer recommendation. Samples were run on a 7890 GC (Agilent Technologies Inc., Santa Clara, CA) with 5977A MSD (Agilent Technologies Inc., Santa Clara, CA). Samples were injected in the splitless mode at an injection port temperature of 270 °C. Helium was used as the carrier gas at 1 mL/min constant flow. The separation was accomplished on a VF-5MS fused silica column (30 m × 0.25 mm i.d. × 0.5 μm film thickness, Agilent Technologies). The oven temperature was programmed to start at 40 °C with a 5 min hold, increase to 110 °C at a rate of 5 °C min^{-1}, and increase to 270 °C (with a 3 min hold) at a rate of 40 °C min^{-1}. The mass spectrometer was operated in the scan mode (50-500 m/z) with electron impact ionization (ionization voltage: 70 eV). For quantitative analysis of lemon tree VOCs, limonene (Sigma-Aldrich, MI, USA), linalyl acetate (Sigma-Aldrich, MI, USA), geranyl acetate (Sigma-Aldrich, Missouri, USA), ocimene (Sigma-Aldrich, MI, USA), α-terpineol (Sigma-Aldrich, Missouri, USA), nerol (Sigma-Aldrich, MI, USA), linanol (Alfa Aesar, MA, USA), cartophyllen (Sigma-Aldrich, MI, USA), α-pinene (Sigma-Aldrich, MI, USA) were used as a standard reference.

2.2 Preliminary Time Course

A preliminary time course study was done to compare passive SPME sampling, active SPME sampling with the built sampler at a flow rate of 0.5 L/min, and passive no flow sampling with the built sampler. 10 μL of a 1.2 ng/ μL chemical mixture were placed in a 1.9L jar (Part# GLC-01858, Qorpak Bridgevill, PA) using two 5 μL Drummond Microcaps (Drummond Scientific Company, Broomall, PA) and allowed to equilibrate for 30 min. The jar's lid had multiple holes drilled into it (five 0.026" and two 1/8" diameter holes) to enable both active and passive sampling. The chemical mixture was sampled for 1, 3, 5, 7, and 10 min with two replicates for active and passive sampling and one sample for no flow. Short sampling times were used to ensure extraction occurred under nonequilibrium conditions and to minimize competitive adsorption. Once the chemical mixture had equilibrated, the jar

was sampled. For passive sampling, one jar was used for all five time points per replicate. The five SPME fibers were inserted through the lid of the jar using the 0.026” holes. They were removed one at a time at each of the five time points. For active and no flow sampling, a different jar was used for each time point. In each case, a 1/8” OD PTFE tube was inserted over halfway into the jar and was connected to the built sampler using compression fittings. With active sampling, the SPME was deployed in the built sampler which then sampled for the give time duration at a flow rate of 0.5 L/min. In the passive no flow case, the SPME fiber was deployed in the built sampler but the device was left off for the time duration. The jars were rinsed with ethanol and baked in a vacuum oven for at least three hours at 100 °C between runs.

2.3 Active Sampler Calibration

Calibration curves were developed for α-pinene, limonene, and ocimene. These calibrations were performed using a syringe pump to mix a known mass of the analytical grade mix into an airflow that was then sampled with a SPME fiber. Briefly, 1 μL of a diluted chemical standard was placed into a 10 mL gas tight syringe (1010 RN, Hamilton Robotics, Reno, NV) using 1 μL Drummond Microcaps (Drummond Scientific Company, Broomall, PA) and allowed to evaporate and equilibrate for at least 15 min. A custom syringe heater using nichrome heater wire and an Omega CN7533 controller (Omega, Stamford, CT) was used to maintain a syringe temperature of 30.0 °C ± 0.5 °C. A model SYR-101 syringe pump (Brandel, Gaithersburg, MD) with a custom built syringe holder was used to inject the equilibrated chemical mixture headspace at various rates into a dilution flow of ambient air controlled by a MC-5SLPM-D/5M mass flow controller (Cole Parmer, Vernon Hills, IL). The syringe pump was controlled using a laptop and an A-Star 32U4 microcontroller (Pololu, Las Vegas, NV) and calibrated prior to use. For each sample, the syringe pump was started and allowed to inject for 1 mL or 1 min prior to sampling. The PTFE sample lines were rinsed with ethanol after each run to ensure there was no carryover. Four samples were collected at each concentration with a blank performed after two sample collections. All samples underwent gas chromatography/mass spectrometry analysis within the same day of sampling. Linear regression was then performed.

The concentration of each compound sample was calculated by dividing the mass of the standard inserted in the syringe by the percentage of the syringe injected per minute which gave the mass injected per minute. This was divided by the dilution flow to determine the concentration in μg/min.

The theoretical mass uptake for each chemical was calculated using equations from Koziel [17] in which the extracted mass is calculated with the following equation

$$n = \frac{2\pi D_g L t}{\ln\left(\frac{b+\delta}{b}\right)} C_g \quad (1)$$

Where n is the extracted mass in ng, D_g is the gas-phases molecular diffusion coefficient (cm^2/s), L is the length of the sorbent (cm), t is the time sampled (s), b is the radius of the sorbent (cm), δ is the fiber boundary layer thickness (cm), and C_g is the sampled analyte

concentration (ng/mL). The diffusion coefficient was calculated by the following equations from Fueller, Schettler, and Giddings [25]

$$D_g = \frac{0.001T^{1.75}\sqrt{\frac{1}{M_{air}} + \frac{1}{M_{VOC}}}}{p\left[\left(\sum V_{air}\right)^{1/3} + \left(\sum V_{VOC}\right)^{1/3}\right]^2} \quad (2)$$

