FINAL RESEARCH REPORT
(JANUARY 1, 2019 – DECEMBER 31, 2020)

Project Title: IDENTIFICATION OF DRUGS IN POWDERS, LIQUIDS, AND PLANT MATERIAL VIA TOTAL VAPORIZATION SOLID PHASE MICROEXTRACTION (TV-SPME)

Award Amount: $96,469

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SUMMARY OF THE PROJECT

MAJOR GOALS AND OBJECTIVES

This project concerns the development of TV-SPME to derivatize and analyze drugs in solid or liquid form without sample preparation, including tablets and plant material.

There were four specific aims in this proposal:

1) Design SPME methods to identify drugs in solid/powder form using a combination of solvent and derivatization agent.
2) Achieve the complete derivatization of the solvent and analysis of drugs in aqueous systems such as alcoholic beverages and urine.
3) Adapt TV-SPME to the analysis of cannabinoids in marijuana as well as synthetic cannabinoids
4) Optimize a representative method for each sample type (i.e., powders, liquids, and plant material) that can be adapted by practicing forensic scientists.

RESEARCH QUESTIONS

The main research questions for this project were:

1) Can TV-SPME be a viable replacement methodology for current protocols that involve strong acids or bases or “dry” extractions using organic solvents?
2) Are controlled substances volatile enough so that a simple headspace experiment can detect them?

RESEARCH DESIGN, METHODS, ANALYTICAL AND DATA ANALYSIS TECHNIQUES

We divided the project according to the physical phase of the samples: liquids, powders, and plant material. The primary instrument was a gas chromatograph / mass spectrometer. Data analysis was accomplished through Microsoft Excel.

EXPECTED APPLICABILITY OF THE TECHNIQUE

We expect that any laboratory that is equipped with an automated SPME sampler can enjoy the benefits of headspace SPME.

PARTICIPANTS AND OTHER COLLABORATING ORGANIZATIONS

This project formed most of the M.S. and Ph.D. work for Alexandra Train and Kymeri Davis, respectively, who are receiving training in instrumental analysis, experimental design and statistical methods via one-on-one work with Dr. Goodpaster.

Name	Project Role	Time Worked (person months)	Contribution	Funding
Davis, Kymeri	research assistant	12	Assists with sample analysis and data interpretation	Graduate Student (IUPUI)
Goodpaster, John	principal investigator	2	Direct supervision of the graduate student, experiments, results and interpretation.	This grant (10% summer salary)

None of the personnel listed above collaborated with an individual in a foreign country or traveled to a foreign country as a part of this project.

CHANGES IN APPROACH FROM ORIGINAL DESIGN AND REASON FOR CHANGE, IF APPLICABLE

Nothing to Report.

OUTCOMES

ACTIVITIES/ACCOMPLISHMENTS

Our major accomplishments were:

1) Illustrating that headspace SPME can extract and identify a wide variety of controlled substances.
2) Demonstrated that on-fiber derivatization can allow for aqueous samples to be vaporized and derivatized.

RESULTS AND FINDINGS

LIQUIDS

On-fiber derivatization was performed using TV-SPME, where the fiber was first exposed to the headspace of a vial containing the derivatization agent, then exposed to a new vial containing the sample. ɣ-Hydroxybutyric acid (GHB) and ɣ-butyrolactone (GBL) are drugs of concern in that they may be used in drug facilitated sexual assault by surreptitiously spiking them into a victim's beverage. These drugs cause sedation, memory loss, and are difficult to detect in biological samples. One challenge in their analysis is that they can interconvert in aqueous samples, which was demonstrated in samples allowed to stand at room temperature for long periods. A volume study of GBL in water was performed with volumes ranging from 1 – 10,000 µL to compare the efficacy of TV-SPME, headspace SPME, and immersion SPME. Lastly, water, beer, wine, liquor, and mixed drinks were spiked with either GHB or GBL with realistic concentrations (mg/mL) and microliter quantities were analyzed using a TV-SPME Gas Chromatography-Mass Spectrometry method. The GBL volume study demonstrated an increased sensitivity in GBL detection when TV-SPME was utilized. Additionally, GHB and GBL were identified in various beverages at realistic concentrations. Overall, TV-SPME was beneficial because it required no sample preparation and used smaller sample volumes than immersion and headspace SPME.

