Evaluation of a New Technology for the Collection of Breath Components in the Detection of Marijuana Use

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INTRODUCTION

- An interest in the use of exhaled breath for non-invasive drugs-of-abuse testing has motivated investigations into:
  - •Breath sample matrix complexity
  - •Adequate breath sample collection and analysis
- As marijuana usage in the United States rises with legalization, there is a need for new field devices to address the public safety concern of driver impairment under the influence of marijuana.
- Previous methods analyzing the active ingredient of marijuana, Δ^9-tetrahydrocannabinol (THC), and its metabolites utilized polymeric filter pads for breath collection, followed by liquid extraction and LC/MS/MS analysis **[1-2].**
- This method, along with immunoassay saliva field tests, has demonstrated poor detection limits for THC and its metabolites.
- In hopes of achieving a better representation of marijuana intoxication, we propose to investigate cannabis-related terpenes in addition to cannabinoids as terpenes constitute a large portion of cannabis and act synergistically with cannabinoids often increasing the psychoactive effects of the drug **[3].**
- This investigation will test out a novel sorbent device, Capillary Microextraction of Volatiles (CMV), using a thermal desorption gas chromatography method.
- We have also developed a vapor generation device to simulate the conditions of exhaled breath for the evaluation of the CMV's efficacy for exhaled breath collection.

MATERIALS

- Liquid standard solutions of 2,5-Dimethylfuran (2,5-DMF), Tetradecane and β-caryophyllene (Sigma-Aldrich).
- GC grade methanol (MeOH) solvent (Fisher Scientific).
- Thermally conditioned CMVs (manufactured in the Almirall lab **[4]**).
- Standard emission permeation tubes (VICI Metronics).

WHAT IS CAPILLARY MICROEXTRACTION OF VOLATILES (CMV)?

- Pre-concentration device based on PSPME **[5-6]**
- 2 mm x 2 cm open ended glass capillary tube filed with sol-gel polydimethylsiloxane (PDMS) coated strips

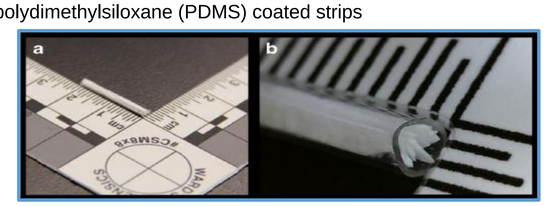

Figure 1. Image of CMV device A) overview B) detailed close up. **[5]**

BENEFITS OF CMV

- Offers dynamic sampling of volatile organic compounds (VOCs)
- Thermally stable at 300˚C
- Offers 5000X increase in surface area improvement in capacity over the static sampling single-fiber SPME **[4-5]**

METHODS

Vapor Generation

- Over a one week period, uncertified permeation devices of neat chemicals were gravimetrically calibrated using a Dynacalibrator Model 150 (VICI Metronics) with a chamber temperature setting of 37˚ C.
- Generated vapors were sampled for 10 min at nitrogen gas flow of 500 mL/min to determine the breakthrough percentage of two CMV's in series.

CMV Analysis

- CMVs were directly thermally desorbed into an 7890A Gas Chromatograph and 5975C Mass Spectrometer (GC-MS) using a thermal desorption probe (Agilent).
- Analyte recovery was determined by spiking 1 µL standard solutions onto the CMV.

INSTRUMENTAL SETUP

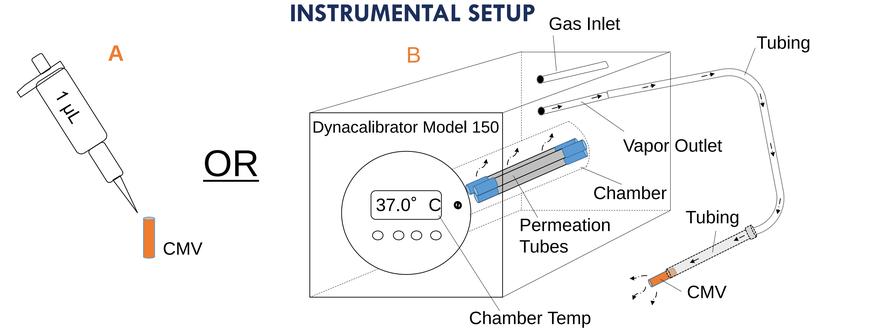

Table 1. Instrumental Parameters

Optimized GC-MS Parameters	
GC Inlet	250˚C, Splitless
Oven Temperature Program	Initial: 50˚C (2 min hold) Ramp: 10˚C/min to 240˚C, 5˚C/min to 280˚C, (7 min hold)
GC Column	ZB5-MS 60 meters
Gas Flow	1.5 mL/min
Aux. Temp	280˚C
MS Quad Temp	150˚C
MS Source Temp	230˚C
Acquisition mode	Fullscan 30-450 m/z

Figure 2. Schematics of the experiment instrument setup. Analytes are absorbed to the CMV device by A) spiking of liquid solution or by B) collection of vapors from the gas generator's outlet. CMV's are placed into a C) thermal desorption probe and undergo D) splitless analysis by gas chromatography – mass spectrometry (GC-MS).