Where T is the temperature (K), M_{air} and M_{VOC} are the molecular weights of air and the chemical of interest (g/mol), p is the pressure (atm), and V_{air} and V_{VOC} are the molar volumes of air and chemical of interest (cm^3/mol). The boundary layer is given by

$$\delta = 9.52\left(\frac{b}{Re^{0.62}Sc^{0.38}}\right) \quad (3)$$

Where Re is the Reynolds number and Sc is the Schmidt number. The Reynolds number is given by

$$Re = \frac{ub}{v} \quad (4)$$

Where u is the linear flow over the fiber (cm/s) and v is the kinematic viscosity of air (cm^2/s). The Schmidt number is given by

$$Sc = \frac{v}{D_g} \quad (5)$$

2.4 Plant Sampling

Plant sampling was performed on a Meyer lemon tree (Citrus meyeri or Citrus limon ‘Meyer’) located at the University of California, Davis (Davis, CA) at the Good Life Garden. The tree was approximately 2 m tall and was flowering but did not have fruit. Sampling occurred on two separate spring afternoons. A background air sample was taken within 20 m of the tree. The tree was sampled three times for 5 min at 0.5 L/min flow using the active sampler device by sampling the space around the leaves and branches. Passive and active SPME sampling was then performed. For passive sampling, SPMEs were placed in stainless steel tea strainers (Harold Import Co., Lakewood, NJ) that were conditioned in a vacuum oven overnight at 110° C. They were then hung from the tree for 5 min. Afterward, the same general space that was used for passive sampling was sampled with the active sampler.

After sampling, the retracted SPMEs were partially inserted into a septum (Restek part number 27157) to prevent further air exchange and possible contamination. Preliminary storage experiments indicated that storage losses were within SPME sample variations.

2.5 Chemical Identification

Lemon tree field sample data were analyzed using MassHunter Workstation software (Agilent Technologies Inc., Santa Clara, CA) including MassHunter Qualitative Analysis ver B.06.00 chromatographic data processing. Qualitative Analysis analyzed all the samples as a batch with parameters selected in an acquired scan data with library search method. The program began the analysis by creating an ion chromatogram for every nominal ion. It integrated each ion chromatogram and created a peak list that was put through a deconvolution algorithm. Thus, for each compound there was an associated deconvoluted spectrum that contained far fewer ions from noise and adjacent peaks. Ions 73, 207, and 281 m/z were excluded since they represent GC column bleed.

3. Results and Discussion

3.1 System Design

Our new active air sampler couples custom-designed parts with inexpensive and commercial-off-the-shelf components that are readily available to allow for controlled chemical sampling using concentration onto a SPME sorbent through a custom designed vacuum manifold. The total system cost for the prototype was ~$360 with about 32 hours of labor. Our system consists of three main modules (Figure 1): the hand vacuum base system, a custom designed SPME holder, and control circuitry. The hand vacuum base system (Black and Decker Model SPV1800) has been modified to accommodate a flow sensor inside the dust receptacle (Figure 2). A custom PTFE adapter was made to channel airflow through the sampling attachment and flow sensor. As the hand vacuum is a relatively cheap mass produced device, all of the flow generated by the impeller will not flow through the sampling attachment but instead leak through parts of the vacuum base and dust receptacle. This leakage does not affect the sampling flow measurement but results in slightly more power used to generate the necessary sampling flow. Low off-gassing adhesive could also be used to seal any leaks which would result in a simpler and cheaper adapter design. The use of an impeller to generate the flow also eliminates the need of additional components to steady the flow like what is needed with diaphragm pumps. The custom designed SPME holder was constructed from compression fittings and tubing. The SPME is placed in the 0.25 in (0.635 cm) compression fitting and is held in place using a front ferrule and compression fitting cap. When attached firmly, the compression fitting creates a sufficient seal such that the flow is directed only through the PTFE tubing. The brass tee was machined such that the 0.5 in (1.27 cm) PTFE tubing could be inserted past the juncture of the third side which resulted in the SPME being surrounded solely by the more inert PTFE tubing and being perpendicular to the flow. The SPME holder attaches to the hand vacuum by compression fittings and stainless steel tubing. The PTFE tubing has been machined to form a 1/16 in (0.15875 cm) slot to increase the linear air velocity across the SPME while the remaining tubing has an inner diameter of 0.375 in (0.9525 cm). The SPME opening on the PTFE tubing was countersunk to help guide the SPME to the opening and limit the chance of the fiber breaking during deployment.

The control circuitry enables flow control which is critical for the active air sampler. Normally, flow control could be standardized by timing the motor within the vacuum to be

active for fixed periods of time. However, the commercial vacuum battery continuously discharges during the use of the device, leading to variable power output. If unregulated, airflow through the system would vary during active sampler use. We achieved flow control in our system using a PID control algorithm and D6F-02A1 flow sensor (Omron, Kyoto, Japan), coupled with a motor driver circuit with an Arduino Nano v3 (Gravitech, Minden, NV) microcontroller (Figure 3). The Arudino provided an inexpensive, simple to use, open-source microcontroller that can easily be reprogrammed to adjust sampling time, flow rates, and PID terms. It also enables the addition of other sensors such as temperature and humidity and an SD card for data logging as part of future work. The Arudino provided enough computational power to enable the PID control algorithm to operate every 10 ms which enables rapid adjustment to any flow disturbances from wind or wild movement of the sampler.

For active SPME sampling, the linear velocity of air across the SPME fiber should exceed 10 cm/s as above this velocity the boundary layer of air surrounding the SPME fiber is minimized and thus the sample collection is primarily dependent only on the adsorption rate of the chemical of interest [17]. The flow rate was set to 0.5 L/min which results in an average velocity of ~95 cm/s linear air velocity. While higher flow rates can be achieved, they must be balanced with the power requirement to reach such flow rates and will reduce the number of samples per battery charge. Additionally, there is a limited amount of plant VOCs of interest surrounding a specific agricultural target, which should not be sampled too rapidly such that the sorbent does not adsorb a sufficient amount. Finally, excessive flow could cause physical damage to SPME and should be avoided.

