Enabling Direct Sample Analysis of Sorbent-based Microextracrtion Fibers with DART-MS for Rapid Generation of Unique Chemical Attribute Signatures

Robert Goguen[1], Crystal Hart[1] and Brian Musselman[1]
[1] IonSense, Inc., Saugus, MA, USA

Introduction

Ambient ionization ideally provides a very rapid means to characterize the chemical composition of a sample without the need for sample prep. Unfortunately, in many experiments the method fails to produce a complete picture of what is in the sample. This is often due to matrix effect and ion suppression with certain analytes. Understanding that SPME has long been a tool for collection of trace contaminants from urine we spiked synthetic urine with sets of drugs of abuse and commercial pharmaceutical products and analyzed those urines by multiple sorbent SPME followed by DART. Detection limits for each chemical as collected by different sorbents varied widely, however the use of multiple sorbents permitted detection of all of the drugs while DART alone could not detect the lower concentration components.

Methods

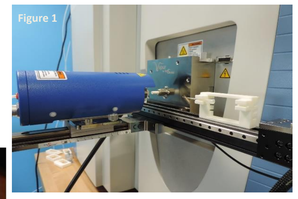
SPME Extraction:

Two different SPME fibers were used for these experiments. The fiber coatings were C18 and PDMS-DVB. The fibers were conditioned in 50:50 water:methanol for 1 hour on a shake plate. For an extraction the fibers were submerged in the sample for 1 hour on the multiplex SPME sampling apparatus(figure 3). The fibers are washed in water for 30 seconds prior to analysis to remove any surface bound components.

DART analysis:

The fibers are analyzed by DART with the SPME fiber module(figure 2). The module allows for a more consistent positioning of the fiber in the ionization region, shown in figure 1. The DART was run at select gas temperatures to allow for the desorption of different analytes. The DART data was collected in positive and negative ion detection modes using a Thermo Fisher Exactive+ MS.

FIGURE 1. DART SVP ionization source coupled to a Thermo Fisher Exactive+. A SPME fiber is inserted into the SPME fiber module. This is placed on the rail and moved into the DART ionizing gas by hand.



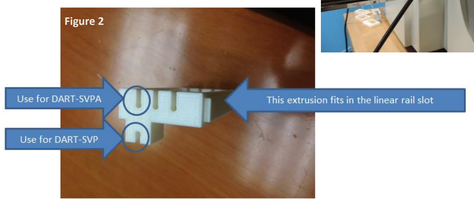


FIGURE 2. SPME fiber module. The module has positions to run SPME with a DART-SVP or a DART-SVPA as well as 6 positions for storing SPME fibers for transport.

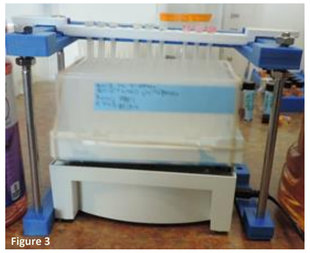
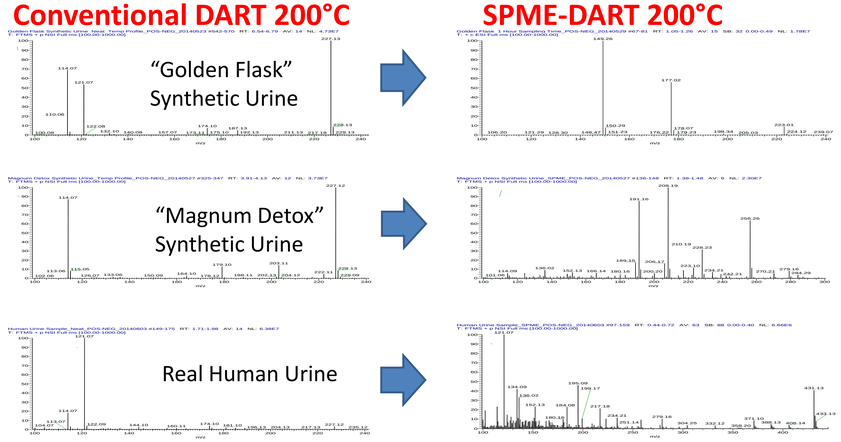


