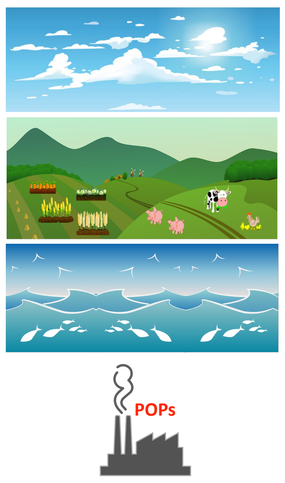
Sliding windows in ion mobility (SWIM): a new approach to increase the separation power in trapped ion mobility-mass spectrometry hyphenated with chromatography

Hugo Muller, Georges Scholl, Johann Far, Edwin De Pauw, and Gauthier Eppe

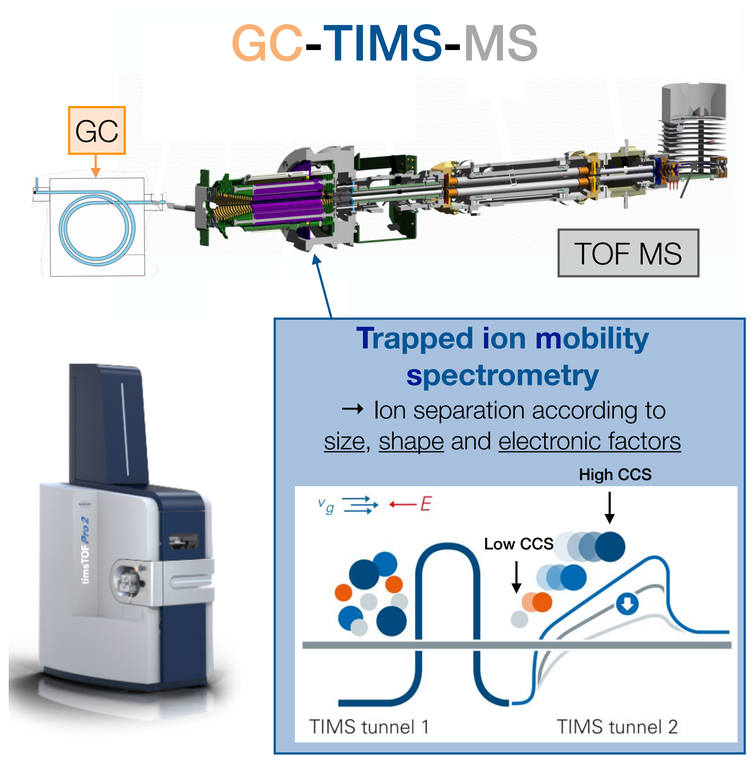
Mass Spectrometry Laboratory, MolSys Research Unit, Department of Chemistry, University of Liège, Liège, Belgium

Introduction

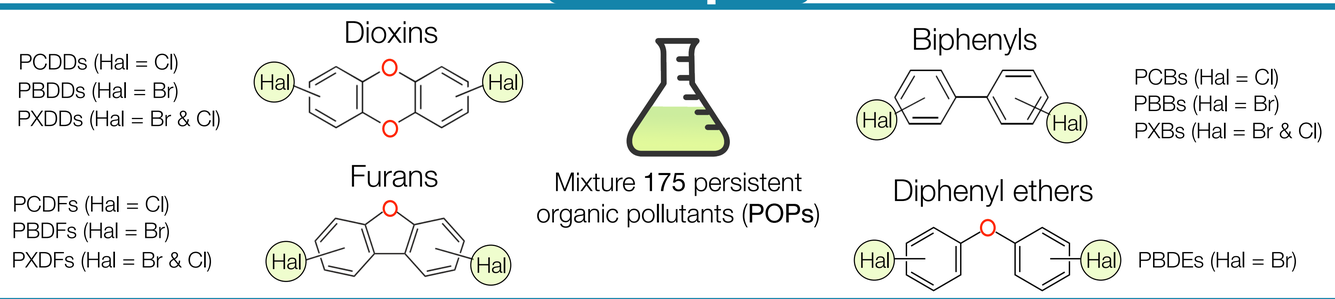
- Persistent organic pollutants (POPs) are chemicals that are released (un)intentionally from industrial activities, and have raised global concern for both human and wildlife owing to their toxic, persistent, and bioaccumulative properties.
- Their monitoring in environmental and food samples is analytically challenging due to the complexity of the sample matrix and the extremely low concentration levels. This necessitates the utilization of exceptionally selective and sensitive analytical methods, typically chromatography hyphenated mass spectrometry techniques.
- The integration of ion mobility within GC-MS systems is a promising approach for the monitoring of halogenated POPs, due to its enhanced capabilities in separation and identification (CCS).
- However, the fast time scale of the front-end chromatographic separation combined with the broad range of CCS values displayed by POPs often restrict the achievable resolving power on high resolution IM platforms, such as TIMS. To overcome this limitation, an innovative SWIM mode has been developed, providing significantly enhanced separation power.