3.2 Time Course

The time course results for limonene are shown in Figure 4. Curves for α-pinene and ocimene are shown in Figures S1 and S2. The curve is not strictly linear which may be a factor of how the experiment was setup. Within the jar, there is a limited amount mass of the chemical present which is diluted over time during active sampling as more air is introduced into the jar. Thus, the concentration of the chemical decreases over time rather than remain steady. This was chosen as the experimental method as it may reflect sampling at a tree where the sample air space is diluted over time as more air is collected. A 5 min sampling time was selected as it provided a balance of sample time and sample variability.

3.3 Calibration

Quantitative assessment of the active sampler performance was carried out by building a calibration curve of the abundance (represented by the ion chromatogram) of the test compounds, α-pinene, d-limonene, and ocimene. These compounds were selected as they are major components of VOC emissions from multiple plants, including citrus. Figure 5 shows the calibration plots developed from the standards based off of the total ion chromatogram (TIC) of the deconvoluted peaks. Variations in the samples may have been due to the sample setup. The syringe plunger was lubricated with a small amount ethanol per manufacturer's recommendations; however, the additional ethanol may have resulted in the sample not completely evaporating within the syringe. Additionally, some of the sample may have escaped from the syringe during the equilibration process.

It is worth noting that the analytical performance of the sampler is affected by a variety of parameters, including sample flow rate, sample matrix, analyte, SPME fiber and GC-MS instrument/method. We have ensured that the device will sample at its programmed flow for a programmed duration, reducing the amount of error that the sampler contributes to the analytical performance. While this study demonstrates that the sampler can measure common VOCs at expected concentration ranges, researchers will need to demonstrate analytical metrics, such as limits of detection and retention capacity, in their applications using this sampler.

3.4 Field Sampling

Using the calibration curve developed, the estimated concentrations and extracted masses for α-pinene and limonene are shown (Table 1). Ocimene was not detected in the field samples. Chromatograms for the field samples are shown in figures 5-9. There have been a limited number of studies on the volatiles produced by Meyer lemon trees. In terms of concentrations, a Meyer lemon branch enclosure setup reported concentrations up to 0.9 ppb [26]. The samples in this study would have concentrations ranging from 0.3 to 3.3 ppb. Additionally, others have collected volatiles from Meyer lemon flushing shoots and reported the total mass collected [27]. Assuming perfect extraction and constant concentration, concentrations ranged from 0.02 to 0.05 $\mu g/m^3$. However, it is unlikely this is an appropriate representation of the concentration as the shoots were enclosed in a 100 mL flask that was sampled at 100 mL/min. Other studies collected Meyer lemon volatiles but did not provide specifics for each compound [28].

This difference in concentrations is likely a result of the different sampling methods. The present method sampled the volume closest to the leaves which could naturally be concentrated if there is minimal wind. Therefore, the measured concentration of the target VOC is expected to be significantly higher than that for the enclosure scenario. It is possible that some other event was occurring within the trees during sampling which caused a significant increase in the VOCs off gassed by the trees. There were no obvious signs of pests present on the trees. Also, air temperatures were different between the calibration samples (25 °C) and the tree samples (19 and 16 °C). Temperature has competing effects for collection. Higher temperatures result in higher diffusion coefficients but also can decrease the sorbent effectiveness although that typically applies to at equilibrium [17]. The relative humidity was higher on site as well but that would have decreased the amount collected by the SPME [17].

Comparisons between the active and passive SPME samples can only be made based on the extracted mass collected because calibration curves were not developed for passive sampling. Passive SPME sampling extracted more chemical mass which was due in part to wind, which caused the tea-strainers to move back and forth throughout the sampling time, effectively creating active sampling conditions. Additionally, to provide the closest comparison between the sampling methods, active sampling was performed in the same area as the passive sampling. The earlier active samples were collected in areas of denser foliage. These same areas could not be sampled passively as hanging tea strainers in these locations would have disturbed the tree and induced a defensive response from the tree and produced a

different VOC profile. Furthermore, although the passive SPMEs were held in place due to the clamping action of the tea strainer, they moved after being hung in the tree due to the motion caused by the wind. So while the active sampling did not perform as well as the passive sampling, the security of the SPMEs was never in doubt as with the passive sampling.

Additional plant chemicals such as linalool and alpha-terpineol were also detected from the plant samples. However, they either did not appear in the calibration curves samples or showed no correlation with the calibration curve. Further pre-concentration and detection of additional compounds may be feasible with extended sampling times.

It can be concluded that the device performed adequately as it was able to collect Meyer lemon VOCs. With a sample time of 5 min and under 1 min needed to switch out SPME fibers between samples, the device shows promises as a high throughput volatile sampler. However, only a limited number of compounds were detected. The limonene concentration was found to be significantly higher than reported literature levels due to the differences in the sampling approach. There were also some variations in the calibration curve that may have come from the system setup. The device was portable; however, the weight from the battery began to be a factor for the user after repeated samples were taken and could be problematic for extensive sampling.

This device could potentially be used in large-scale plant diagnostics for precision agriculture, as it would enable rapid sampling of a tree to determine its health or other factors through the use of a low cost sampling unit. By monitoring the VOC profile of the plants, the grower could determine if the plants are stressed from pests or nutrient deprivation and promptly respond. Furthermore, the device could be used in other air sampling situations such as pollution monitoring or for other chemicals of interest. The device is also adaptable to different types of SPMEs as well as other sorbents that could be placed in housing with a 0.25” compression fitting connection. Thus, we suggest the present sampler design as a viable low-cost sampling method that may be easily implemented and deployed by both researchers and growers alike.

