MASS SPECTROMETRY LABORATORY

LIÈGE université

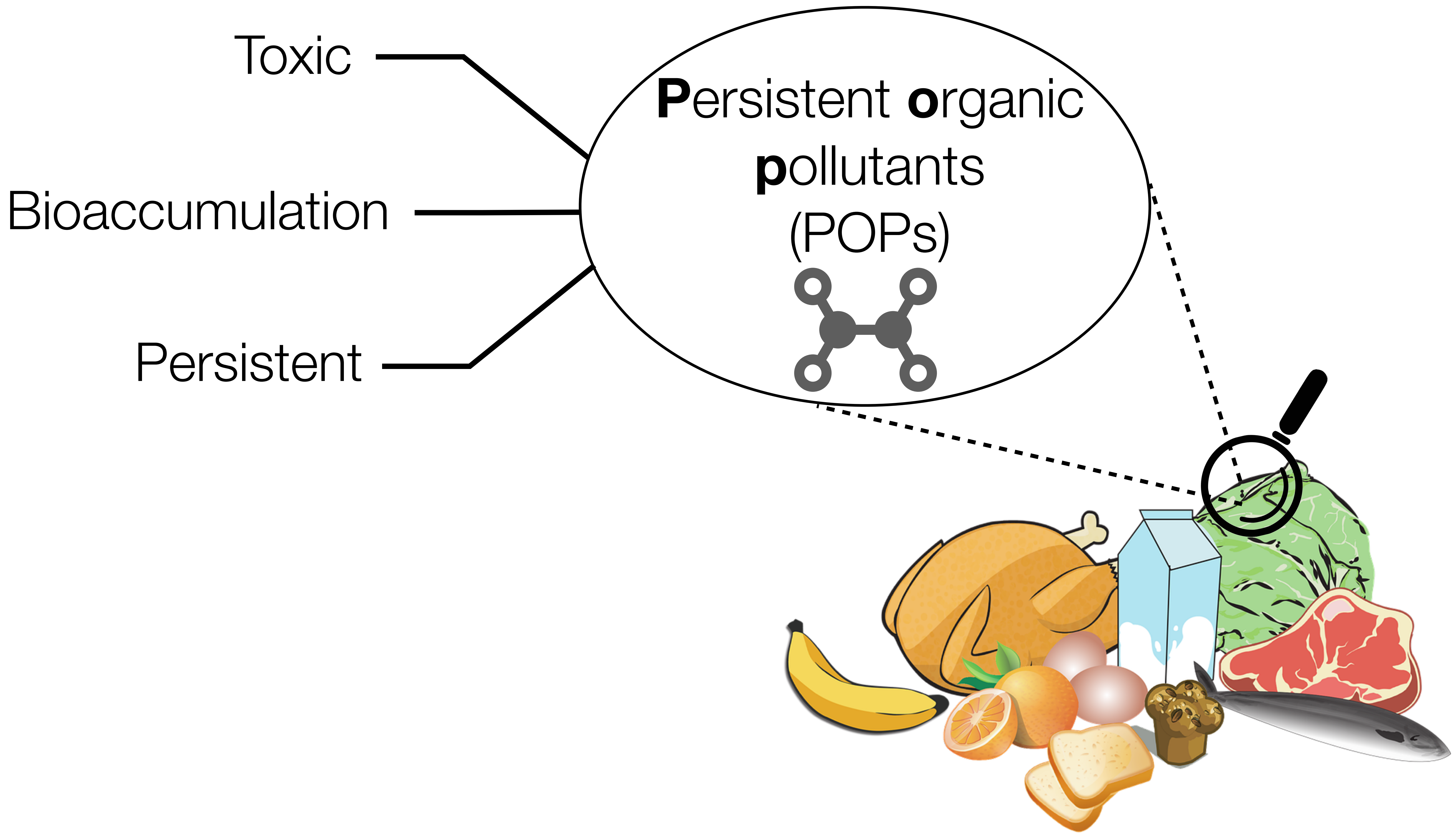
SEPARATION OF COELUTING ISOMER AND ISOBAR COMPOUNDS FROM COMPLEX HALOGENATED POLLUTANT MIXTURES BY GC-APCI-TIMS-TOFMS

