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ENTECH INSTRUMENTS — APPLET

Beyond THC and CBD:

Solvent Free Headspace Extraction and GC-MS Profiling of Terpenes and Cannabinoids in Cannabis Flower and Products

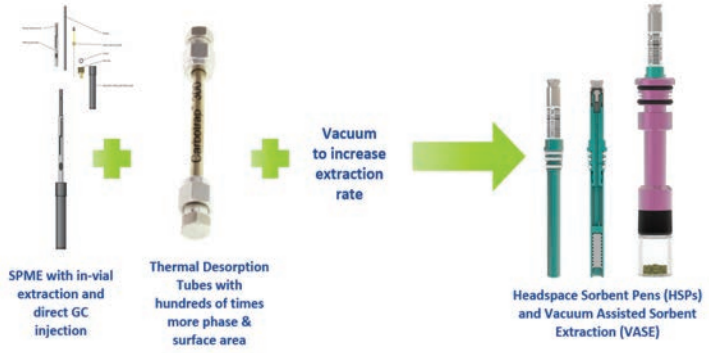


Figure 1 *The Headspace Sorbent Pen (HSP) combines the in-vial extraction convenience of Solid-Phase Micro Extraction (SPME) and larger capacity of Thermal Desorption (TD) tubes to extend the range of applications suitable for solvent-free headspace extraction.*

Introduction

Compositional analysis of products, including any contaminants present, from raw materials to finished products is crucial to ensure quality and safety.

Headspace Sorbent Pens (HSPs) are used with the technique, Vacuum Assisted Sorbent Extraction (VASE), to extract volatile organic compounds (VOCs) to semi-volatile organic compounds (SVOCs) in solid, liquid, and gas matrices.

Many existing headspace techniques are only quantitative for volatiles (Boiling point (BP) range <200°C). VASE-TD is a technique that increases the compatibility of many applications with solvent-free headspace extraction by combining the strengths of SPME and TD tubes. After placing the sample in the vial and inserting the HSP containing an adsorbent, a vacuum source is applied, bringing the in-vial pressure to about 0.3 atm.

Advantages of Headspace Sorbent Pens (HSPs)

- ✓ In-vial headspace extraction of VOCs & SVOCs
- ✓ Micro to exhaustive extraction
- ✓ Compatible with both liquids and solids
- ✓ Very large volatility range (<100°C up to 550°C)
- ✓ Robust and quantitative: Sorbent Pens can be used interchangeably
- ✓ Resistant to traditional headspace matrix effects due to large sorbent capacity

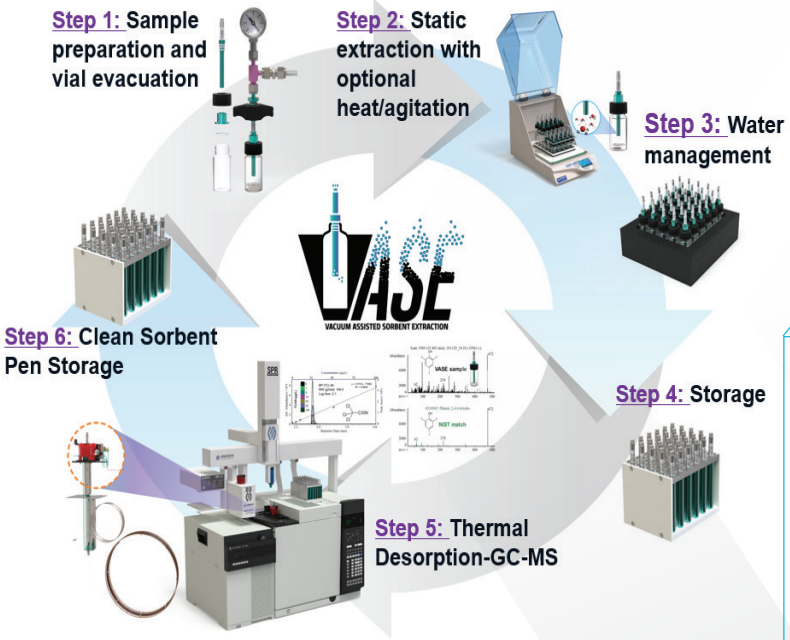


Figure 2 *The VASE workflow from sample to results.*

Overlay of 4 HG cannabis replicates (100:1 Split) with 4 re-desorptions of the same HSPs for carryover test (10:1 Split) shows negligible carryover!

