A New Thermal Desorption Tube for Sampling Terpenes in Air

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Introduction

There is a growing interest in sampling terpenes from air.[1,2,3]. Since gas chromatography is the most common technique used for analyzing terpenes, a new thermal desorption (TD) tube specific for sampling those terpenes relevant to cannabis and hemp was developed. This provides a means to monitor/determine terpene concentrations in the cultivation environment.

Thermal desorption is less waste intense/more environmentally friendly than single use devices since the TD tubes can be reused multiple times and no (toxic) solvents are required for the sample preparation workflow. TD is amendable to sampling a wide range of terpene concentrations by either adjusting the sample volume (how much air is pulled through the tube during sampling) or by adjusting the split flow ratio of the thermal desorber prior to analysis to transfer more or less of the sample to the GC instrument and detector.

Air sampling near live plants or dried plant materials provides a simple way to determine the concentration of the different terpenes being released by the plant at a given time and specific growing or drying conditions. With thermal desorption, only the volatile compounds like the terpenes are collected by the TD tubes because less volatile compounds, such as tetrahydrocannabinol (THC), and cannabinoids, are not released into the air by the plant due to their much higher boiling points. So, for analysis only the TD tubes are sent to the laboratory, not any plant material. The technique is also non-invasive/less destructive than removing valuable parts from the plants and shipping plant material for terpene analysis.

Knowing the terpene concentration being emitted from the dried plant material could provide valuable information to growers, dispensaries since the terpene odor can influence the customers purchasing decision.

Below are examples of where thermal desorption tubes could be used for the determination/quantification of terpenes:

- **Workplace Exposure** – Industrial Hygiene
  - To measure greenhouse worker's exposure to terpenes.

- **Emission & Odor Testing** – Regulatory
  - To quantify terpene emissions from a cultivation area (greenhouses or outdoor farms).

- **Terpene Profiling** – Growers & Testing Labs
  - To characterize different strains
  - Does a certain terpene ratio provide answers to questions like:
    - When is the right time to harvest?
    - When are the plants in distress?
  - Testing terpene profiles can also be useful for other sources such as hops, fruits, and essential oils.

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What is Thermal Desorption?

Thermal Desorption (TD) is a sample preparation technique for gas chromatography that can be used to analyze volatile and semi-volatile organic compounds (VOCs and SVOCs).

Typically, an instrument called a Thermal Desorber is connected to a GC instrument and in most cases, it replaces the common GC inlet/injector port.

There is a variety of ways to collect samples onto TD tubes (active & passive). The most common way is to pull air through the TD tube using an air sampling pump. As the air travels through the tube the VOC's and SVOC's of interest are retained by one or more adsorbents packed into the tube while the main components of air (nitrogen, oxygen, argon etc.) passes through the adsorbents un-retained. Essentially the more volume of air is pulled through the tube the more VOC and SVOC's will be retained on the adsorbents in the TD tube (if no breakthrough occurs).

After sampling the TD tube is sealed and sent to a laboratory where it is placed on a thermal desorber to be analyzed. During analysis the tube is rapidly heated to 250 – 330 °C while an inert carrier gas sweeps the VOC /SVOCs (thermally desorbed from the TD tubes adsorbent) onto the GC column where they are separated and transferred to a detector such as flame ionization detector (FID) or a mass spectrometer (MS).

Experimental

To quantify the terpene concentration a thermal desorption tube must be able to retain the terpenes during sampling, but it also must efficiently release them during the desorption step. During our research we discovered no single adsorbent could provide good recoveries for all terpenes relevant to cannabis and hemp samples. Therefore, a new multi-bed TD tube was designed, the Carbotrap® T420, which contains two different graphitized carbon black adsorbents that offer different surface areas and retentivity (weak and medium), resulting in excellent recoveries of the target terpenes (see **Figure 1** for a schematic of the new tube). To demonstrate the performance of this new Carbotrap® T420 tube we tested it alongside a TD tube packed with Tenax® TA, which is a commonly used adsorbent in the field of thermal desorption.
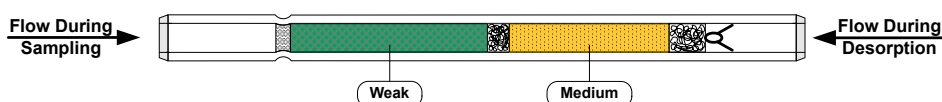
Terpene Test Standard

We combined two multi-component terpene test mixes and then added neat β-myrcene to the final mix to create a comprehensive terpene test mix for calibration and to challenge the TD tubes. See **Table 1** for the specific details.