4. Conclusions

An active SPME sampler using commercial-off-the-self components was developed to sample plant volatiles and evaluated by generating a limonene calibration curve and sampling a Meyer lemon tree. The device successfully captured plant VOCs and represented a quicker and cheaper means of collecting plant volatiles than the use of plant enclosures and sampling pumps. The amount of VOCs collected is known to increase with increased sampling time. However, in the applied field sampling environment, shorter sampling times are demanded. A five min active sampling SPME device that can collect chemicals at a quantitative analysis level has a high potential to be used for applied environment.

Future work is preferred before the device could be practically applied for specific applications. Systematic studies are needed to verify that the sampling methodology can generate reproducible results from sampling in the field and also identify the differences

between healthy and unhealthy trees. Further upgrades could include adding a temperature sensor to adjust for temperature variations. However, the proposed approach could form a basis for standardized sampling device that could be employed both in plant research and agriculture. The described sampling manifold is designed to be low cost and requires minimal custom manufacturing to make it suitable for wide adoption and use.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

- Low cost, plant volatile compound active sampling method with SPME is proposed
- A commercial hand-vacuum was modified as a base for sampling module
- Calibration curves were developed for α-pinene, limonene, and ocimene
- Meyer lemon tree was sampled for field validation

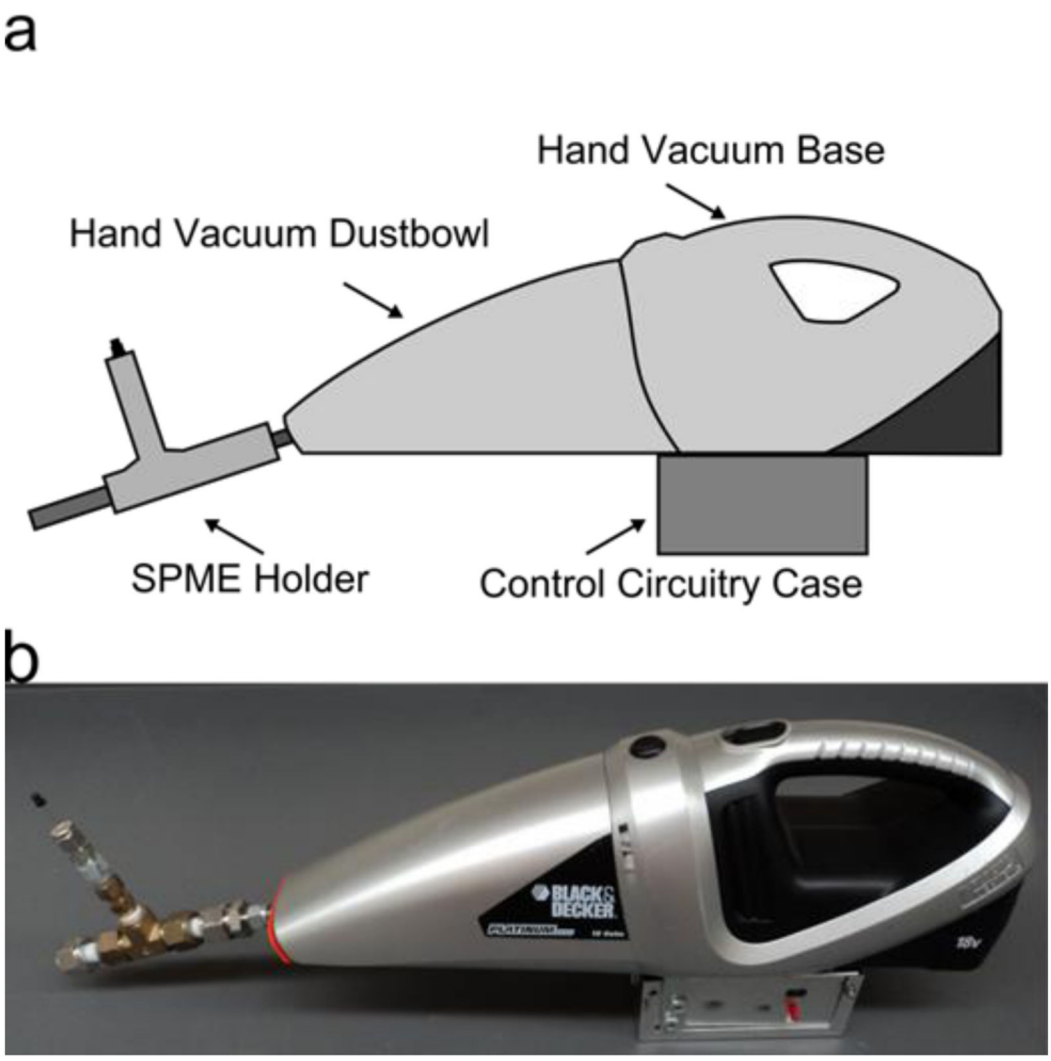

Figure 1:
a) System layout of the active air sampler b) Prototype version of the device