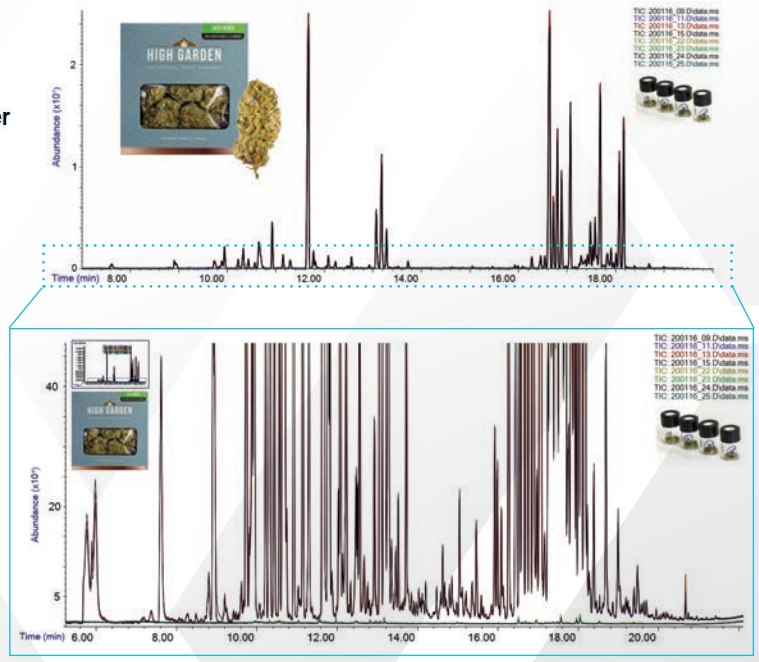


Figure 3 *Re-run of HSPs shows negligible carryover.*

Following extraction, the HSP is the isolated in an air-tight sleeve and transferred to a unique thermal desorption (TD) unit via an autosampler for thermal desorption onto a gas chromatography (GC) column for separation and detection by mass spectrometry (MS) or flame-ionization detection (FID). Typical steps from sample to results are outlined in **Figure 2**.

Application to Complex Matrix of Cannabis

A five-minute HSP extraction of cannabis flower at 100°C and an initial sub-ambient vial pressure of 0.36 atm resulted in qualitative profiling of numerous compounds found within cannabis flower. Over 40 of the most abundant volatile organic compounds, monoterpenes, sesquiterpenes, and cannabinoids were identified via spectral match to the NIST library.