Table 1. Overview of the composition of the terpene test mixes used for challenging the TD tubes

Compound Name	Mix A	Mix B	Neat	Final Conc.
α-Pinene	✓			400 µg/mL
Camphene	✓			400 µg/mL
β-Pinene*	✓	✓		800 µg/mL
β-Myrcene			✓	400 µg/mL
3-Carene*	✓	✓		800 µg/mL
α-Terpinene	✓			400 µg/mL
p-Cymene		✓		400 µg/mL
D-Limonene*	✓	✓		800 µg/mL
γ-Terpinene	✓			400 µg/mL
Terpinolene		✓		400 µg/mL
L-Fenchone	✓			400 µg/mL
Linalool		✓		400 µg/mL
Fenchol	✓			400 µg/mL
Camphor*	✓	✓		800 µg/mL
Isoborneol	✓			400 µg/mL
Borneol		✓		400 µg/mL
DL-Menthol	✓			400 µg/mL
α-Terpineol		✓		400 µg/mL
Citronellol	✓			400 µg/mL
Pulegone	✓			400 µg/mL
Geraniol		✓		400 µg/mL
Geranyl Acetate	✓			400 µg/mL
β-Caryophyllene		✓		400 µg/mL
α-Cedrene	✓			400 µg/mL
α-Humulene	✓			400 µg/mL
Nerolidol I*	✓	✓		800 µg/mL
Nerolidol II		✓		400 µg/mL
Cedrol	✓			400 µg/mL
β-Eudesmol	✓			400 µg/mL
α-Bisabolol	✓			400 µg/mL

* The concentrations of these terpenes are doubled when the A&B mixes are combined.

A final concentration of 400 µg/mL and 800 µg/mL was made by adding the following mixes to 5 mL glass volumetric flask:

- 1 mL Terpene Mix A 2000 µg/mL (**CRM40755**)
- 1 mL Terpene Mix B 2000 µg/mL (**CRM40937**)
- 2.53 µL Myrcene neat (**64643**) *
- Fill flask to the 5 mL mark with methanol

* Volume calculated by using the density of myrcene 0.791 g/cm³ at 25 °C

Flow During Sampling → **Weak** **Medium** ← **Flow During Desorption**

Figure 1. Schematic of the glass Carbotrap® T420 thermal desorption tube.

Analytical Conditions

For the analysis of the collected samples on the TD tubes the conditions and instrument parameters outlined in **Table 2 & 3** were used.

Table 2. Thermal desorber parameters

Thermal Desorber	
Instrument:	PerkinElmer® TurboMatrix 150
Carrier gas:	Helium
Temperatures	
Primary tube desorption:	300 °C
Focusing trap low temperature:	0 °C
Focusing trap desorption temperature:	300 °C
Heating rate of focusing trap:	99 °C/s
Valve & transfer line temp:	175 °C
Timings	
Pre-purge prior to desorption:	2.0 min
Primary tube desorption time:	5.0 min
Focusing trap desorption time:	8.0 min
Pneumatics	
Column pressure:	13.8 psi (analyzed at constant pressure, the calculated flow rate is 1.7 mL/min at 45 °C)
Desorb flow:	10 to 25 mL/min*
Inlet split (between primary tube and the focusing trap):	50 to 75 mL/min*
Outlet split (between focusing trap and GC column):	10 to 50 mL/min*
Dry-purge:	Not Used

*The desorption flow and split flow varied based on the application on how much sample was collected on the TD tubes, and the anticipated concentration expected from the samples.

