Study of the formation of perfluoroalkyl carboxylic acid (PFCA) dimers in gas phase by coupling ion mobility with mass spectrometry (IM-MS)

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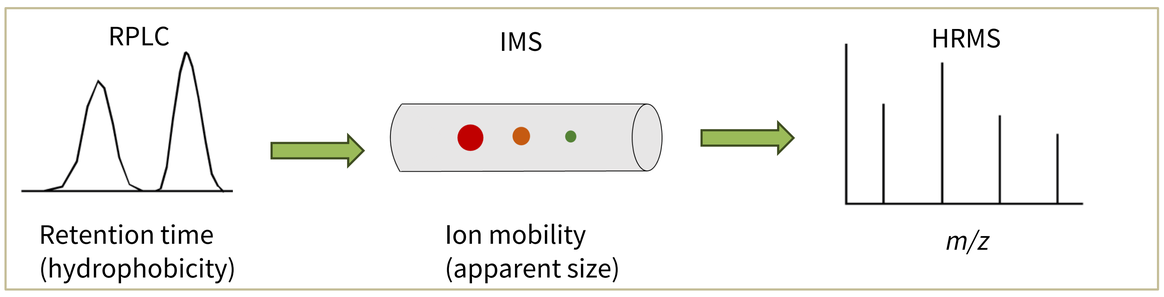
PFAS: Forever chemicals

Per-and polyfluoroalkyl substances (PFASs) are emerging pollutants of great concern. Since the 1950s, they have been extensively used in industrial and commercial applications due to their attractive properties. Due to their inherent stability and widespread use, these compounds are found and prevail in all environmental matrices, raising concerns about health safety. Only a few of these substances are regulated (e.g. perfluorooctane sulfonic acid, PFOS) and in response to growing concern about legacy PFASs, major manufacturers have turned to alternative PFASs, and approximately 5,000 compounds have been inventoried to date. There is therefore a great need for large-scale suspect and non-targeted screening approaches for these compounds.

Perspectives offered by IMS

- Additional separation dimension

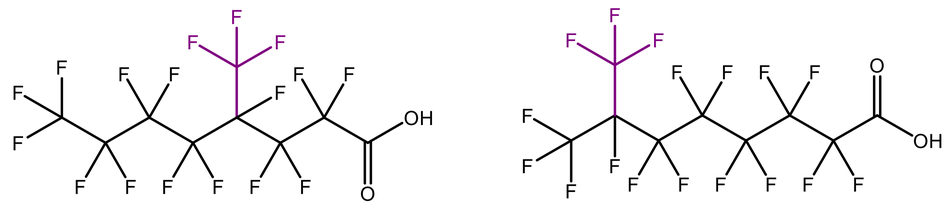


- Additional identification factor : CCS (Å^2)
- CCS-*m/z* trendlines
  - Increase confidence in homologue identification **[2]**
  - Structural information **[3,4]**
  - Can be combined with Kendrick mass defect analysis to further increase confidence in homologue identification **[2]**
- Easier data pre-filtering as PFASs have a distinct position in CCS-*m/z* space **[2]**

Limitations of RPLC-HRMS

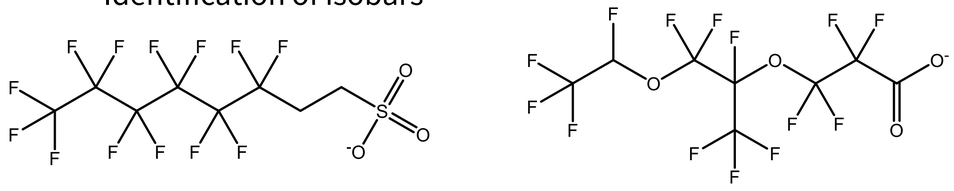
Among current challenges **[1]**:

- Separation of isomers



PFNA isomers

- Identification of isobars



6:2 FTS
m/z 426.9674

Hydro-EVE
m/z 426.9651

Materials and methods

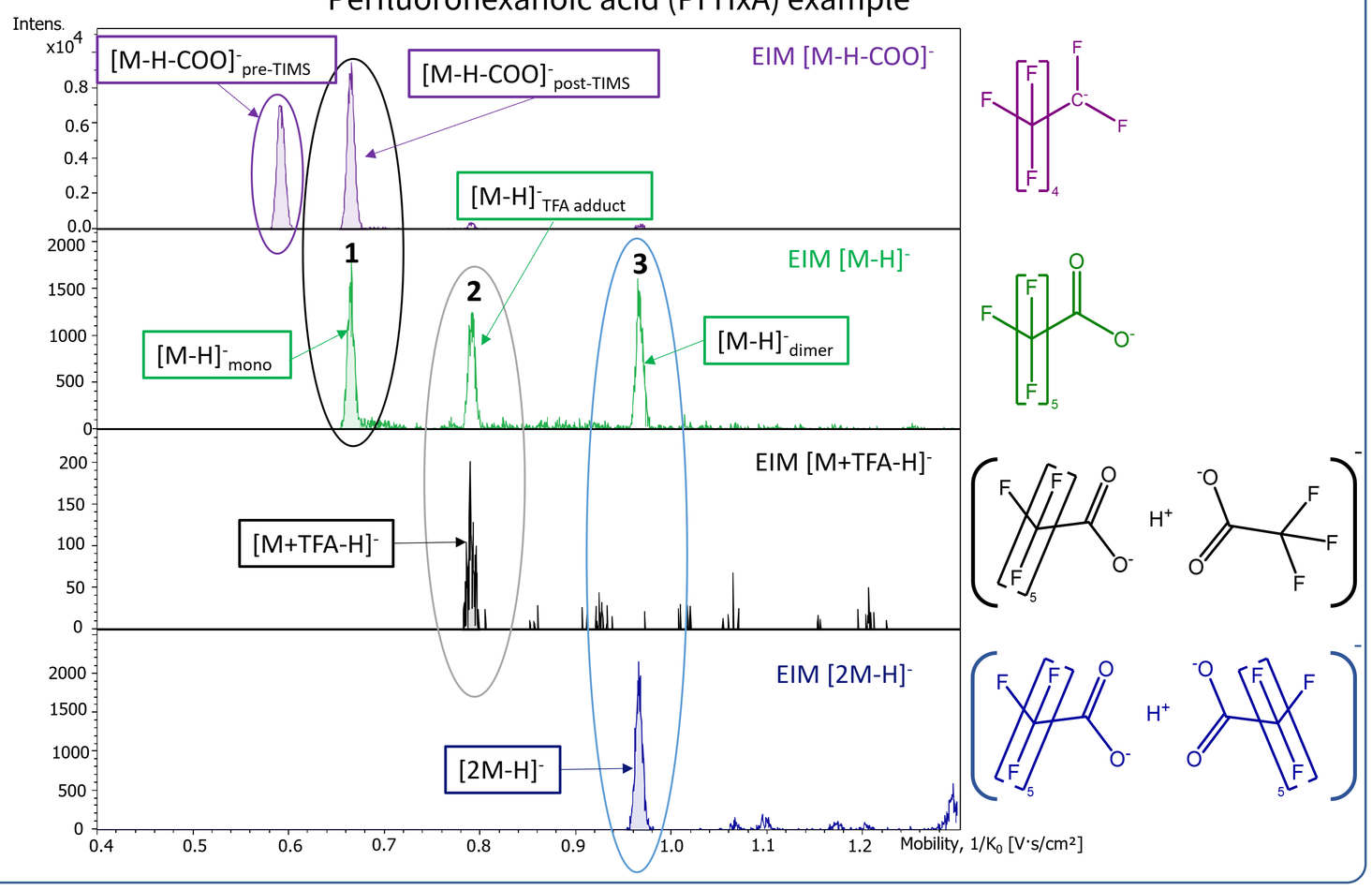
- Direct injection of 300ng/mL PFCA standards solutions in methanol with 0.1% formic acid, in the negative electrospray ionization mode.
- 3 IMS set-ups:
  - Agilent 6560 DTIM-QTOF
  - Bruker timsTOF Pro2
  - Synapt G2 HDMS (TWIMS)

Aims of the study

1) Confidently assign the multiple mobility peaks in the mobilogram of deprotonated perfluoroalkyl carboxylic acids (PFCAs).
2) Determine whether the CCS trendlines of the monomeric and dimeric ions obtained with three different IMS set-ups (drift tube, trapped, and traveling wave IMS) are similar or not.