24th IMSC conference, 1 September 2022

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

Introduction

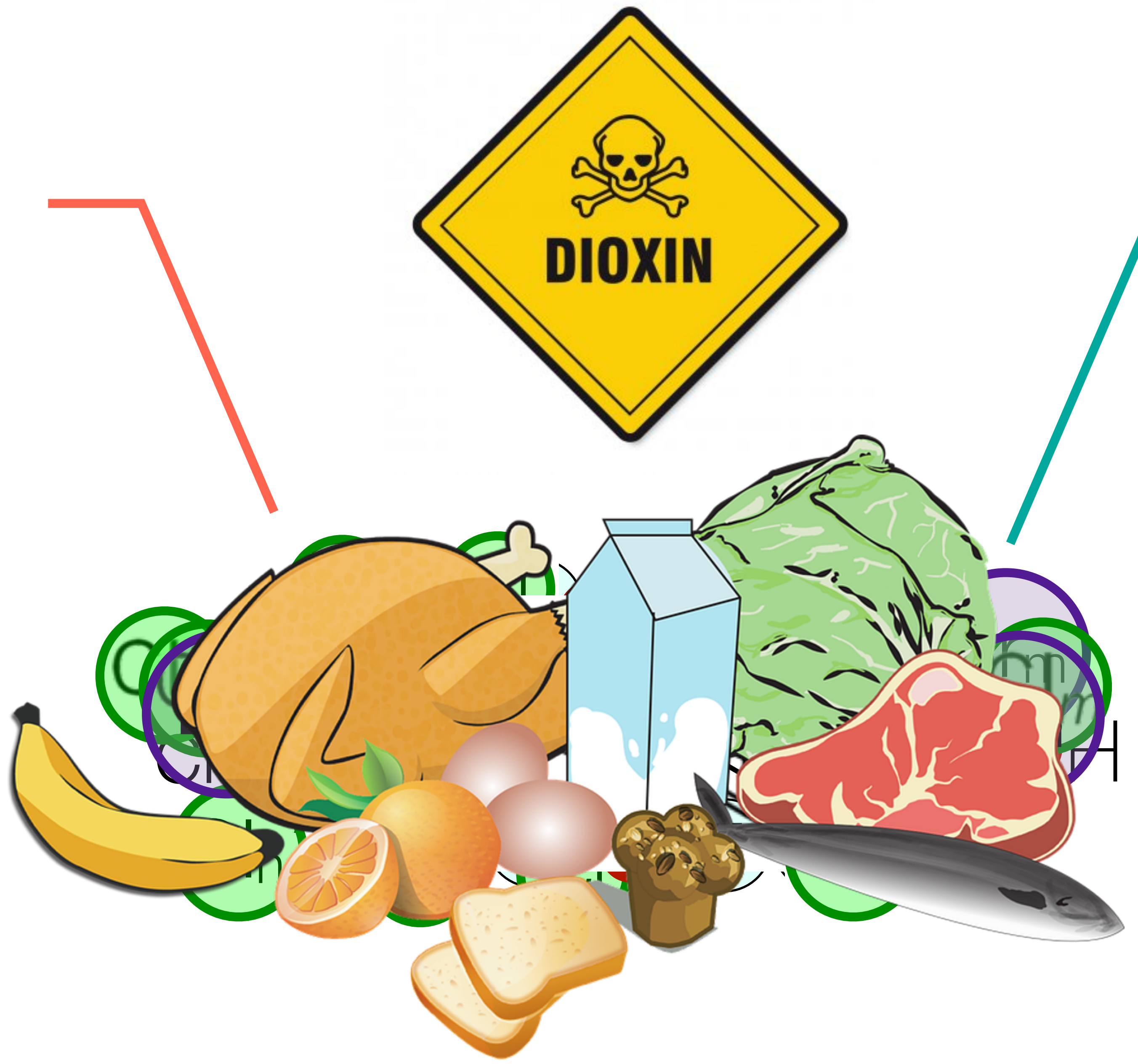
Halogenated POPs



Halogenated POPs

Legacy

Emerging



PCDDs (Dioxins)
Poly**c**hlorinated **D**ibenzo**d**ioxins
n+m = 1 to 8
75 congeners

PFAS
Per**f**luoro**a**lkyl **s**ubstances

PCBs
Poly**c**hlorinated **B**iphenyls
n+m = 1 to 10
209 congeners

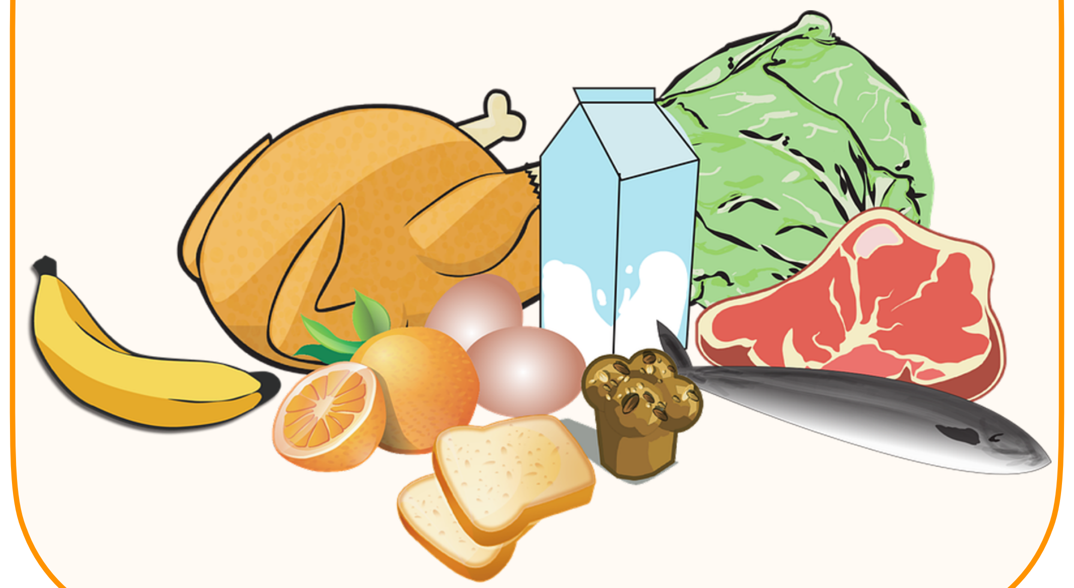
CPs
Chlorinated **p**araffins

PBDEs
Poly**b**rominated **D**iphenyl **E**thers
n+m = 1 to 10
209 congeners

Mixed **Cl-Br** dioxins

Analysis in food

Food sample



Sample prep

Grinding

Freeze-drying

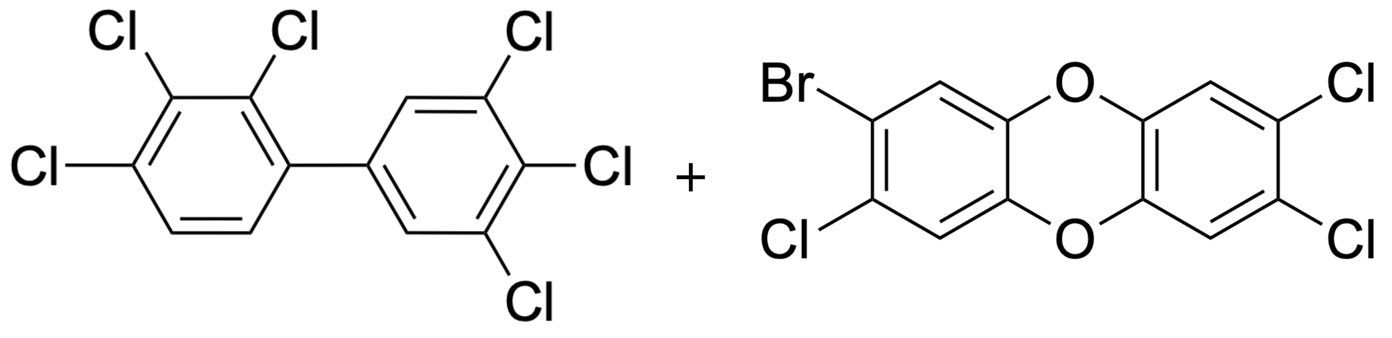
Extraction

Clean-up

How to deal with such challenging coelutions

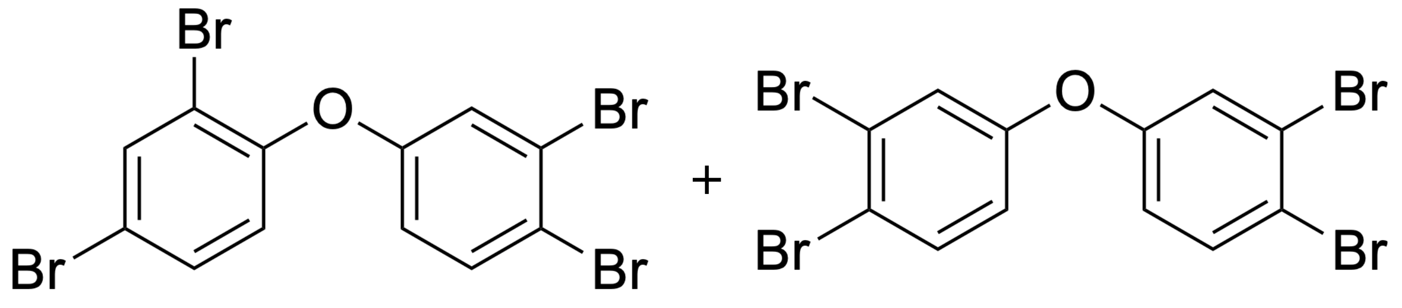
- More intensive sample prep
- Higher mass resolving power
- Additional dimension of separation
  - GCxGC
  - GC-**IMS**
- MS/MS