Table 3. Gas chromatograph parameters

GC Conditions	
Instrument:	Agilent 7890B GC / 5977A (Single Quadrupole)
Column:	SLB®-5ms 30 m x 0.25 mm ID x 0.25 µm (**28471-U**)
Oven:	45 °C for 2 min, 10 °C/min to 120 °C hold for 3 min, 30 °C/min to 30 0°C hold for 2 min
Column flow:	Column Pressure was controlled by the thermal desorber (**Table 1**). The transfer line of thermal desorber was connected directly to the GC Column, thus by-passing the inlet of the GC
Detector:	MS
Mass Spec Parameters	
Tune EMV:	1912
Transfer line:	230 °C
MS Source:	230 °C
MS Quad:	150 °C
Scan range:	40-265 Da
Solvent delay:	0 min

The chromatogram in **Figure 2** is showing a 0.5 µL of the terpene test standard (as describe above) spiked onto a glass Carbotrap® T420 tube and then desorbed.
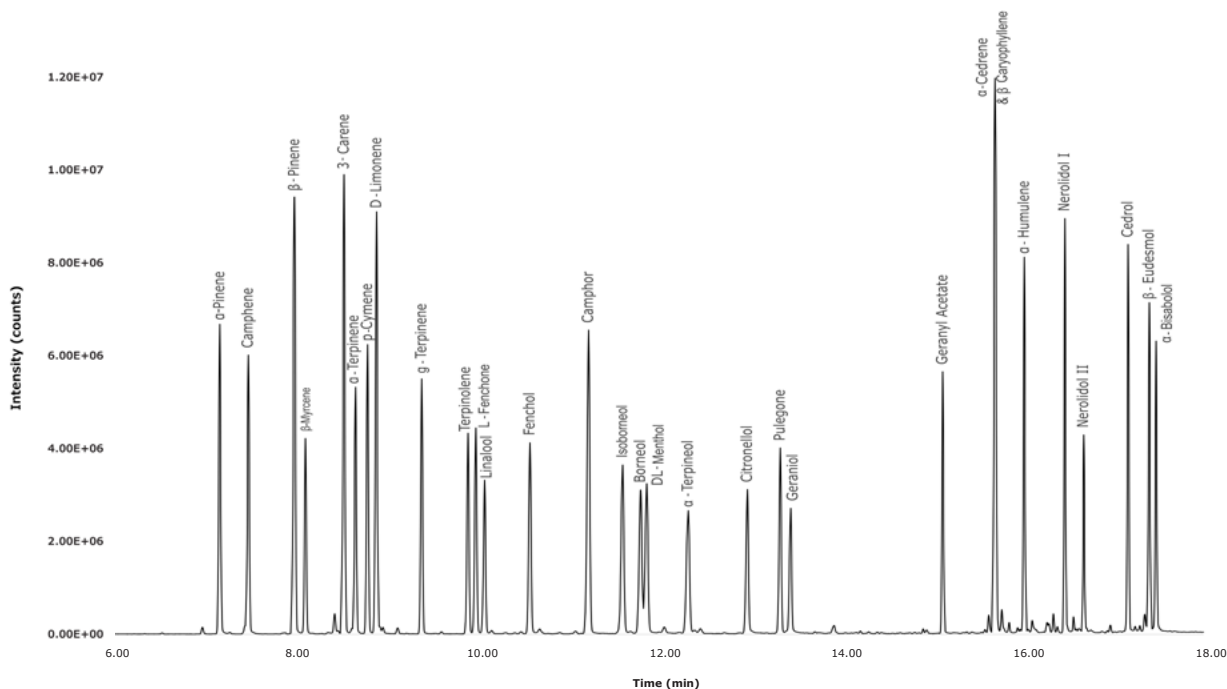

Figure 2. Desorption of the terpene test mix from the Carbotrap® T420 TD tube.

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Results & Discussion

Recovery Experiments

To test the recovery, we spiked each of the TD tubes with the 0.5 µL of the terpene test mix described above and challenged them with 2 and 10 liters of nitrogen gas. To challenge the TD tubes, they were attached to an Adsorbent Tube Injector System (ATIS) with a constant flow of 0.1 L/min of dry nitrogen gas flowing through the hot glassware of the ATIS and through the TD tube attached to the outlet of the ATIS. (**Figure 3** illustrates how the TD tubes were spiked). The temperature of the ATIS glassware was set to 100 °C. Using a Hamilton® 7000 series syringe a 0.5 µL volume of the terpene test mix was injected in the ATIS glassware. The hot glassware vaporized the terpenes which were then carried to the TD tubes by the nitrogen gas. The tubes remained attached until a total of 2 liters passed through the tubes.