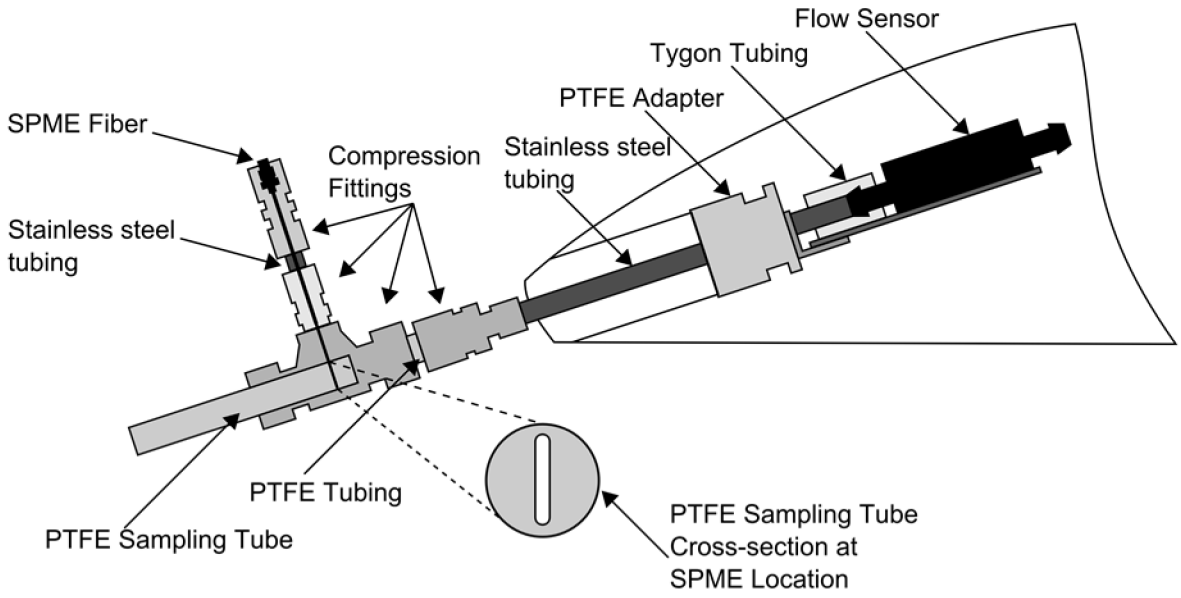

Figure 2:
Detailed view of the custom SPME holder, sampling module, and custom tubing interface

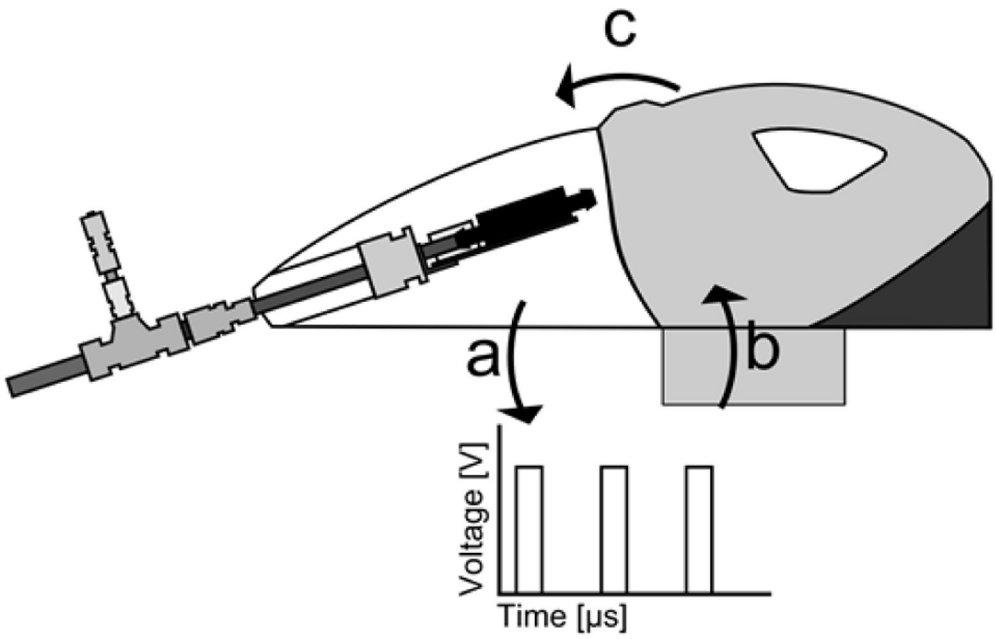

Figure 3:

Flow control is achieved by first measuring the flow with the sensor. a) The flow sensor signal is interpreted by an Arduino Nano microcontroller which applies the PID control algorithm which updates every 10 ms and determines the new motor speed. b) The motor driver circuit then controls the motor through pulse width modulation (PWM) at a frequency of 31.25 KHz. c) With the new motor setting, the flow rate through the sampler is adjusted.