Isobars coelution
(same **nominal** mass)



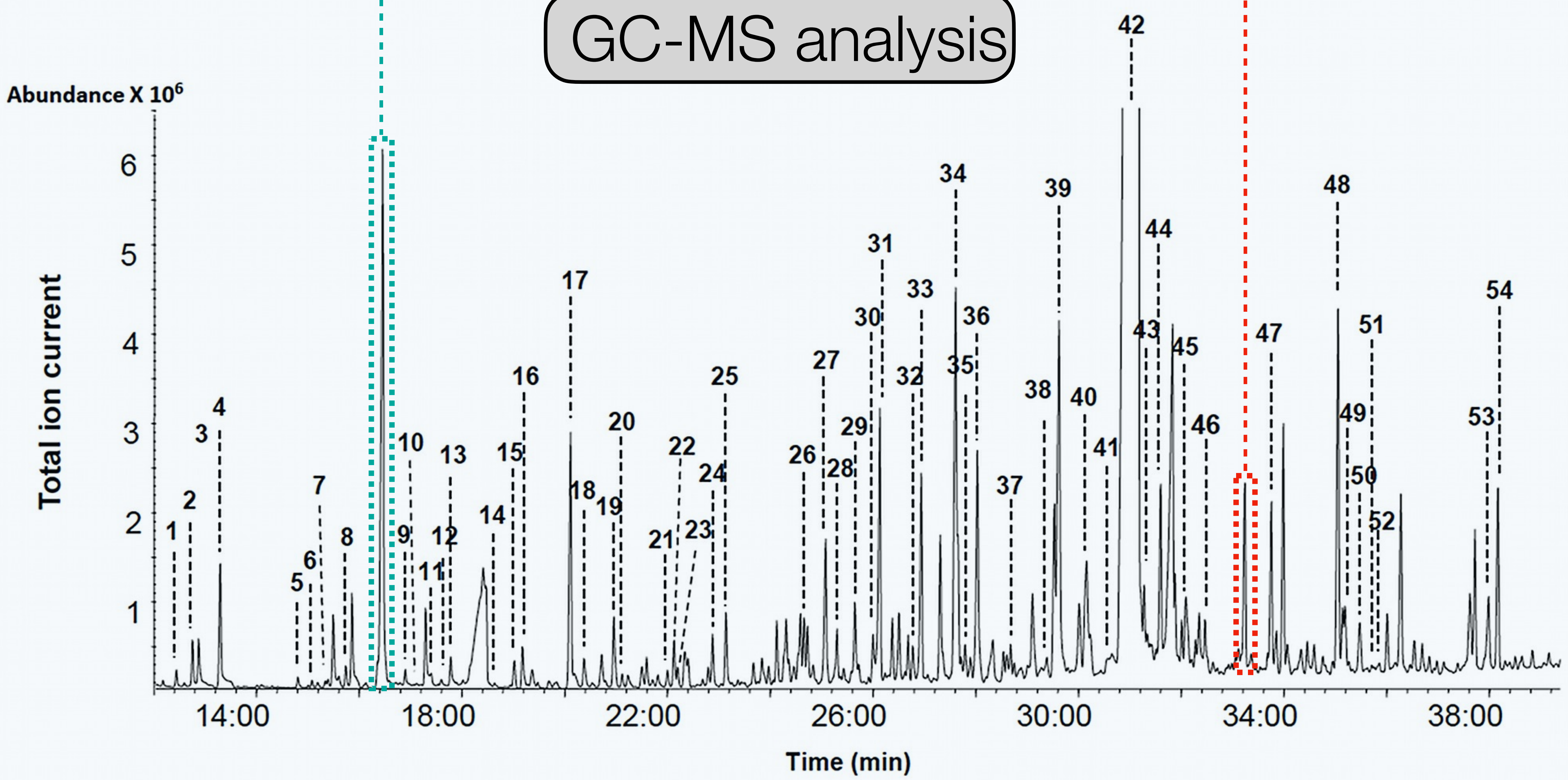
m/z 365.83 m/z 365.84

Isomers coelution
(same **exact** mass)