These steps were repeated with another TD tube, but the tube remained attached until a total of 10 liters has passed through the tube. After the tubes were challenged, they were analyzed to determine the recovery of each terpene desorbed from the TD tubes. To determine the recovery a four-point calibration curve was created by spiking four Carbotrap® T420 tubes with 0.25, 0.35, 0.5 and 0.6 µL of the terpene test mix. For the calibration curve the amount of nitrogen gas was reduced to a very small "challenge volume" of only 0.2 Liters. This is enough to transfer the terpenes to the adsorbents packed in the tube but doesn't present any sort of real challenge for the adsorbent since the volume is very low.

Table 4 lists the results of this challenge experiment and compares the recoveries of those terpenes relevant to cannabis and hemp from a single bed TD tube packed with Tenax® TA vs the new Carbotrap® T420 tube. Recoveries greater than 92% were achieved with the Carbotrap® T420 tubes at both 2 and 10 liters. Whereas the recovery on the Tenax® tube for α-pinene and camphene was less than 80% only after the 2-liter challenge and dropped to less than 25% together with β-pinene to 42% after challenged with 10 L.
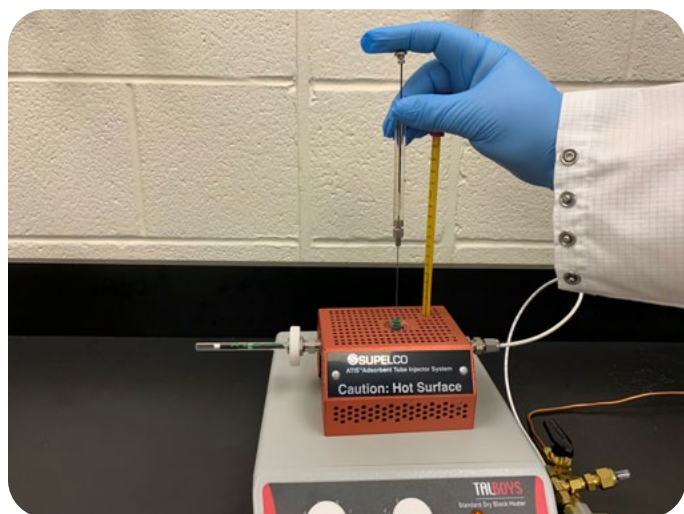

Figure 3. Spiking the Carbotrap® T420 tube with the terpene test mix using Supelco® Adsorbent Tube Injector System (ATIS).

Table 4. Comparison of the terpenes recoveries from Tenax® and Carbotrap® T420 TD tubes at two challenge volumes

Compound/ Challenge Volume	Carbotrap® T420		Tenax® TA	
	2 L N_2	10 L N_2	2 L N_2	10 L N_2
α-Pinene	97%	97%	78%	24%
Camphene	99%	104%	74%	16%
β-Pinene	93%	92%	94%	42%
β-Myrcene	109%	107%	95%	103%
3-Carene	97%	94%	101%	101%
α-Terpinene	96%	94%	88%	98%
p-Cymene	98%	97%	101%	103%
D-Limonene	99%	97%	100%	101%
γ-Terpinene	97%	94%	99%	100%
Terpinolene	97%	94%	90%	96%
α-Terpineol	97%	96%	100%	99%
β-Caryophyllene	101%	97%	96%	94%
α-Humulene	99%	97%	100%	98%

To compare the performance of the Carbotrap® T420 tubes under actual field conditions, we collected air samples from inside the trim room of a cannabis greenhouse using both the Carbotrap® T420 and Tenax® TA TD tubes. The air sample collection took place with both TD tubes positioned side by side each other at the flow rate of 0.1 L/min for a total sample volume of 10 Liters. **Table 5** shows that the concentration obtained from the Tenax tubes was significantly lower for α-pinene, camphene, and β-pinene. Typically, a difference of +/- 25% suggests that breakthrough (insufficient retention) could be occurring. This large difference suggests that with Tenax® TA an underestimation of the concentration for these more volatile terpenes can occur. This issue was not detected with the Carbotrap® T420 tube. The two employed Graphitized Carbon Blacks (GCB) adsorbents in the Carbotrap® T420 tube with increasing adsorption strengths making the tube more efficient and suitable for sampling a wider range of terpenes compared tubes packed with just Tenax® TA

