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Real and Synthetic Urine by DART-SPME

Introduction

Urine has long been the sample of choice for drug screening of employers and law enforcement investigators. This of course has led to the development of synthetic urines as a means for people to supply for the drug screen test to falsify results. These synthetic urines often contain the major components of real urine diluted in water: urea and creatinine. Higher quality synthetic urines also contain various metabolites and salts.

When urine is analyzed by direct liquid injection LC/MS or DART-MS, significant matrix effects are encountered and the mass spectrum is dominated by the urea and creatinine. In order to minimize the matrix effect, solid phase micro-extraction (SPME) probes were utilized to extract the metabolites and analytes of interest, separating them from the matrix.

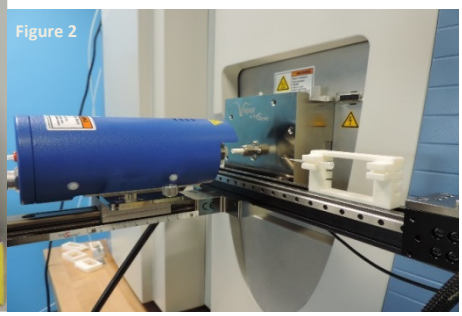
The SPME probes were treated as desorption probes for Direct Analysis in Real-Time (DART) in order to use the resulting spectrum to differentiate real urine from synthetic urine samples. If a sample is deemed real, the mass spectrum provides a means to screen for drugs of abuse.

Analysis of one sample is rapid with the extraction taking 1 hour or less and the DART analysis only taking 1 minute per sample. The extraction and analysis can be run in parallel to reduce experiment time.

Materials and Methods

A collection of synthetic urines were analyzed for this experiment (Figure 1). All were bought online with the exception of one, which was bought at a local smoke shop. The human samples were provided at different times during the day.

The DART was coupled to a Thermo Exactive Plus Mass Spec (Figure 2).



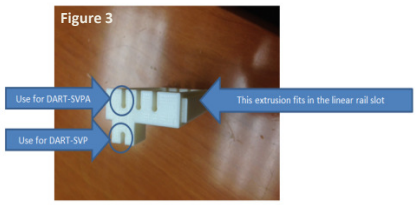
Experimental

Extraction:

The sorbents used were PDMS-DVB coated stainless steel fibers (Sigma-Aldrich). SPME fibers were pre-conditioned in 50:50 Water:Methanol solution for 30 minutes. A 1ml aliquot of urine was dispensed into a 2ml vial and placed on a shake plate set to approximately 2000RPM. The coated end of the SPME fiber was inserted into the vial containing the liquid. The sample and SPME were shaken for 1 hour.

Analysis:

After the extraction the fibers were removed from the vial and rinsed in water for 15 seconds to remove compounds not strongly bound to the sorbent. The DART source was operated with the desorption ionization gas set to 200°C with the MS switching polarities. Fibers were placed into a SPME fiber holder (Figure 3) and moved into the DARTs ionization region by using the robotic sampling arm. (Figure2).

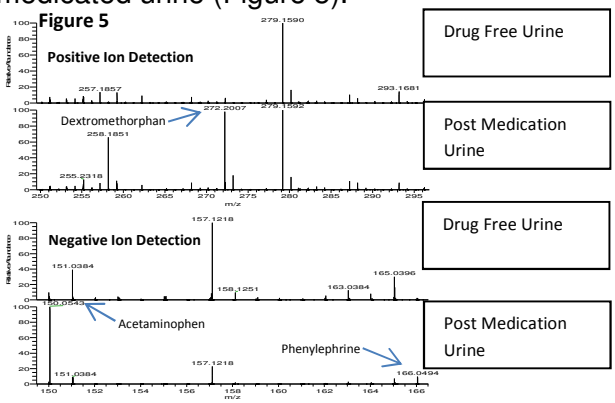


Human Urine Vs. Synthetic Urine

With DART-SPME it is easy to determine if a urine sample is real or synthetic. When analyzed, the synthetic urines give a spectrum that typically contains only a few peaks (Figure 4), these peaks correspond to the major components found in urine. When real urine is analyzed, the same major peaks are present but there are also many more peaks from compounds excreted by the body. The complexity of the urine spectrum makes it easy to differentiate real from synthetic urine samples (Figure 4).

Detection of Drugs in Urine

To assess the ability of DART-SPME to detect drugs in urine, a volunteer provided urine samples before and after administration of an over-the-counter cold medication. One hour after administration of the tablet, the subject provided a second urine sample. Both samples were analyzed by SPME-DART. The three drugs contained in the medication were detected in the post-medicated urine and not the pre-medicated urine (Figure 5).



Conclusions

The use of SPME in combination with DART allows for the rapid determination of the authenticity of a urine sample along with the detection of drugs present. All this can be done in a single analysis, saving time and resources. The SPME sampling of urine can be multiplexed to provide 96-samples per hour by using a microtiter plate and suitable number of probes.

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Figure 4