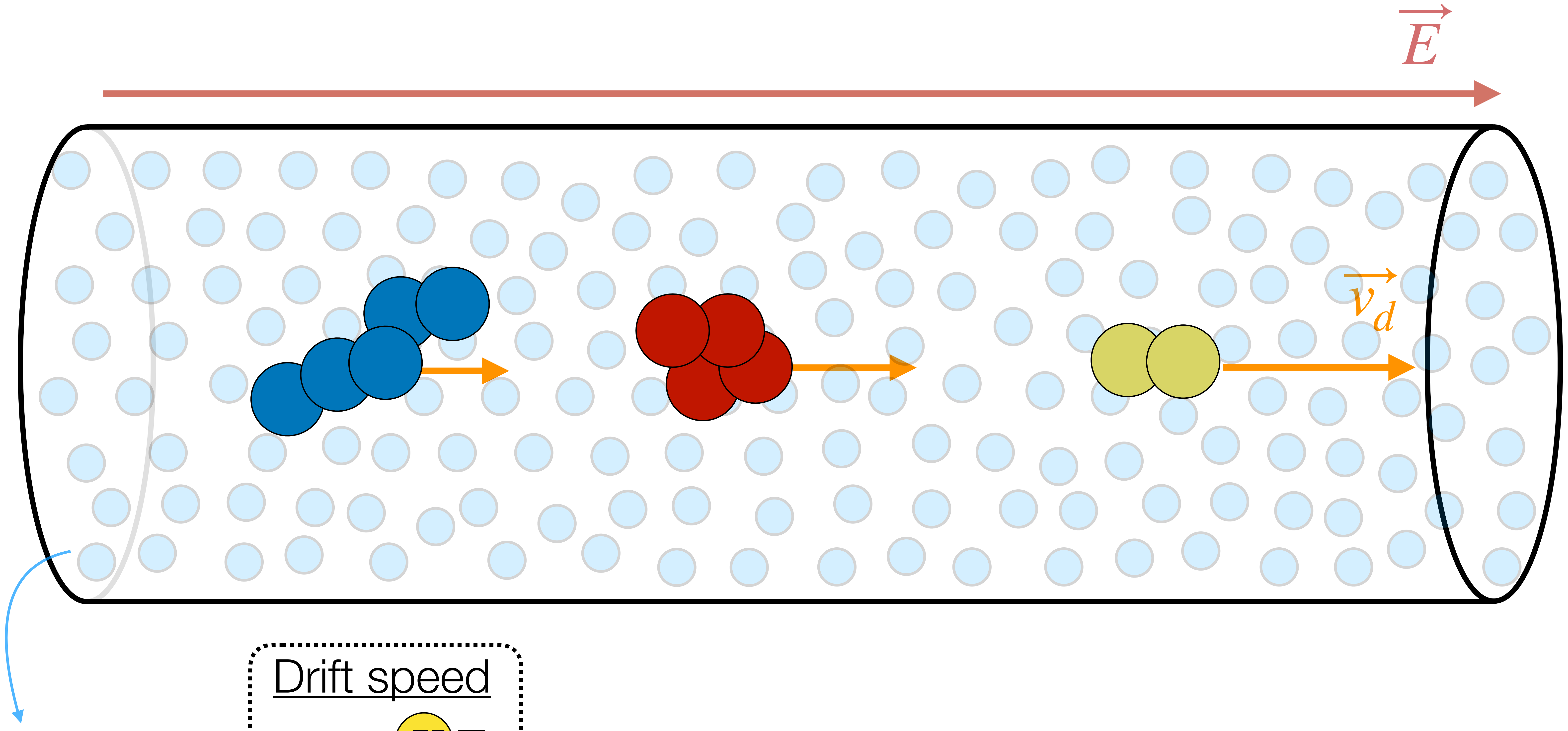
m/z 485.71 m/z 485.71

GC-MS analysis

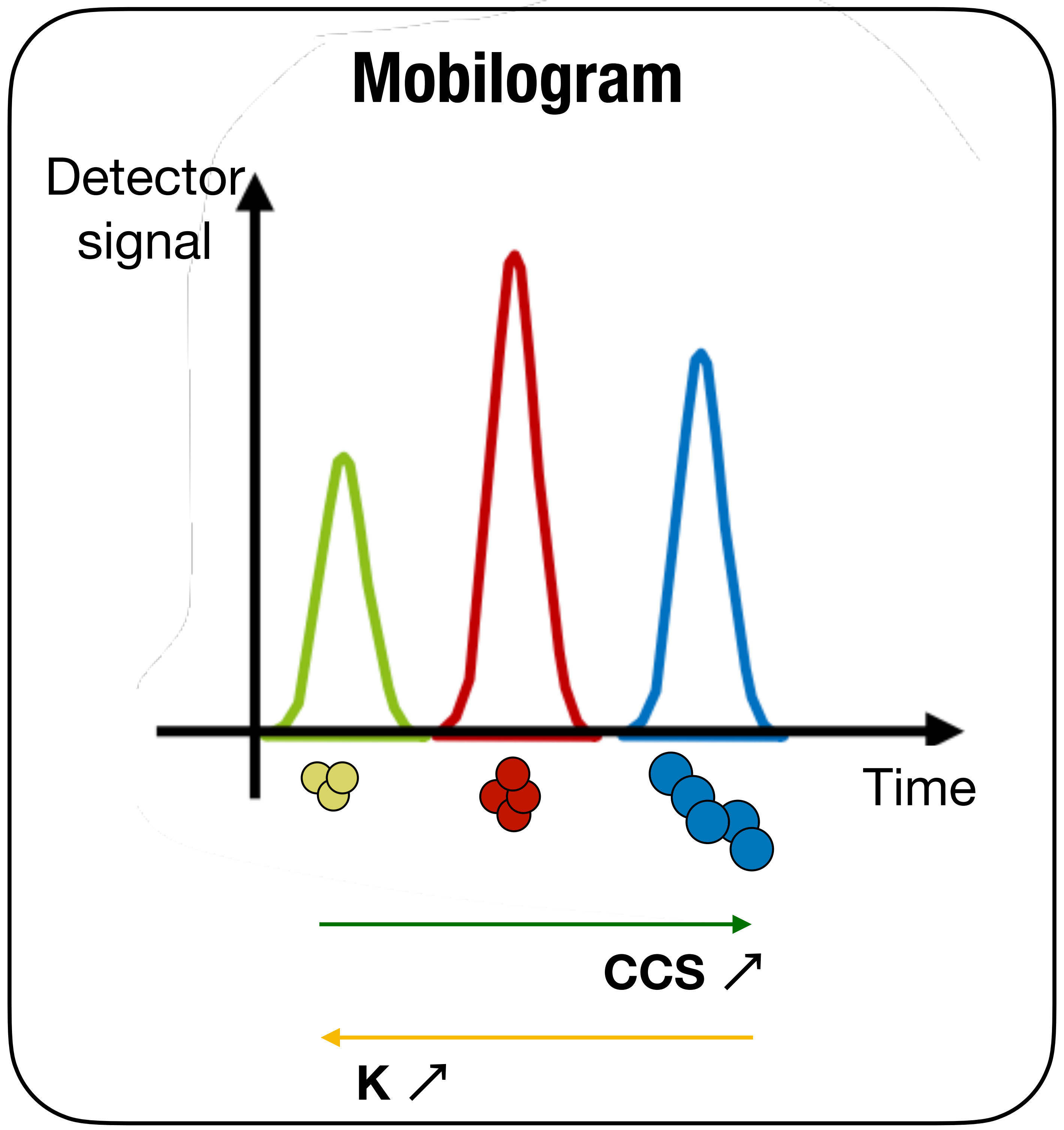


Hugo Muller et. al, "Separation of coeluting isomer and isobar compounds from complex halogenated pollutant mixtures by GC-APCI-TIMS-TOFMS", IMSC 2022

Ion mobility



Drift gas
(He, N_2)



Drift speed

$$v_d = KE$$

Ion mobility constant

Fundamental low-field mobility equation

$$K = \frac{3}{16}\sqrt{\frac{2\pi}{\mu k_b T}}\frac{ze}{N\Omega}$$

→ **C**ollision **c**ross **s**ection (CCS)

