Advances in Mass Spectrometry for the Analysis of Emerging Persistent Organic Pollutants

av

Lauren Mullin

Akademisk avhandling

Avhandling för filosofie doktorsexamen i kemi,
som kommer att försvaras offentligt
fredagen den 25 oktober 2019 kl. 09.15,
Hörsal M, Örebro universitet, Örebro

Opponent: Prof. Jean-François Focant
Université de Liège, Belgium

Örebro universitet
Institutionen för naturvetenskap och teknik
701 82 ÖREBRO

Abstract

Lauren Mullin (2019): Advances in Mass Spectrometry for the Analysis of Emerging Persistent Organic Pollutants. Örebro Studies in Chemistry 24.

Mass spectrometry (MS) is a technique widely implemented for the measurement of environmental pollutants. A critical tool for the analysis of persistent organic pollutants (POPs) over several decades, MS as coupled with liquid and gas chromatography (LC and GC) techniques enables the analysis of emerging POPs. The aim of this thesis was to investigate the use of alternative MS-based techniques to assist specific analytical challenges including separation of stereoisomers using supercritical fluid chromatography (SFC), reduced ionization competition with appropriate mobile phase additives, and applied rotationally averaged collision-cross section (CCS) of ions via ion mobility measurements of emerging POPs.

Chromatographic efficiency improvements for the brominated flame retardant, hexabromocyclododecane (HBCDD), were implemented through the development of two supercritical fluid chromatography (SFC) methods. Based on the inherent qualities of supercritical fluids, separation of both predominant diastereomers and respective enantiomers was performed in a shorter time with wider chromatographic resolution using SFC than existing LC methods.

Turning next to MS ionization considerations, the emerging perfluoroalkyl substance hexafluoropropylene oxide-dimer acid (HFPO-DA) was investigated. Following a survey of analytical methodologies for HFPO-DA, the challenge of extreme dimer formation, in-source fragmentation and very low $[M\text{-}H]^-$ production was described. Method development using alternative mobile phase additives in currently used LC-MS acquisition techniques was deployed.

Finally, ion mobility spectrometry (IMS) was implemented in a non-targeted acquisition study of indoor dust samples. This study used IMS coupled with quadrupole time-of-flight MS to identify a wide range of contaminant classes, including emerging POPs. Identification confidence is a challenge currently facing non-targeted studies, and the use of prediction mechanisms of analyte IMS gas-phase separations was explored.

Through applying diverse alternative techniques, increased method performance was explored for emerging POPs analyses.

Keywords: Mass Spectrometry; Liquid Chromatography; Supercritical Fluid Chromatography; Ion Mobility; POPs; Electrospray Ionization

Lauren Mullin, School of Science and Technology
Örebro University, SE-701 82 Örebro, Sweden