Investigating the Polarity Range of Dielectric Barrier Discharge Ionization: Detection of Organic Microcontaminants in Water

A. K. Huba[1], M. F. Mirabelli[1], R. Zenobi[1]*

[1]ETH Zürich

Ambient mass spectrometry enables a fast and direct analysis, requiring minimal or no sample preparation; these attributes have established it as the preferred technique for applications in numerous fields (e.g., biomedical, forensic, and environmental). A very efficient ambient ionization method that has been developed and optimized in our research group involves an active capillary plasma ionization source based on a dielectric barrier discharge (DBD) [1]. By directly coupling this source to solid-phase microextraction (SPME), a simultaneous clean-up and enrichment of compounds of interest can be achieved, further simplifying and accelerating the analysis. The versatility and sensitivity of our source and method were previously demonstrated, for example for the sub-ng/L detection of pesticides [2]. Nonetheless, poorer ionization efficiencies for low-polarity compounds (such as polycyclic aromatic hydrocarbons, PAHs) precluded their detection at comparably low levels. The goal of this study was, thus, to explore ionization efficiencies across a wide polarity range, under varying plasma conditions. Results show that the presence of different solvents (e.g., acetonitrile, chlorobenzene, acetone) greatly affects ionization efficiencies and mechanism. For example, depending on the presence of solvent vapors, the preferential formation of radical versus protonated cations from PAHs was observed. This behavior will be further investigated and exploited towards the potential use of solvent as “dopants” in order to increase ionization efficiencies.

Additionally, the findings obtained will aid in further developing a detection method of organic microcontaminants in different water matrices (such as tap, ground, and treated wastewater) via the direct coupling of SPME to the previously mentioned DBDI source. Preliminary results show that a high-throughput analysis, with detection limits in the low ng/L range for specific compounds (e.g., N,N-dimethyl toluamide), good repeatability, and excellent linearity on ≥ 3 orders of magnitude, can be achieved. These promising results show that this approach has the potential of competing with, and perhaps even replacing, more established techniques such as gas chromatography-mass spectrometry (GC-MS). An increased efficiency for a larger polarity range will further expand the range of possible applications.

[1] M. M. Nudnova, L. Zhu, R. Zenobi, *Rapid Communications in Mass Spectrometry,* **2012,** 26, 1447-1452.
[2] M. F. Mirabelli, J.-C. Wolf, and R. Zenobi, *Analytical Chemistry,* **2016,** 88, 7252-7258.