- Size & shape
- Ion-gas interaction potential

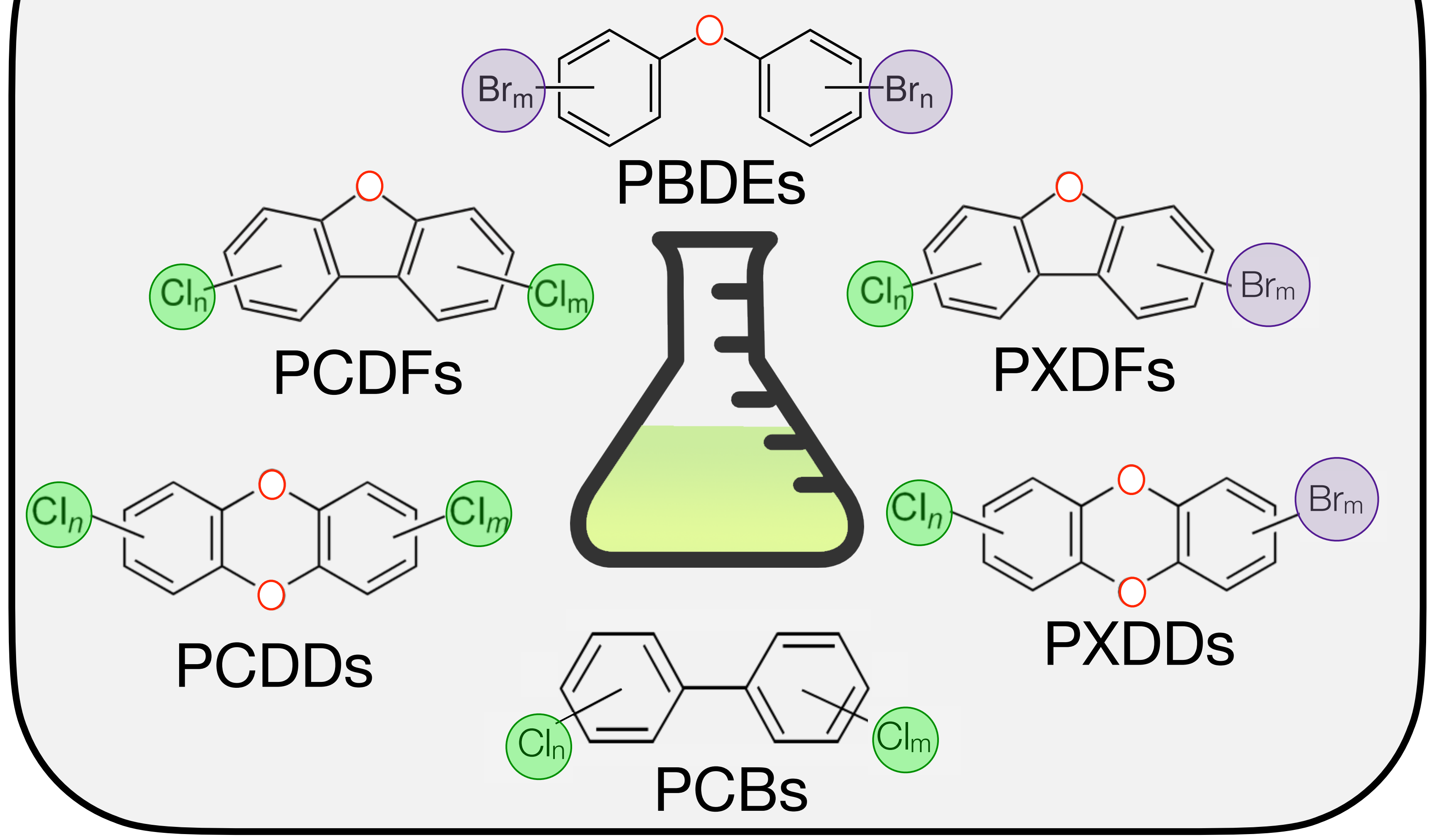
MASS LABORATORY
SPECTROMETRY

LIÈGE université

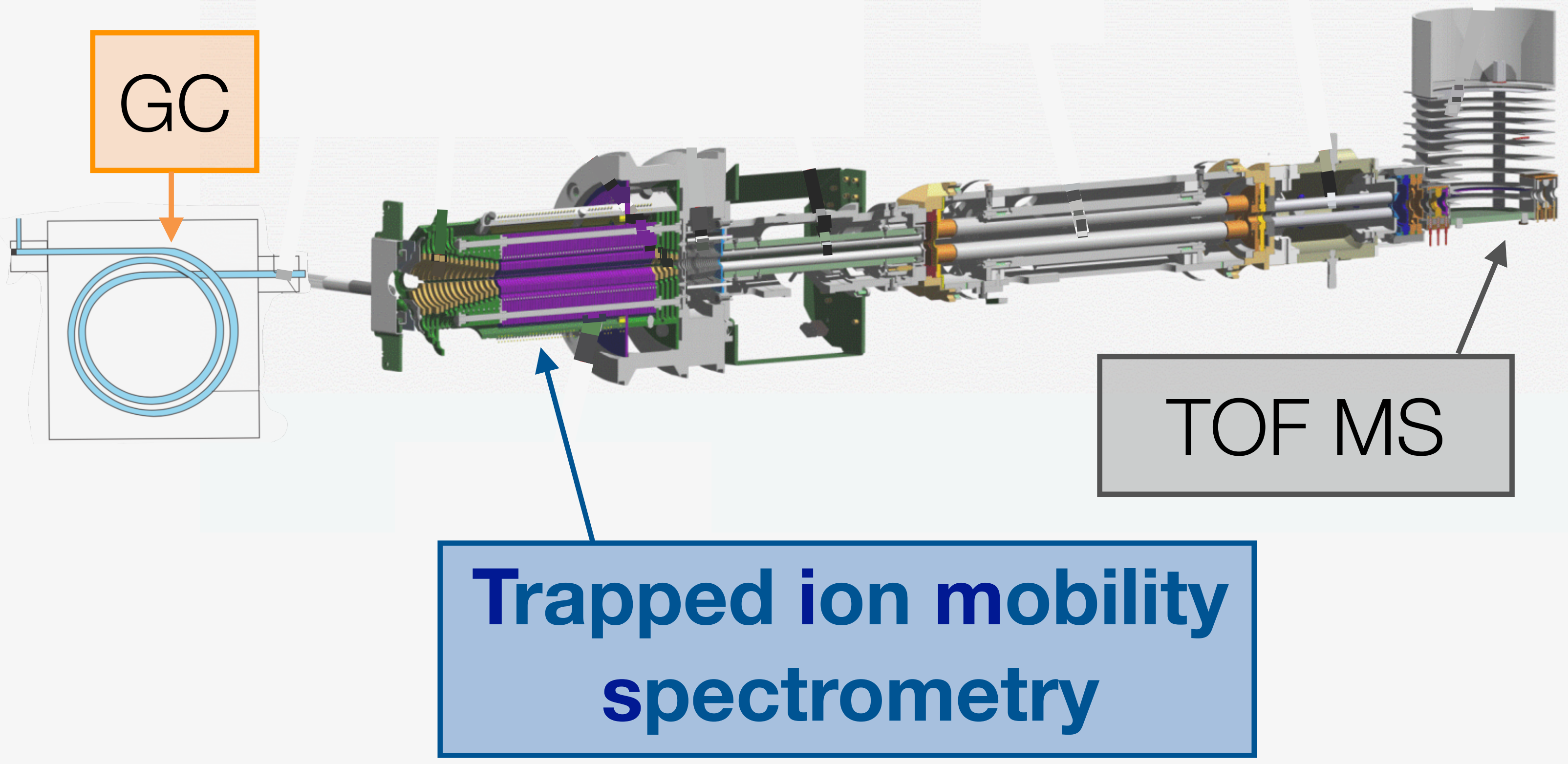
Coeluting isomer & isobar POPs in GC-TIMS-MS