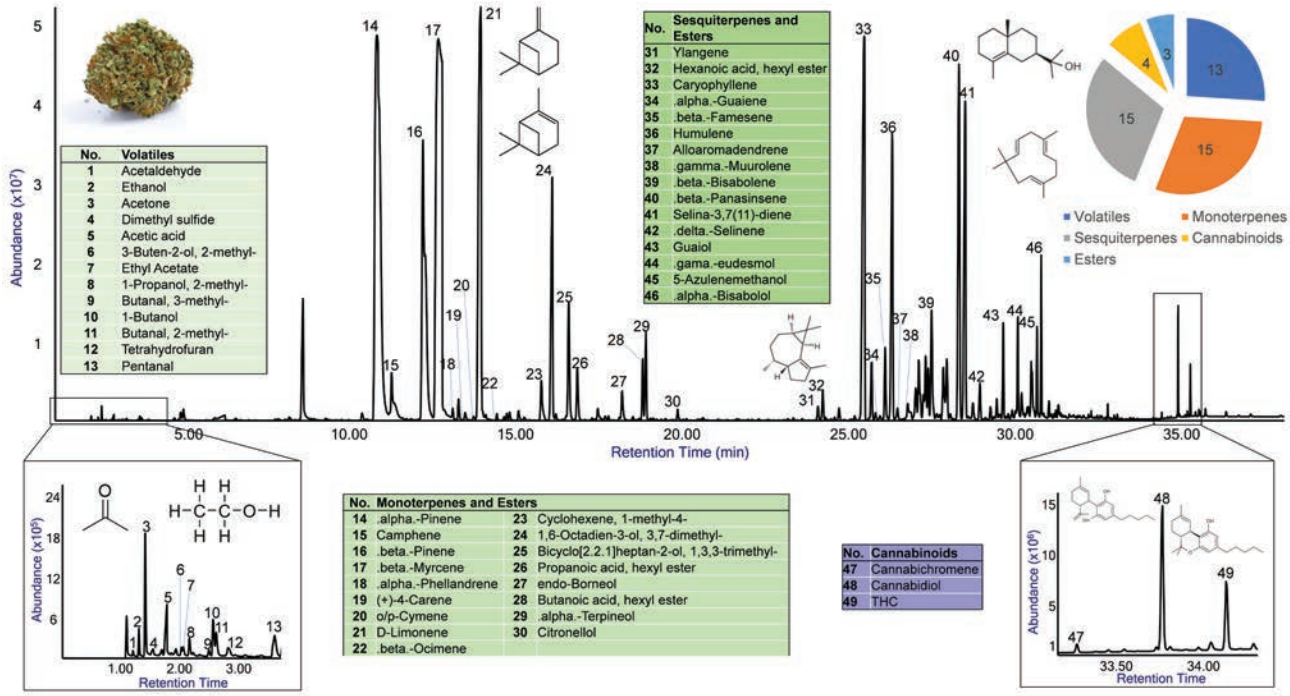


Figure 4 *VASE-TD-GC-MS chromatogram of a 100 mg sample of cannabis flower (Craft Cannabis ACOG Hybrid).*

Consumers express interest in specific strains containing desired terpenes that may enhance the health benefits of products either alone or synergistically with other terpenes, THC, CBD, and other cannabinoids.

Replicate terpene extractions (n=4) shown in **Figure 5** was achieved using unique HSPs. RSDs resulted in 12% or less for each of the 3 distinct cannabis strains tested. The workflow of raw sample to results can be achieved in less than 1 hour. This quick and reliable method allows interpretation of terpene diversity and accurate testing to ensure products contain the terpene ratios desired by consumers.