Instrumentation



Sample



Sliding windows in ion mobility (SWIM)

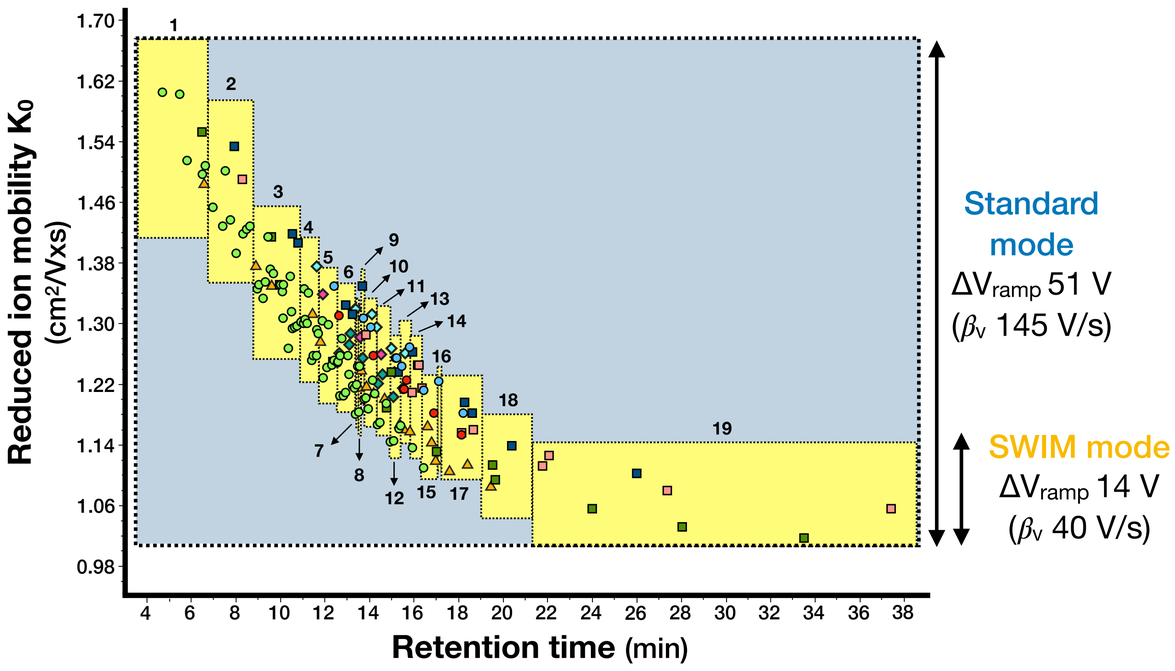


Fig. 1: Experimentally measured reduced ion mobility values K_0 of POPs as a function of their GC retention time. The ion mobility analysis range that was used in standard mode and in SWIM mode is represented by the blue and yellow rectangles, respectively.

- In TIMS, the resolving power R_p depends directly on the scan rate β_V, which corresponds to the rate at which the voltage is decreased during the elution step. The larger the analysis range (ΔV_{ramp}) and the smaller the analysis time (t_{ramp}), the larger the scan rate and the lower the separation power.

$$R_p \propto \frac{1}{\sqrt[4]{\beta_V}} \quad \text{where} \quad \beta_V = \frac{\Delta V_{ramp}}{t_{ramp}}$$

- The reduced ion mobilities K_0 of the halogenated POPs ranged from 1.02 to 1.60 cm²/Vxs (CCS from 133 to 200 Å²)

Standard TIMS mode

Broad (ΔV_{ramp} = 51 V) and constant IM range throughout the chromatographic separation

SWIM TIMS mode

Narrow (ΔV_{ramp} = 14 V) and mobile IM range that adapts to the K_0 vs RT profile of the ions

- The use of shorter ion mobility analysis ranges in SWIM mode resulted in a slower scan rate and significantly improved resolving power (~40%) compared to the standard TIMS mode.

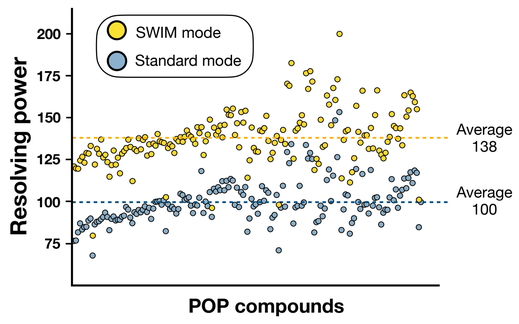


Fig. 2: Comparison of the individual IM resolving power of POPs achieved in standard and SWIM mode.

