Optimizing Ambient Ionization by DART – Solid Phase Microextraction (SPME), Thermal Separation

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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 effects 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 shaker plate. For an extraction the fibers were submerged in the sample for 1 hour using an apparatus that permits multiplex SPME sampling of up to 12 samples at a time (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 Plus MS.

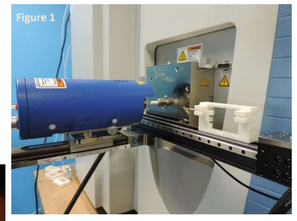


FIGURE 1. DART SVP ionization source coupled to a Thermo Fisher Exactive Plus. A SPME fiber is inserted into the SPME fiber module. This is placed on the rail and moved into the DART

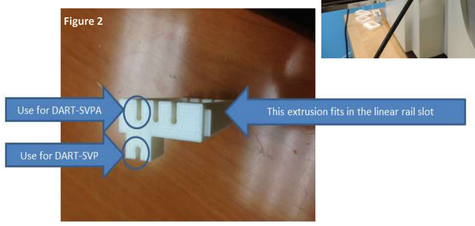
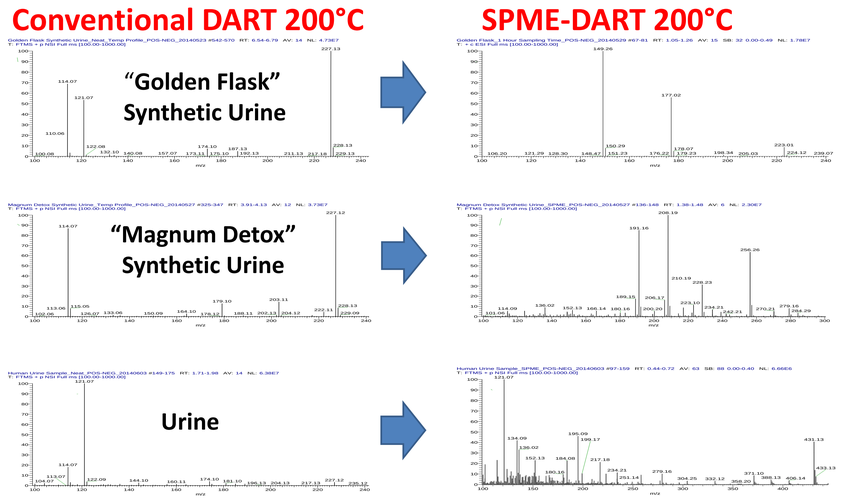


FIGURE 2. SPME fiber module. The module has positions to run SPME with a DART-SVP or a DART-SVPA as well as 6 positions for storing SPME fibers for transport.

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

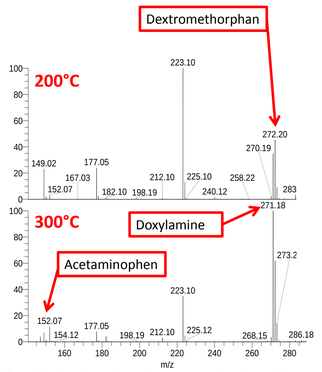
SPME of Synthetic Urine

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.

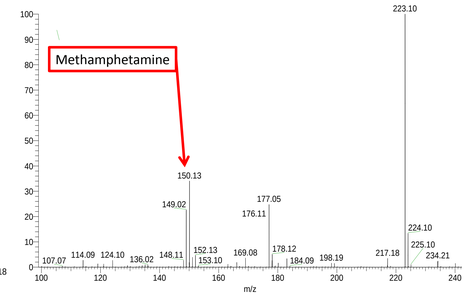


Drugs in Urine

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



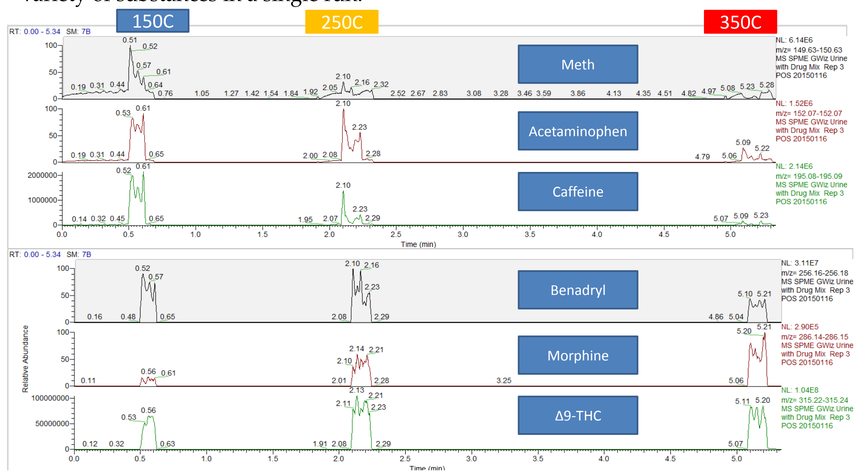
Cold Medication spiked into synthetic urine (different drugs can ionize at different temperatures)



Methamphetamine spiked into synthetic urine

Temperature Profile with SPME

Method development was taken a step further by spiking six drugs into a synthetic urine and performing a temperature profile on the single fiber. The SPME was analyzed at 150, 250, and 350C. This experiment is performed to screen for a wide variety of substances in a single run.



The extracted ion chromatograms above show that the optimum temperature varies depending on the compound in the urine. This method would be quite useful when scanning for multiple substances in urine while only consuming one SPME fiber. The time savings could also be used in eliminating back logs of drug screening in forensics lab with the use of this rapid analysis technique.

Conclusions

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

Future Research

Future goals involve development of high throughput SPME-DART method. Using the multiplex SPME sampling apparatus it is possible to sample up to 12 SPME fibers using a strip of individual fibers for sample screening.