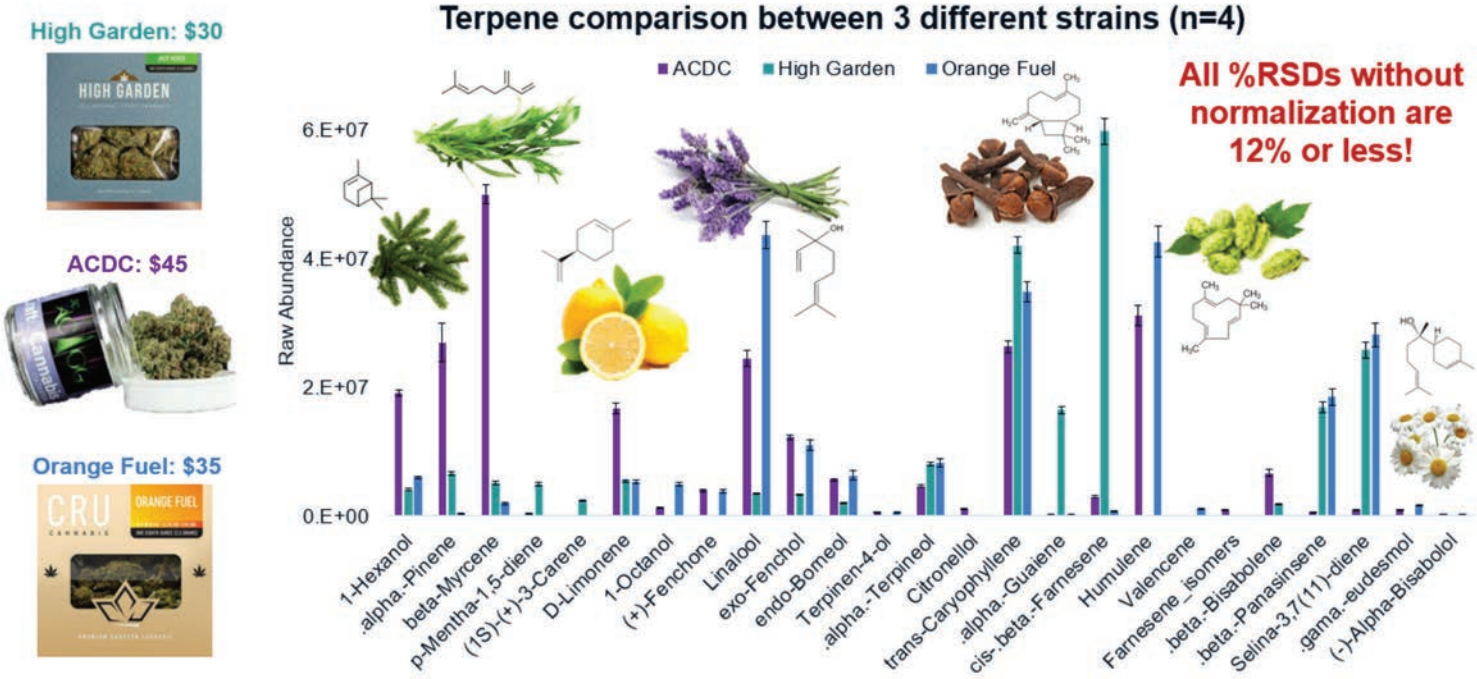


Figure 5 *Strain to strain comparison of terpene profiles between 3 cannabis flower products.*

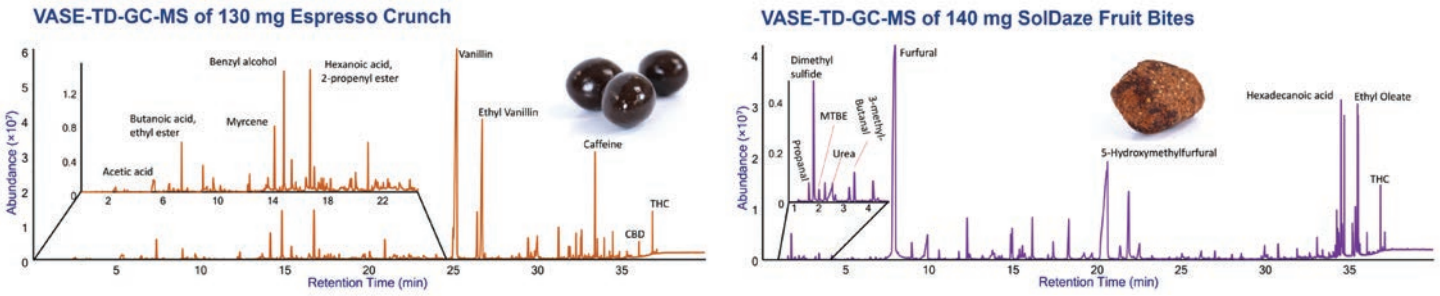


Figure 6 *Qualitative profiling of 2 different cannabis-infused edible products.*

Qualitative profiling of cannabis-infused edible products Espresso Crunch and SolDaze Fruit Bites shown in **Figure 6** above demonstrate a wide range of compounds of interest including volatile contaminants, flavor additives, and active cannabinoids.

Quantitation of Monoterpenes in Cannabis Flower

Table 1 below shows the standard addition method applied to quantitation of monoterpenes within the complex matrix of cannabis flower. Quantification (n=4) resulted in %RSDs between 3.3 – 20.6% for 8 monoterpenes using standard addition applied to cannabis samples. Replicate 2 for Camphene highlighted in yellow is an outlier that may have been caused due to homogenization issues.