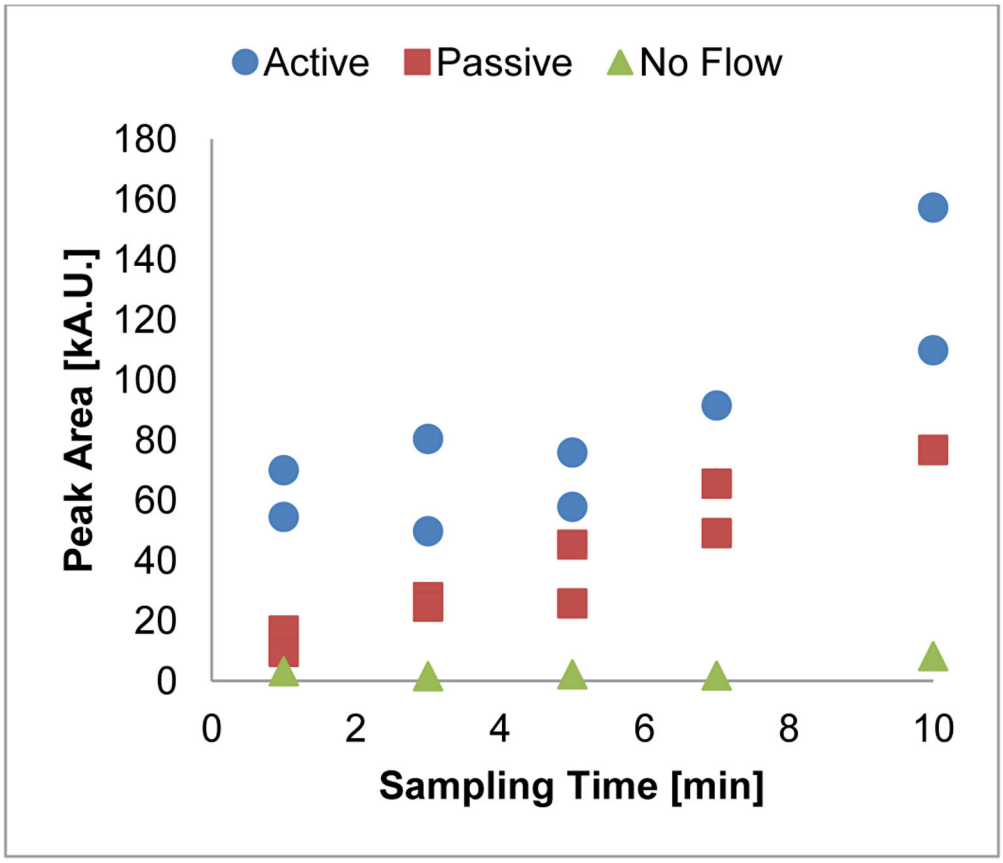

Figure 4:
Limonene time course results. 10 uL of 1.2 ng/uL chemical standard were pipetted in a 1.9 L jar and sampled with the active sampler at 0.5 L/min, passively, and with the active sampler with no flow rate

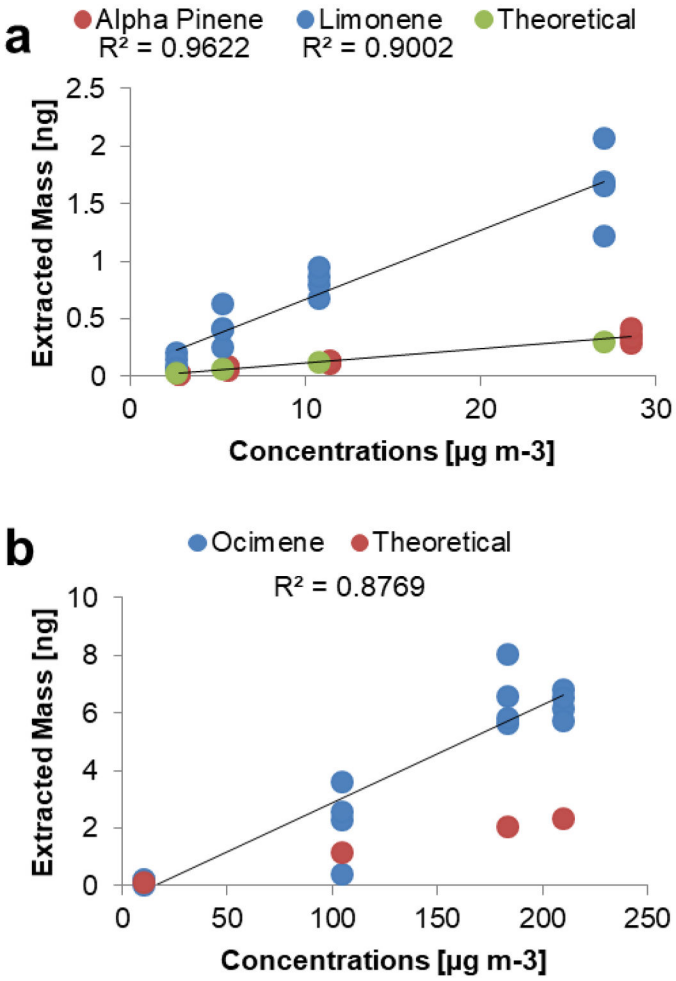

Figure 5:

The gas phase calibration curves developed using CAR/PDMS) SPMEs. The standard mix was sampled for 5 minutes at 500 mL/min. A) Gas phase calibration of alpha pinene and limonene, B) Gas phase calibration of ocimene