POWDERS

For this work, traditional headspace SPME methods were utilized for the detection of various drugs in powder form using a polydimethylsiloxane/divinylbenzene (PDMS/DVB) SPME fiber. It was hypothesized that headspace SPME could be used to identify drugs in powder form by placing the drug into a headspace vial and heating the vial to 120°C. Drugs of interest included methamphetamine, pseudoephedrine, caffeine, cocaine, procaine, inositol, heroin, diphenhydramine, fentanyl, and pharmaceutical tablets including hydrocodone and oxycodone. These drugs were analyzed individually as well as in a realistic mixture. Seized drug samples from the Indiana State Police were also analyzed. To analyze these drugs using a headspace SPME method, a sample of the powered drug or drug mixture (~1 – 2 mg) was placed into a headspace vial with no prior sample preparation or extraction. This vial was then heated to 120°C inside of a Gerstel agitator and the sample was adsorbed onto the SPME fiber for 10 minutes. If derivatization was necessary, the PDMS/DVB fiber was first inserted into a vial containing the appropriate derivatization agent and then inserted into the sample vial for 30 minutes. All drugs, excluding inositol, were identified in powder form using this headspace SPME method without any prior sample preparation and without dissolving the drug in a solvent. These drugs were successfully identified individually as well as within a realistic

mixture. This headspace SPME method is simple, efficient, and cost effective for the detection of legal and illegal drugs.

Plant Material

In this work, samples such as marijuana, essential oils, and CBD oil were utilized to compare the two techniques. The compounds of interest in marijuana were the three main cannabinoids, cannabinol (CBN), cannabidiol (CBD), and tetrahydrocannabinol (THC). The sample preparation and GC-MS parameters were kept the same for the samples to determine which SPME technique works best for these samples. Sensitivity was compared to determine which SPME technique works the best. It was found that TV-SPME shows greater sensitivity with THC and equivalent sensitivity with CBN.

Limitations

The ultimate limitation of Headspace SPME is the volatility of the analytes themselves. The vast majority of controlled substances have sufficient vapor pressure to be detectable. However, some analytes such as the cannabinoids were more difficult to detect using this approach.

Artifacts

List of products

Presentations

1. IUPUI Graduate Student Multidisciplinary Symposium, Indianapolis, IN. Department of Chemistry & Chemical Biology, Indianapolis, IN. “Identification of Drugs in Powder Form with No Sample Preparation Via Headspace Solid Phase Microextraction (SPME) Methods”, August 16, 2019.

2. Midwestern University Analytical Chemistry Conference, Indianapolis, IN. Department of Chemistry & Chemical Biology, Indianapolis, IN. “Identification of Drugs in Powder Form with No Sample Preparation Via Headspace Solid Phase Microextraction (SPME) Methods”, November 8, 2019.

3. Turkey Run Analytical Chemistry Conference, Marshall, IN. Department of Chemistry & Chemical Biology, Indianapolis, IN. “Identification of Drugs in Powder Form with No Sample Preparation Via Headspace Solid Phase Microextraction (SPME) Methods”, September 27, 2019.

4. American Chemical Society: Think Like a Molecule Symposium, Indianapolis, IN. Department of Forensic and Investigative Sciences, Indianapolis, IN. "An Overview of Total Vaporization – Solid Phase Microextraction and its Forensic Applications", April 5, 2019.

5. Pittsburg Conference, Philadelphia, PA. Department of Forensic and Investigative Sciences, Indianapolis, IN. "An Overview of Total Vaporization – Solid Phase Microextraction and its Forensic Applications", March 19, 2019.

6. American Academy of Forensic Sciences Annual Scientific Meeting, Baltimore, MD. Department of Forensic and Investigative Sciences, Indianapolis, IN. "Detection of Various Drugs in Human Urine Samples Via Total Vaporization – Solid Phase Microextraction", February 20, 2019.

PUBLICATIONS

1. Davis, K.E.; Hickey L.D.; Goodpaster, J.V. Detection of gamma-hydroxybutyric acid (GHB) and gamma-butyrolactone (GBL) in alcoholic beverages via total vaporization solid-phase microextraction (TV-SPME) and gas chromatography-mass spectrometry. J. Forensic Sci. (in press)

2. K.E. Davis, J. V. Goodpaster, **"**Gas Chromatography-Mass Spectrometry Paired with Total Vaporization Solid-Phase Microextraction as a Forensic Tool," Journal of Visual Experiments, 2020. In press.

DATA SETS GENERATED

We generated a series of GC/MS date files for each of the relevant drugs of abuse: GHB, GBL, marijuana, methamphetamine, pseudoephedrine, caffeine, cocaine, procaine, inositol, heroin, diphenhydramine, fentanyl, and pharmaceutical tablets including hydrocodone and oxycodone.

DISSEMINATION ACTIVITIES

Our main dissemination activities have been delivering oral/poster presentations at local and national meetings, as well as publishing our results in peer-reviewed journals.