FIGURE 3. Multiplex SPME sampling apparatus. Allows for simultaneous sampling of multiple SPME fibers

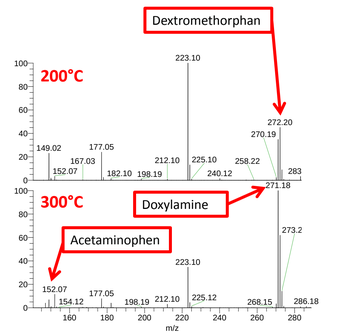
SPME of Synthetic Urine

The need for a cleanup procedure becomes obvious when urine is analyzed neat with DART. Two brands of synthetic urine were analyzed along with a real sample of urine. Without SPME the only major ions present in the spectrum are from the dimer of urea, creatinine and the creatinine dimer. The samples extracted by SPME yield a spectrum with many more important ions. The PDMS-DVB fiber gives a spectrum with the most ions for urine.

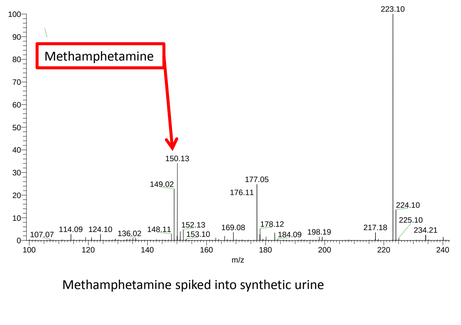


Drugs in Urine

The SPME extraction was evaluated using samples of synthetic urine spiked with different drugs. Prior to SPME extraction each sample was analyzed and none of the spiked drugs were detected in the spectrum. The C18 fiber works best with drugs however the PDMS-DVB fiber gave similar results.



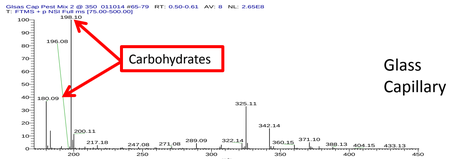
Cold Medication spiked into synthetic urine (different drugs can ionize at different temperatures)



Methamphetamine spiked into synthetic urine

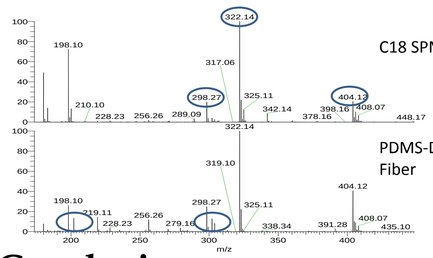
SPME of Pesticides in Juice

Urine is just one of many substances where DART and other analysis techniques fall short due to a high matrix effect and ion suppression. Fruit juices are often difficult to analyze due to the high carbohydrate content which dominate the spectrum. With the addition of SPME, a juice sample can be analyzed without the carbohydrates and much more information can be gained from analysis. For this experiment apple juice was spiked with a pesticide mix at 1ppm.



Glass Capillary

Spectrum of apple juice spiked with a pesticide mix. Note: Due to matrix effect of carbohydrates no pesticide ions are visible when sampling off a glass melting point capillary.



Pesticide Name	Chemical Formula	Molecular Weight
Carbaryl	$C_{12}H_{11}NO_2$	201.220
Spiroxamine	$C_{18}H_{35}NO_2$	297.476
Pyriproxyfen	$C_{20}H_{19}NO_3$	321.369
Fenhexamid	$C_{14}H_{17}Cl_2NO_2$	302.200
Azoxystrobin	$C_{22}H_{17}N_3O_5$	403.390

Conclusions

- The use of SPME fibers in combination with DART it is possible to analyze samples by reducing ion suppression caused by matrix effect.
- Extracting a sample with different SPME fiber coatings allows for different components to be collected.
- Desorbing SPME fibers at different gas temperatures allows for different components of a sample to be ionized independently of each other.
- By varying the sorbent coating and desorption temperature a unique chemical signature can be determined for most samples.

Future Research

The next goal for this research is to evaluate a high throughput SPME-DART method. Using the multiplex SPME sampling apparatus it is possible to sample with up to 96 SPME fibers simultaneously. With a traditional LC-MS SPME method analysis of 96 samples may take hours or days. SPME-DART allows for this analysis to be completed in under an hour.