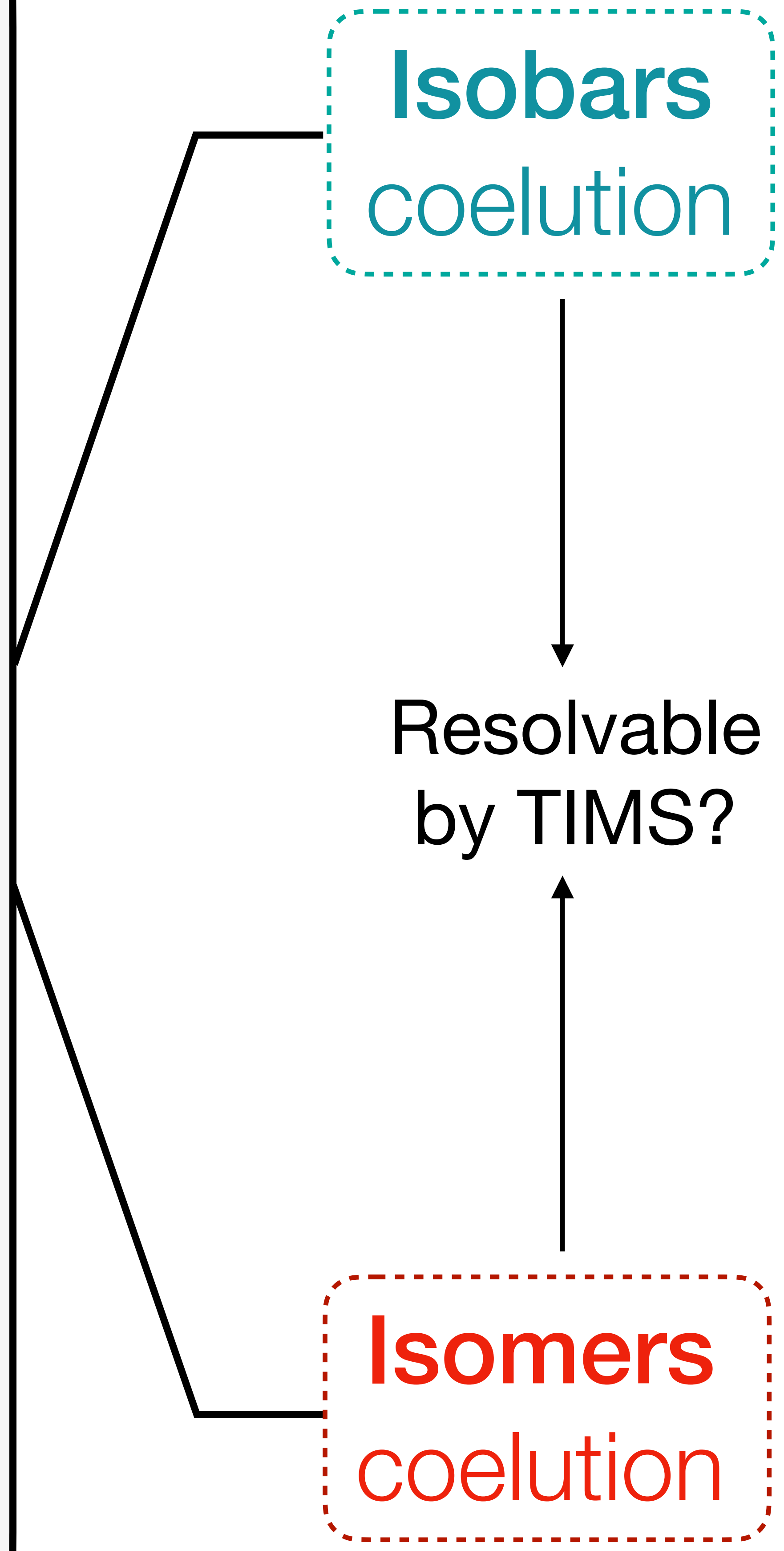
Material & methods

Mixture of 145 POP standards