RESULTS

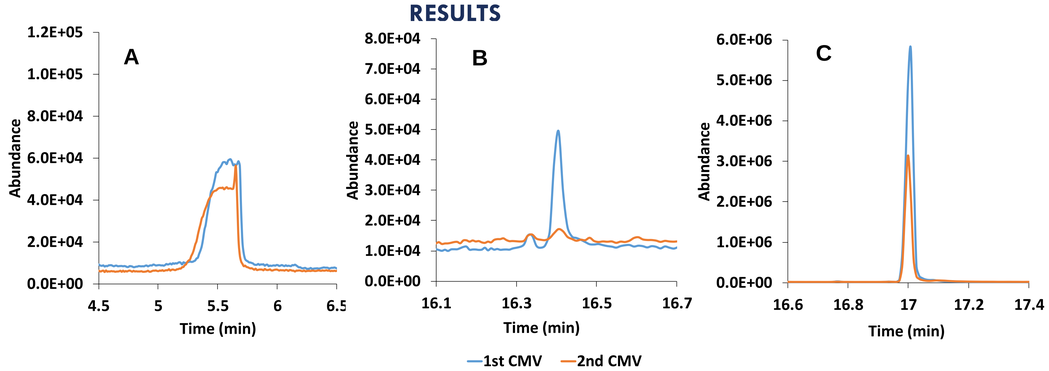

Figure 3. Chromatograms of overlapping responses of two CMV's in series following a 10 minute collection of generated vapors at a 500 mL/min flow. A) 2,5-dimethylfuran (RT = 5.181 min), B) tetradecane (RT = 16.405 min), C) β – caryophyllene (RT = 17.032 min).

Table 2. Calculated figures of merit of a select number of target analytes on GC/MS.

	2,5-Dimethylfuran	ß-Caryophyllene	Tetradecane
Instrument Detection Limit	0.5 ppm	0.6 ppm	4.6 ppm
Instrument Quantification Limit	1.7 ppm	2.1 ppm	15.2 ppm
CMV Direct Analyte Recovery	¥57.6%	ǂ 26.7%	#39.2%
CMV Breakthrough	81.5%	51.7%	10.5%

Calculations based on three replicate averages of SIM peak area datum.
Concentrations of methanolic solutions for recovery determination were 7.6 ppm¥ , 4.9 ppmǂ , and 14.5 ppm# respectively.

DISCUSSION

- Preliminary data shows that the CMV's collection efficiency varies based on the chemicals' physical properties (i.e. volatility and polarity).
- At the 37˚ C temperature of the gas generator, the compounds have decreasing volatility as follows 2,5-Dimethylfuran (2.89E2 mmHg), β – caryophyllene (8.67E-2 mmHg) and Tetradecane (3.53E-2 mmHg).
- Tetradecane showed the lowest breakthrough percentage at a flowrate of 500 mL/min due to its non-polarity and strong interaction with the non-polar CMV surface. β – caryophyllene and 2,5-DMF are more volatile and slightly polar.
- Recoveries were greater than 20% indicating its sampling suitability for thermal desorption applications, considering the breakthrough.
- It is hypothesized that recoveries may improve with enhancement of the CMV's sorbent chemistry by the introduction of a bipolar sorbent coating (i.e. Carboxen/PDMS).

FUTURE WORK & FUTURE APPLICATIONS

- Investigation of other key cannabis-related, tobacco-related and breath related compounds:
  - α-pinene
  - β-myrcene
  - Δ^9-tetrahydrocannabinol (THC)
  - Cannabidiol (CBD)
  - Cannabinol (CBN)
  - Nicotine
  - Acetone
  - Decanal
  - 2-methylbutane
  - 2-butanone
- Improve the collection capacity of the CMV
  - Enhancement of sorbent surface chemistry (i.e. bipolar sorbent)
  - Cryofocused sample collection
- Ethically approved sample collection of exhaled breath of human volunteers using the CMV incorporated into a field sampling device.

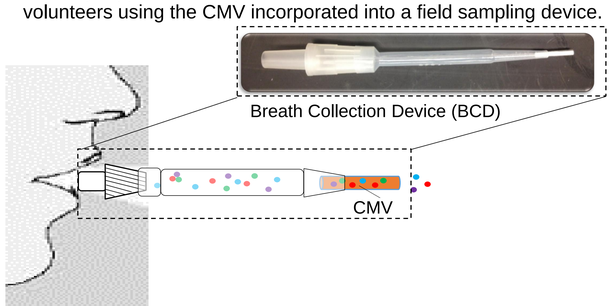

Figure 4. Demonstration of CMV sample collection using the BCD field sampler.

REFERENCES

1. Beck, O., et al. (2011). *J Anal Toxicol.* 35(8): p. 541-4.
2. Himes, S.K., et al., (2013). *Clin Chem.* 59(12):1780-9.
3. McPartland, J. M., & Russo, E.B. (2001). *Journal of Cannabis Therapeutics*, *1*(3-4), 103-132.
4. Patent US 8,668,873 B2 Awarded March 11, 2014 (Disclosed 2008) Inventors: Jose Almirall, Jeannette Perr and Patricia Guerra, Florida International University
5. Fan, W. & Almirall, J.R. (2014). *Anal. and Bioanalyt. Chem. 406(8):2189-2195.*

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