Table 5. Terpene concentrations determined from sampling air inside a cannabis-growing facility

	Carbotrap® T420	Tenax®-TA	Carbotrap® T420 vs. Tenax® TA
	(µg/m³)	(µg/m³)	% Diff
α-Pinene	297.9	165.9	57%
Camphene	20.1	8.8	78%
β-Pinene	229.9	162.9	34%
β-Myrcene	1473.2	1531.7	-4%
3-Carene	8.6	7.8	10%
α-Terpinene	3.8	3.9	-2%
p-Cymene	6.7	5.9	14%
D-Limonene	499.0	522.0	-4%
γ-Terpinene	2.9	2.9	-2%
Linalool	42.1	46.8	-11%
β-Caryophyllene	78.5	86.8	-10%
α-Humulene	18.2	19.5	-7%

The lower recoveries obtained with the Tenax® TA tubes for α-pinene, camphene and β-pinene that were observed from both the laboratory challenge and the real air samples obtained from the field illustrate the importance of choosing a thermal desorption tube that is purpose built for the task of sampling terpenes.

Uptake of Moisture During Air Sampling

Generally, it is important to minimize the amount of water vapor transferred to the GC during a thermal desorption process. As a rule of thumb, it is advisable to make sure the amount of water retained on the TD tubes is always <1 mg prior to desorption. This can be achieved by choosing hydrophobic adsorbents (like used in the Carbotrap® T420 tube) to reduce water pick up during sampling, and/or dry purging the tubes prior to the thermal desorption step. Since humidity inside a greenhouse can easily exceed 50%RH, it is important to keep this in mind when collecting air samples in this environment. Too much water vapor in the desorbed sample can affect split flow ratios as water vapor expands differently than dry helium (used carrier gas) since the water vapor is quickly released from the TD tube during desorption. Water vapor can also cause separation problems on the GC and quench some detectors. A commonly successful way to address this issue is to choose thermal desorption tubes that contain adsorbents that do not retain moisture during sampling. For this study it was tested how much water was retained by the new Carbotrap® T420 TD tube. For comparison, we also included TD tubes packed with Tenax® TA and silica gel. Tenax® TA was selected because it is known to be very hydrophobic. Silica gel was also tested because it is a hydrophilic adsorbent, and it can retain up to ~40% of its own weight in water vapor before it becomes saturated, and therefore it would be indicative on how much water vapor is being pulled through the other TD tubes during this experiment. For the experiment, we thermally conditioned the silica gel tubes at 120 °C and both

the Carbotrap® T420 and Tenax® TA tubes at 320 °C for 1 hour to assure they were completely dry before we obtained the tare weight of each tube using a laboratory balance. Then the tubes were connected to the exposure chamber where a dynamic atmosphere of 70% humidity was generated. We used an air sampling pump to pull the humidified air through the tubes at a flow rate of 0.1 L/min. After every 1 liter of humidified air pulled through the tubes they were removed and weighed on a laboratory balance. This was repeated until a total of 10 liters of the humidified air had passed through the tubes. **Table 6** shows how much water was retained by each type of tube. The results showed no significant amount of water vapor retained on the Carbotrap® T420 or the Tenax® TA tubes. The tare weight of the tubes fluctuated between +/- 1 mg which indicated that the water vapor was passing through these tubes and was not retained. As expected, the silica gel tube did retain a significant amount of water vapor and continued to increase in weight as more humid air was pulled through the tube. Only very little water vapor was retained by the Carbotrap® T420 TD tubes even after 120 mg of water vapor (10 L air sample) had passed through, demonstrating it is on par with the Tenax® TA tube regarding moisture retention. This shows that the Carbotrap® T420 TD tube can be used to sample in high humidity environments. This simplifies the desorption as no dry-purge step is required prior to analyzing the tubes.