Table 1 Standard Addition Method Results for 9 Monoterpenes Tested in Cannabis Flower.

No.	Terpene	RT (min)	Qion	Rep 1	Rep 2	Rep 3	Rep 4	Ave	%RSD
1.	Camphene	9.116	93	213	609	239	209	351	66.7
2.	.alpha.-Phellandrene	10.136	93	40	41	38	40	40	3.3
3.	(1S)-(+)-3-Carene	10.245	93	8	6	7	6	7	9.5
4.	Eucalyptol	10.607	43	200	155	152	153	165	14.1
5.	Ocimene	10.836	93	11	15	14	12	13	13.2
6.	(+)-Fenchone	11.588	81	2202	1781	2427	1914	2081	13.9
7.	Camphor	12.52	95	32	28	33	20	28	20.6
8.	Isoborneol	12.703	95	50	38	42	42	43	11.4
9.	Hexahydrothymol	12.897	71	12	10	8	11	10	15.6

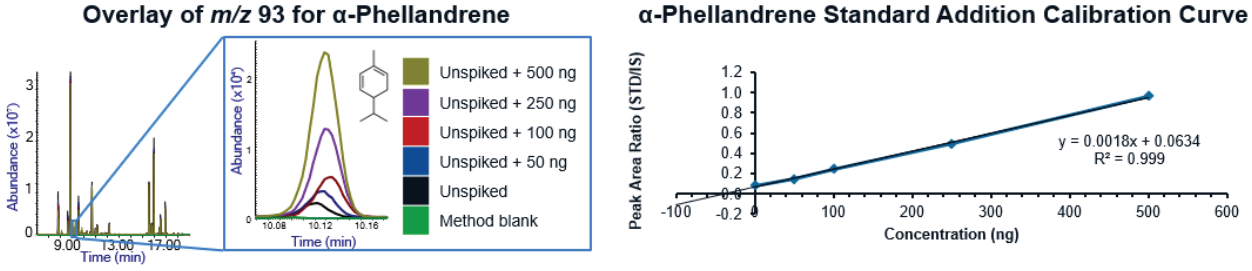


Figure 7 *Standard addition calibration curve for α-Phellandrene.*

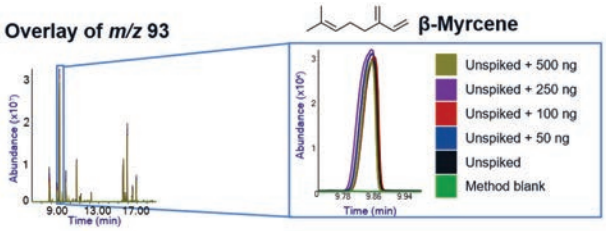


Figure 8 *Overlay of m/z 93 for β-Myrcene.*

Highly abundant monoterpenes such as β-Myrcene shown in **Figure 8** require further dilution to allow the added standards to be at a high enough concentration.