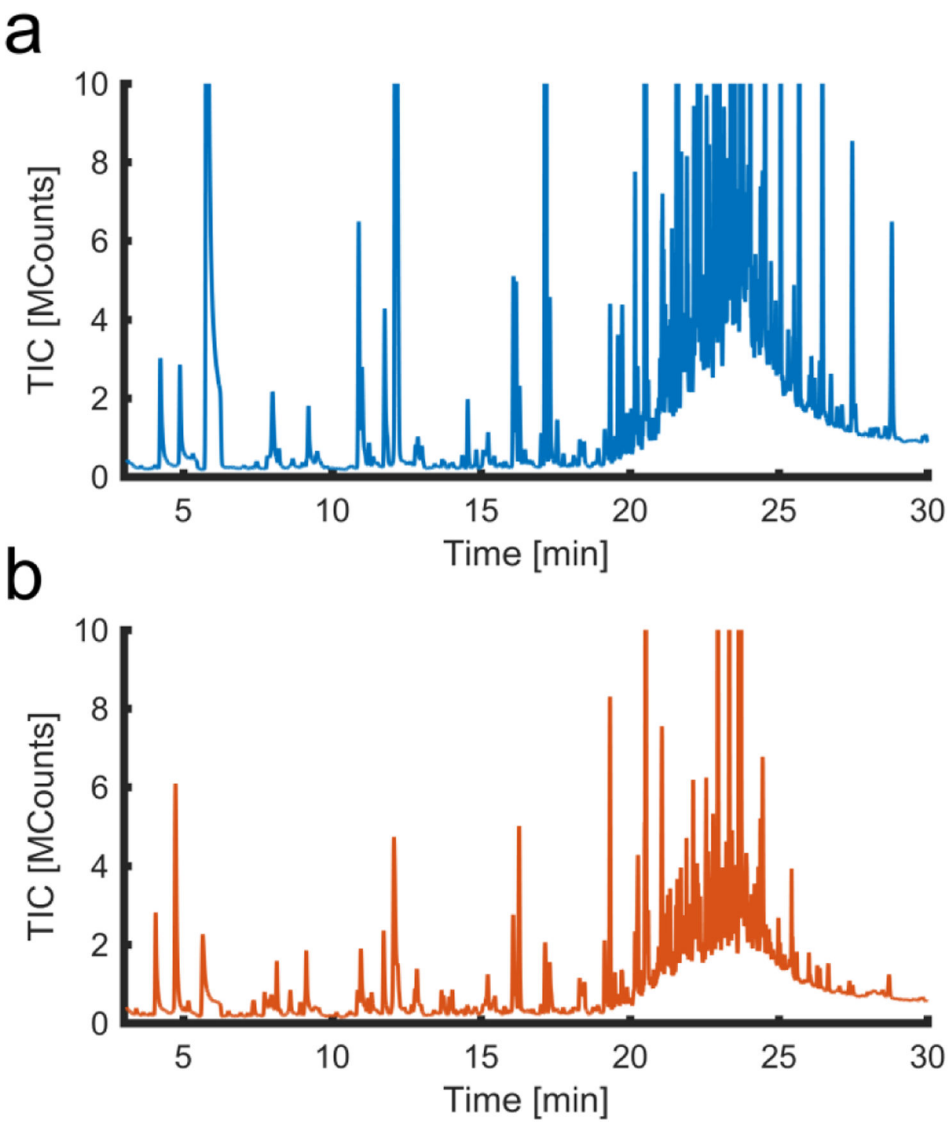

Figure 6:

a) Background chromatogram sample taken within 20 meters of the Meyer lemon tree sampled. b) Chromatogram of active sampling of the Meyer lemon tree

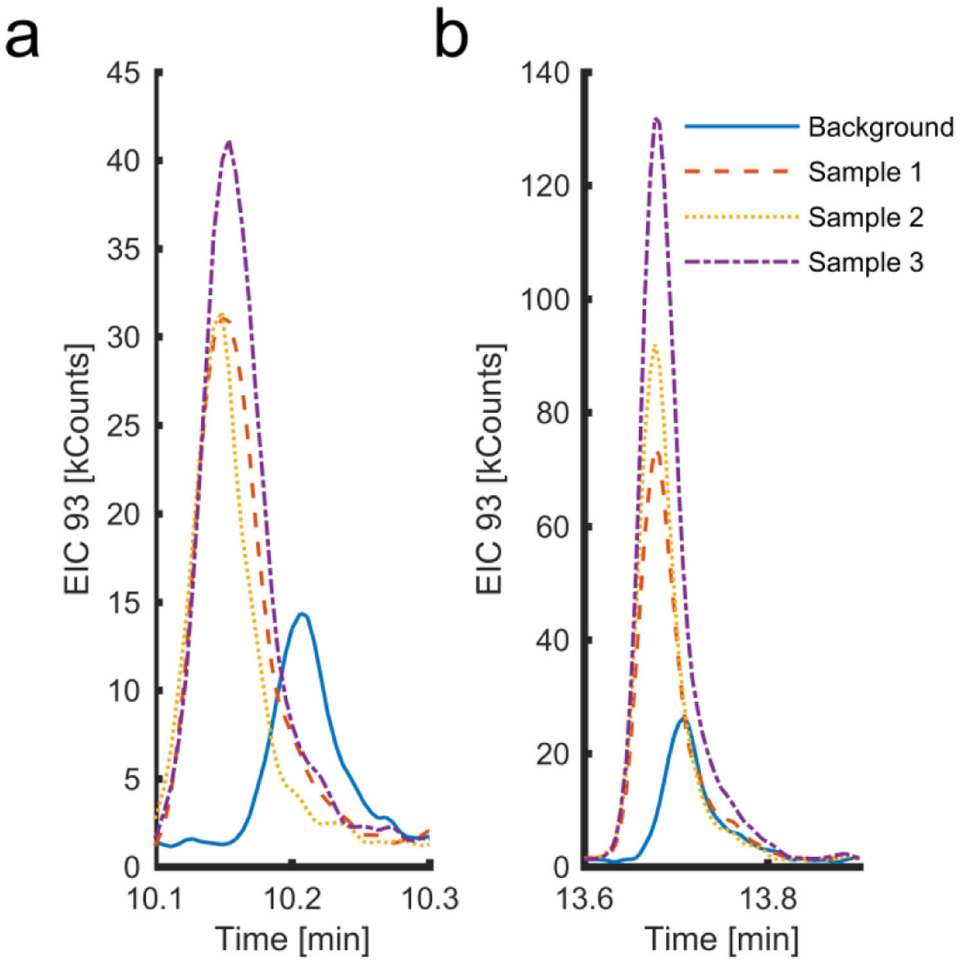

Figure 7:
Extracted ion chromatograms for a) α-pinene and b) limonene peaks from the background and Meyer lemon tree replicates.