Table 6. Amount of water vapor concentrated in TD tube while sampling in high humidity (70%RH)

Volume of Humidified Air pulled through the tubes	Silica Gel	Carbotrap® T420	Tenax® TA
0 Liter	0 mg	≤ 1mg	≤ 1mg
1 Liter	18 mg	≤ 1mg	≤ 1mg
2 Liter	35 mg	≤ 1mg	≤ 1mg
3 Liter	50 mg	≤ 1mg	≤ 1mg
4 Liter	64 mg	≤ 1mg	≤ 1mg
5 Liter	76 mg	≤ 1mg	≤ 1mg
6 Liter	87 mg	≤ 1mg	≤ 1mg
7 liter	97 mg	≤ 1mg	≤ 1mg
8 Liter	106 mg	≤ 1mg	≤ 1mg
9 Liter	113 mg	≤ 1mg	≤ 1mg
10 Liter	120 mg	≤ 1mg	≤ 1mg

Conclusion

The Carbotrap® T420 tube thermal desorption tube has been specifically designed for sampling terpenes in air. It exhibits excellent recoveries of terpenes relevant to the cannabis and hemp industry for sample volumes up to 10 liters of air. This new adsorbent tube is suitable for sampling also in humid atmospheres like greenhouses as it does not retain water.

Thermal desorption can be considered as an eco-friendly sample collection and analysis technique since the used tubes, like the Carbotrap® T420 tube, can be re-conditioned and reused multiple times. Furthermore no (hazardous) solvents are required in the desorption process, that would need to be sourced and later disposed after the analysis.

The Carbotrap® T420 is available as both glass and stainless-steel tubes. Glass tubes do have the advantage of allowing a visual observation of the integrity of the adsorbent packing with repeated use and are generally considered to be more inert. Stainless-steel tubes are more durable and will not break when sampling under harsher conditions in the field. Each TD tube contains a unique barcode for easy sample identification and tracking. The tubes are designed to function with any thermal desorption instrument that accepts ¼ in. O.D. x 3.5 in. long tubes (6.35 mm O.D. x 89 mm length).

Featured Products

Description	Cat. No
Thermal Desorption Sampling Tubes	
Carbotrap® T420 89 mm Glass-Fritted TD Tube, 1/4 in. (6.35 mm) O.D., preconditioned, Pk.10	28689-U
Carbotrap® T420 89 mm SS TD Tube, 1/4 in. (6.35 mm) O.D., preconditioned, Pk.10	28687-U
GC Column	
SLB®-5ms Capillary GC Column, L × I.D. 30 m × 0.25 mm, df 0.25 µm	28471-U
Reference Materials & Standards	
Terpene Mix A, certified reference material, 2000 µg/mL each component in methanol	CRM40755
Terpene Mix B, certified reference material, 2000 µg/mL each component in methanol, ampule of 1 mL	CRM40937
Myrcene, analytical standard, neat	64643
Accessories	
Adsorbent Tube Injector System (ATIS) 110 VAC	28520-U
Adsorbent Tube Injector System (ATIS) 230 VAC	28521-U
ATIS Replacement standard injection glassware	28526-U
Hamilton® syringe 7101, volume 1 µL, needle size 22s ga (bevel tip)	20979

References

1. Urso K, Frazier A, Heald S, Khlystov A. Terpene exhaust emissions and impact ozone modeling from cannabis plants at commercial indoor cultivation facilities in Colorado. J Air Waste Manag Assoc. 2022 Aug;72(8):828-848. https://doi.org/10.1080/10962247.2022.2046206.

2. Wang CT, Wiedinmyer C, Ashworth K, Harley PC, Ortega J, Rasool QZ, and Vizuete, W. Potential regional air quality impacts of cannabis cultivation facilities in Denver, Colorado. Atmos. Chem. Phys., 19, 13973–13987. https://doi.org/10.5194/acp-19-13973-2019, 2019.

3. de Ferreyro Monticelli D, Bhandari S, Eykelbosh A, Henderson SB, Giang A, Zimmerman N. Cannabis cultivation facilities: A review of their air quality impacts from the occupational to community scale. Environmental science & technology. 2022;56(5):2880–2896. http://dx.doi.org/10.1021/acs.est.1c06372.

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