I-Peak identification in TIMS

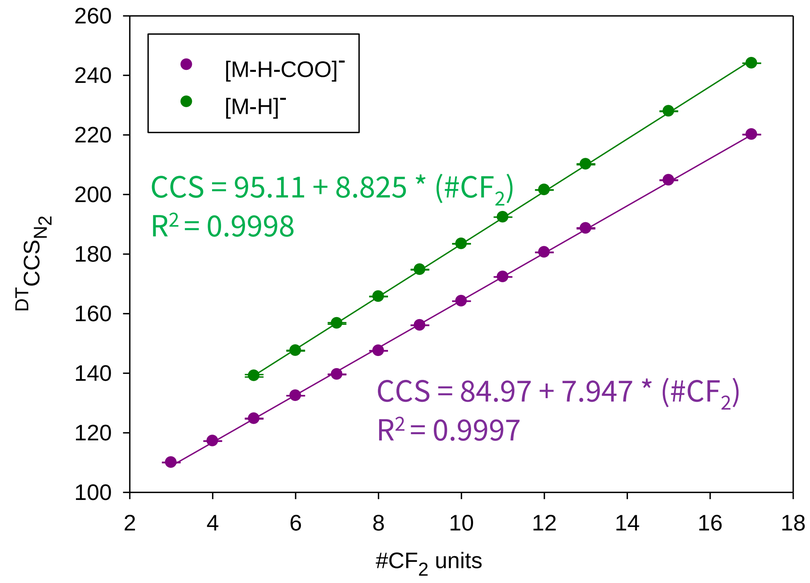
Perfluorohexanoic acid (PFHxA) example



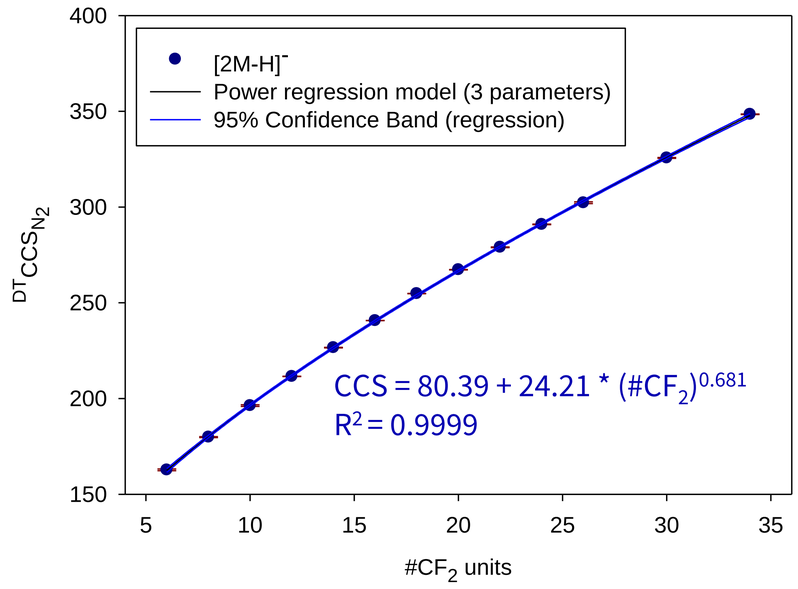
II-CCS-#CF_2 trendlines

CCS trendlines similar between DTIMS, TIMS and TWIMS
⇒ Only the DTIMS data are represented

Monomeric deprotonated and decarboxylated PFCAs:



Proton-bound homodimers:



Conclusions

- PFCA compounds can form proton-bound dimers when analyzed in negative ESI (IMS), which can impact the sensitivity. If these dimers dissociate after their mobility-based separation in the corresponding deprotonated ion ([M-H]$^-$), multiple peaks can be found in the mobilogram of the [M-H]$^-$ ion, preventing unambiguous determination of the CCS value of the deprotonated ion in its monomeric form.
- The CCS trendlines of PFCA monomeric and dimeric ions do not vary notably between the three IMS set-ups (i.e., DTIMS, TIMS and TWIMS), suggesting that their overall shape is not influenced by the difference in effective ion temperature between these three instruments. **[5]**
- The linear CCS trendlines of monomeric PFCA ions suggest an overall cylindric shape **[4]**. However, the power regression model for the CCS trendlines of the homodimeric ions might suggest an overall V-shape, but this should be investigated further.

References

[1] Dodds, J. N. *et al.*, *Anal. Chem.* **2020**, *92* (6), 4427–4435., **[2]** Foster, M. *et al., Environ. Sci. Technol.* **2022**, *56* (12), 9133–9143., **[3]** Haler, J. R. N. *et al., Methods* **2018**, *144*, 125–133., **[4]** Haler, J J. R. N. *et al., J. Am. Soc. Mass Spectrom.* **2022**, *33* (2), 273–283**,** **[5]** Morsa, D. *et al., Anal. Chem.* **2011**, *83* (14), 5775–5782