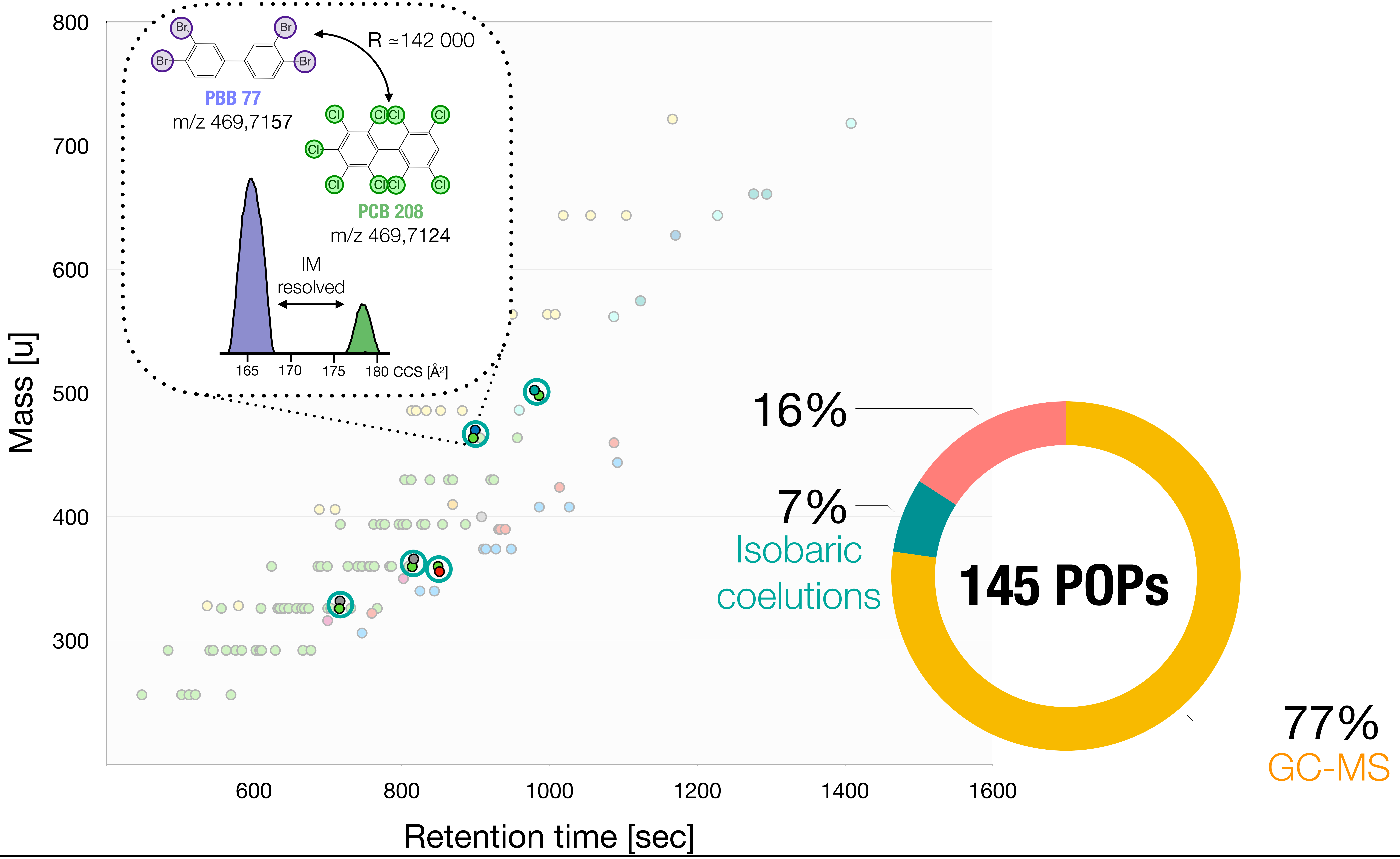


GC-TIMS-MS analysis



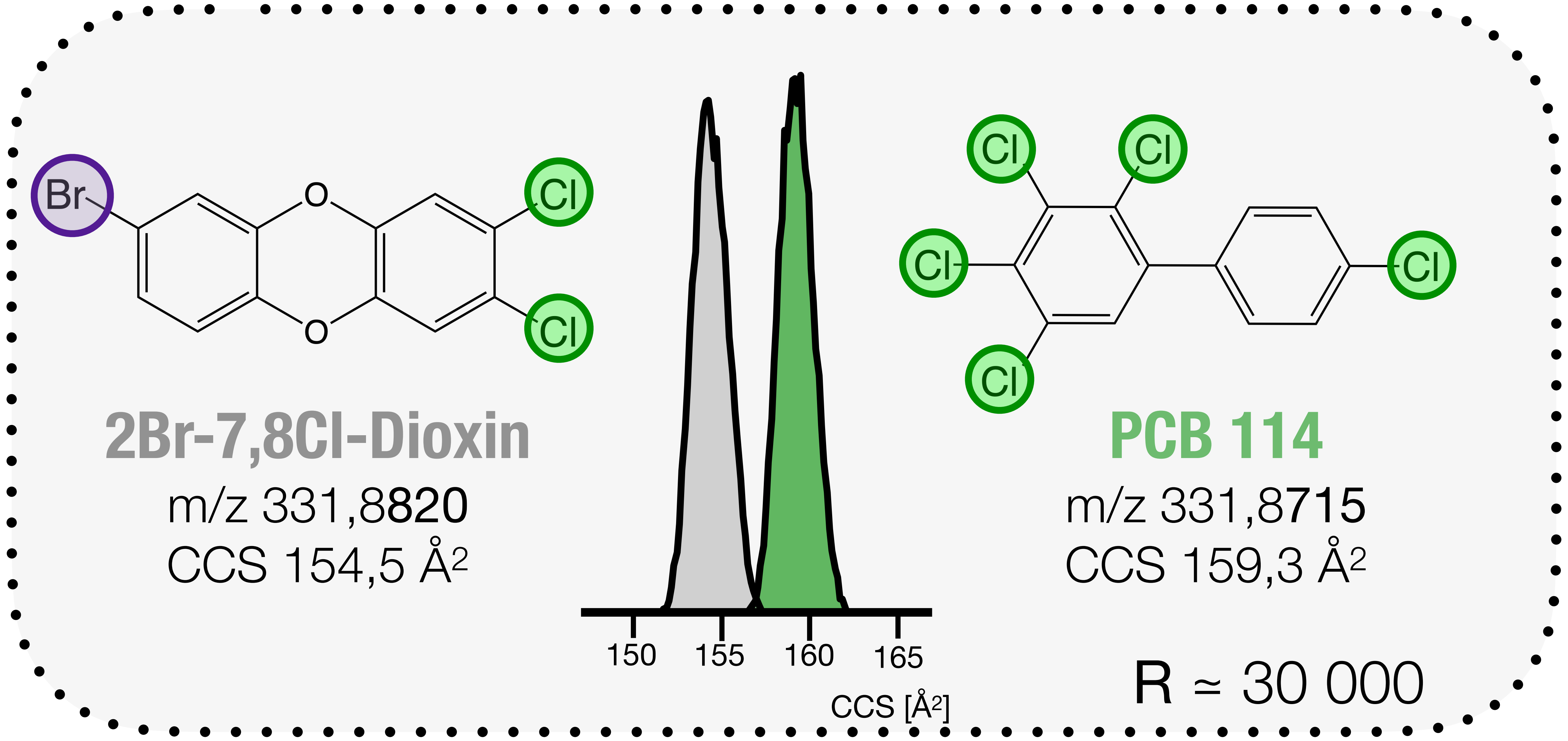