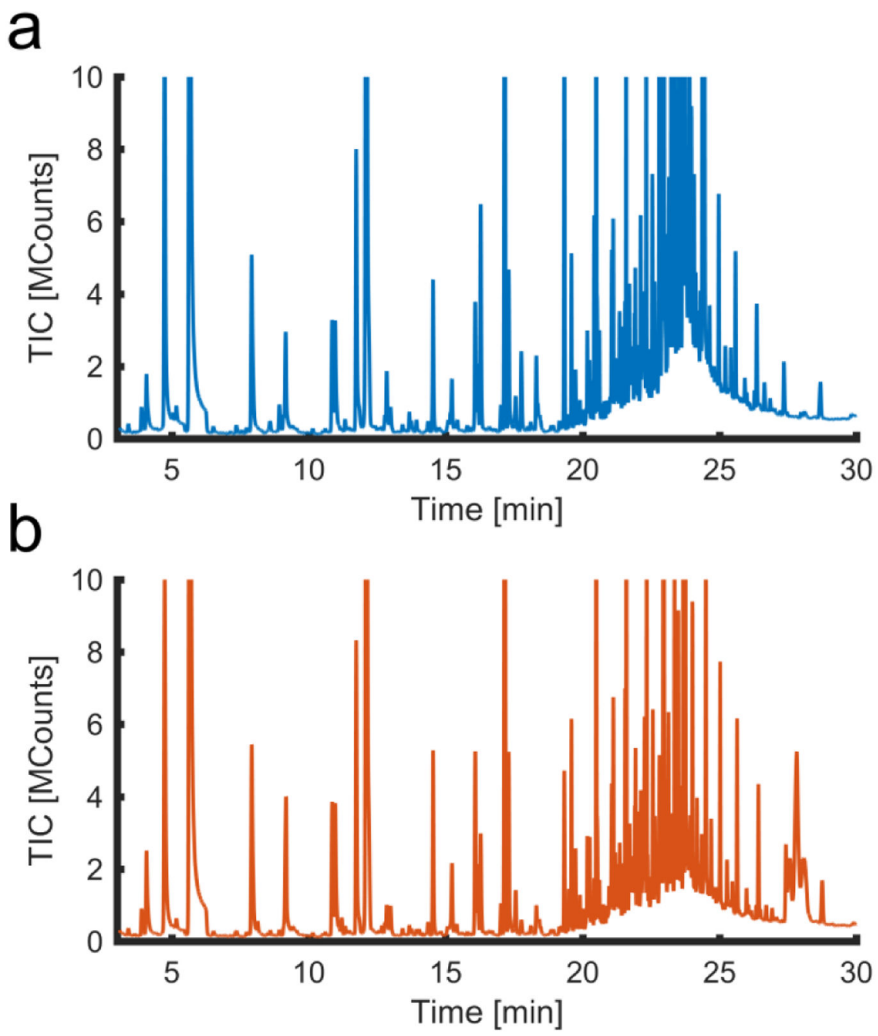

Figure 8:
Chromatograms from a) passive and b) active sampling of a Meyer lemon tree

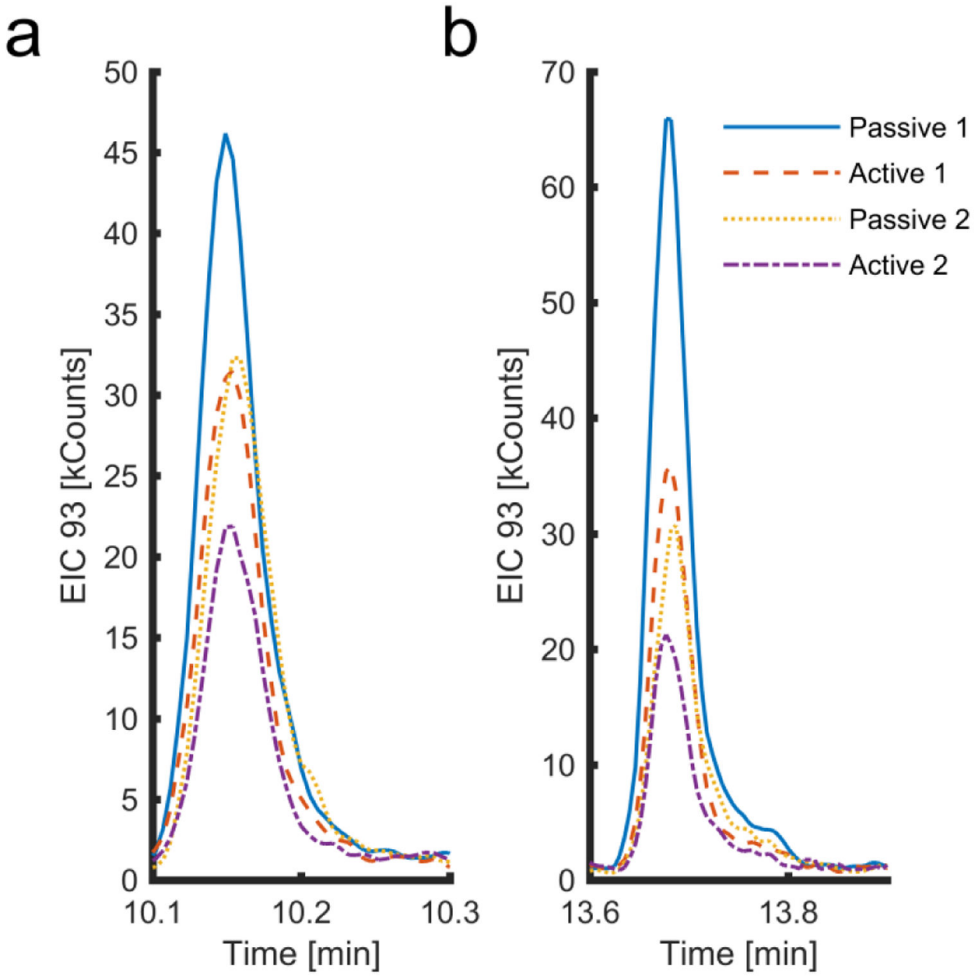

Figure 9:
Extracted ion chromatograms for a) α-pinene and b) limonene peaks from the passive and active samples of the Meyer lemon tree

Table 1:

Concentrations and extracted mass from Meyer lemon tree. Results where the calculated extracted mass or concentration were below 0 were deemed negligible.

	Concentration [μg m^{-3}]		**Extracted Mass [ng]**	
Sample	α-pinene	Limonene	α-pinene	Limonene
Day 1 Blank	2.8	Negligible		
Active Sample 1.1	7.7	9.3	0.09	0.63
Active Sample 1.2	6.5	12.0	0.07	0.79
Active Sample 1.3	9.6	18.1	0.11	1.15
Active Sample 2.1	6.8	3.4	0.07	0.27
Active Sample 2.2	Negligible	1.5	Negligible	0.16
Passive Sample 2.1			0.12	0.58
Passive Sample 2.2			0.09	0.24