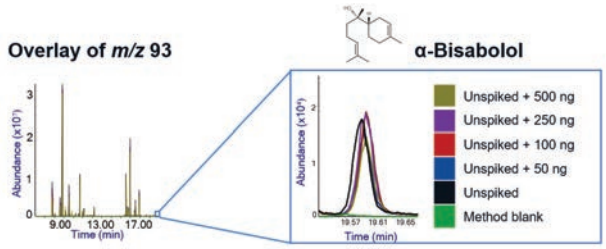
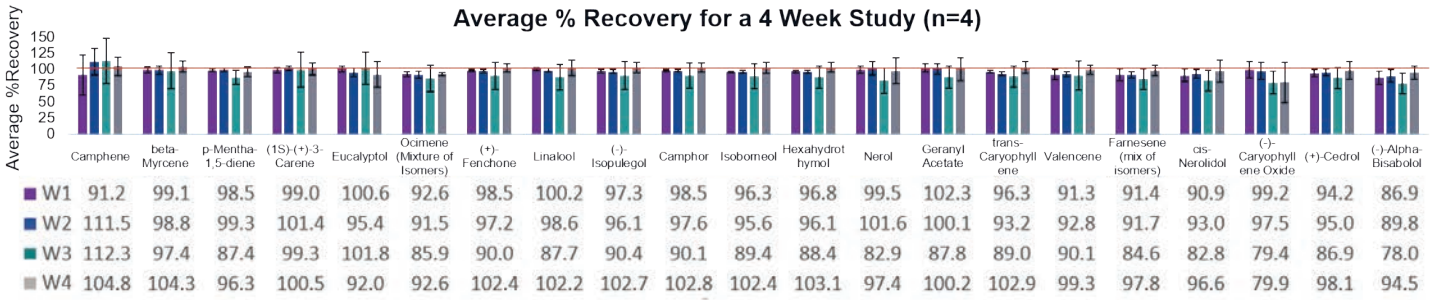


Figure 9 *Overlay of m/z 93 for α-Bisabolol.*

Sesquiterpenes, such as α-Bisabolol shown in **Figure 9**, may be a levels higher than standard addition concentrations. Further method optimization is required for quantitation of sesquiterpenes.

Terpenes Extracted on HSPs are Stable for up to 4 Weeks



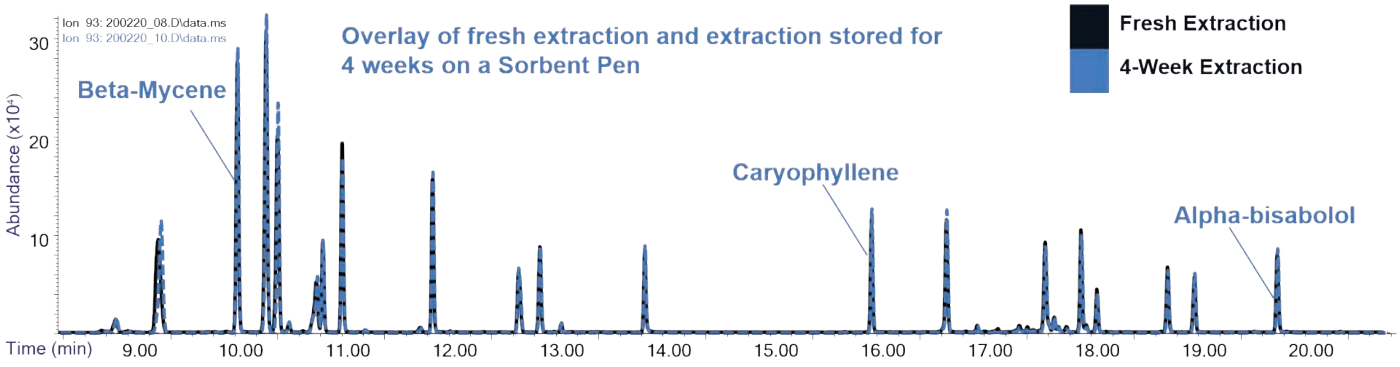


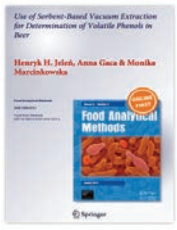
Figure 10 *Results show average recoveries for tested terpenes extracted on HSPs are 80-105% for up to 4 weeks.*

Stability tests show terpenes are stable (80-105%) for up to 4 weeks when extracted onto HSPs enabling samples to be extracted at the source and shipped to a testing lab for analysis.

Conclusions

- ✓ A new headspace technique has been developed for qualification of terpenes to cannabinoids in one run.
- ✓ Workflow of raw sample to results can be achieved in less than 1 hour.
- ✓ Stability studies show that the range of terpenes tested are recovered at 80-105% after being stored in isolation sleeves for 4 weeks prior to desorption when compared to recoveries of desorptions performed on the same day as extraction.

VASE Publications



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