Capillary DBDI and APPI as efficient ionization sources for direct interfacing between SPME and MS

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Direct interfaces of solid-phase microextraction (SPME) with mass spectrometry (MS) are rapidly spreading in the MS community thanks to ambient ionization sources developed in recent years such as DART, DESI and DBDI. One of the limitations that needs to be addressed when dealing with complex sample matrices is the matrix effect, which can severely affect reproducibility and sensitivity. Two of the most promising approaches to directly ionize compounds extracted from SPME, i.e., DBDI-MS and APPI-MS, were compared in terms of tolerance towards different kinds of sample matrices. This approach enabled results to be available within minutes, rather than hours required when chromatography is used, saving precious time when fast and accurate results are needed.

Both sources were built in-house, in a capillary format that can be directly connected to the MS using a leak-tight connection. The compounds were thermally desorbed from the SPME device and the resulting gas phase ionized. Quantitation was performed by high-resolution mass spectrometry using a Thermo LTQ Orbitrap. Commercial SPME fibers, including matrix compatible PDMS/DVB/PDMS fibers, were employed for quantification from complex sample matrices. Compounds of different polarity and chemical classes were employed in this study. Quantitation of several classes of molecules in complex samples was achieved. Several complex matrices were spiked with target compounds. Among these, fruit juices, milk, body fluids (urine and blood plasma) and soil were chosen. Illicit drugs, pesticides and other environmental pollutants were considered.

The matrix tolerance observed with both sources allowed the analysis of complex samples while avoiding the need for sample pre-treatment, derivatization and, notably, permits one to skip conventional and time-consuming chromatographic separation. A complete (>99%) thermal desorption of the compounds from the SPME devices usually required less than 1 minute, enough time to perform quantitation, with no need for any cryofocusing system. Matrix component could be retained on the fiber for longer times. For example, sugars or phenolic compounds from food matrices were highly persistent on the SPME fiber. Our results show that chromatography can be circumvented in many cases where the complexity of the sample matrix is not extremely high, especially when adequate pre/post-extraction procedures are employed. A thorough comparison of the efficiency and selectivity (compounds of different polarity) of the DBDI and APPI ionization mechanisms in the direct ionization of complex samples is being carried out and will be used to extend this approach to more complex samples matrices.