Application: coeluting isomer & isobars

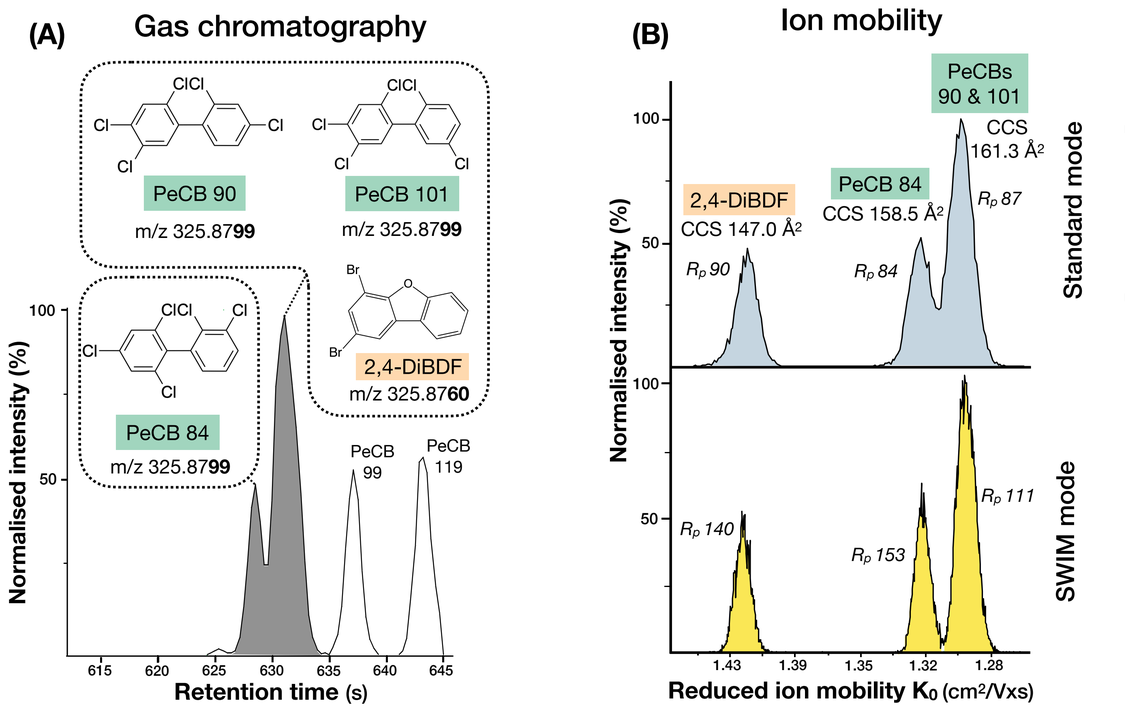


Fig. 3: (A) GC chromatogram of pentachloro biphenyls (PeCBs) and dibromodibenzofuran (DiBDFs) highlighting the (partial) coelution of PeCBs 84, 90, 101 (isomers) and 2,4-DiBDF (isobar). (B) Corresponding ion mobility spectra in standard mode (upper spectrum) and SWIM mode (lower spectrum).

- Coeluting isobars: the 2,4-DiBDF was baseline separated from the PeCBs in the ion mobility dimension (ΔCCS > 7%) due to significant difference in structure (halogenation degree).
- Coeluting isomers: the PeCB 84 was partially separated from PeCBs 90-101 in standard mode, but baseline separated in SWIM mode. However, no separation was observed for the isomeric pair PeCBs 90-101, even in SWIM mode.
- Overall:
  - all coeluting isobaric pairs could be baseline separated in IM dimension (9/9)
  - the great majority of coeluting isomeric pairs remained unresolved in the IM dimension (2/13)

Conclusion & Perspectives

SWIM mode

SWIM is an innovative approach to significantly increase the overall IM separation power of chromatography hyphenated TIMS-MS applications where analytes display a wide range of CCS values, such as POPs.

Coeluting isomers & isobars

TIMS is a powerful technique to resolve coeluting isobaric POPs. However, the separation of coeluting positional isomeric POPs that display very similar CCS values (ΔCCS < 0.5%) will require higher resolving power.

HM acknowledges financial support from the F.R.S.-FNRS (FRIA grant FC 47331). The authors also thank Bruker for their support and the Belgian Federal Public Service of Health, Food Chain Safety and Environment through the contract RT22/06 TEQFOOD.

H. Muller hugo.muller@uliege.be I **Prof. G. Eppe** g.eppe@uliege.be Mass Spectrometry Laboratory (MSLab) I www.mslab.uliege.be I MSLab_ULiege