LAUREN MULLIN is currently a PhD candidate in the Environment and Health Group of MTM Research Centre at Örebro University, and a Principal Scientist at Waters Corporation. Her research is grounded in advances in mass spectrometry and liquid, gas and supercritical fluid chromatography, and their applications for the analysis of emerging environmental contaminants, biomedical research and metabolite identification.

Mass spectrometry (MS) and coupled chromatographic techniques are critical tools in the identification and measurement of environmental contaminants. One group of these contaminants, the persistent organic pollutants (POPs), are of exceptional importance for monitoring due to their propensity for bioaccumulation, toxicity, potential for long-range transport from the source of use, and resistance to biotic and abiotic clearance. Though a number of these compounds have been known and analyzed for many years, due to the introduction of various chemical classes for consumer product improvements which may also share POPs attributes, the characterization of emerging POPs is an active area of research.

MS-based approaches for the analysis of this wide-ranging chemical landscape have historically used magnetic sector with gas chromatography and electron ionization for selective and sensitive legacy POPs monitoring. Some new and emerging POPs, however, require the use of liquid chromatography due to properties precluding successful separation in their native state with gas chromatography. Atmospheric pressure ionization sources facilitate this coupling to MS and greatly enhance the detection of these emerging POPs. Moreover, the adoption of tandem quadrupole and time-of-flight mass spectrometry MS systems for both legacy and emerging POPs analysis has also occurred. Numerous challenges and opportunities still exist in the field of MS-based POPs analysis and can be summarized in part as the need for increased sensitivity, selectivity among isomeric species, and challenges in identification confidence for compounds found during non-targeted analyses.

The aim of this thesis was to develop methods addressing specific analytical gaps of emerging POPs using alternative chromatographic approaches, ionization methods and complementary gas-phase separations. Harnessing advances in MS-based couplings, this was achieved through implementing supercritical fluid chromatography with tandem quadrupole MS for the enhanced separation of hexabromocyclododecane stereoisomers, a brominated flame retardant and new POP. The method was tested against the analysis of whale blubber and human serum extracts. Following this, an exploration of the recently detected hexafluoropropylene oxide-dimer acid ionization behavior describes the undesirable formation of homodimer and in-source fragmentation which diminish protonated precursor ion formation and adversely impact sensitivity for this compound when using current liquid chromatography-electrospray ionization conditions. To address this, an alternative mobile phase composition showed improved detection sensitivity and was implemented in the analysis of water extracts. Lastly, the use of ion mobility spectrometry coupled to time-of-flight MS detection was assessed for its utility in non-targeted screening of various organic contaminants in indoor dust samples. This work specifically focused on the use of unique averaged rotational gas-phase derived measurements of ions, the collision cross section, and how experimentally derived values compare to two predictive model values as a tool to increase confidence in proposed compound identification.

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