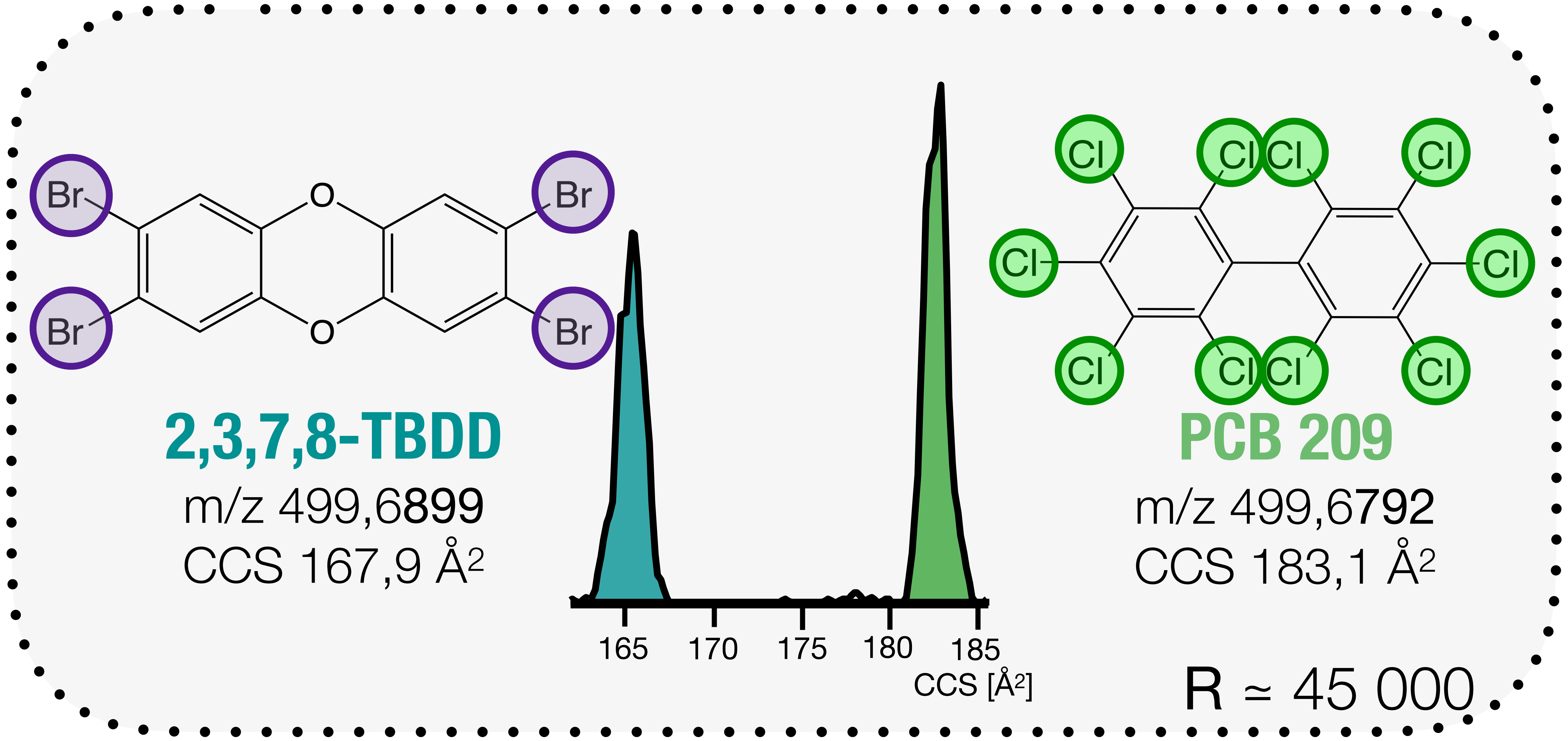
Coeluting isobars

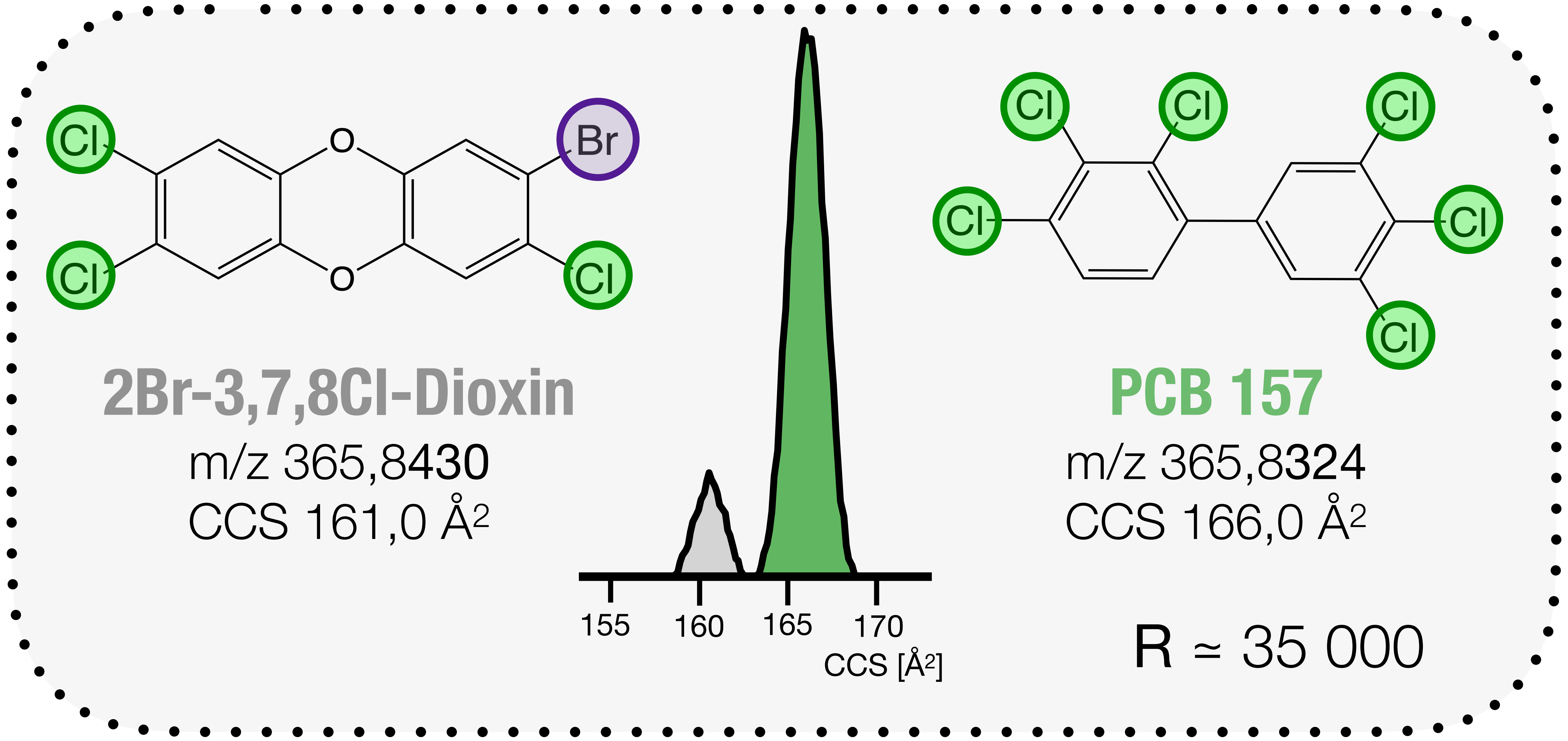


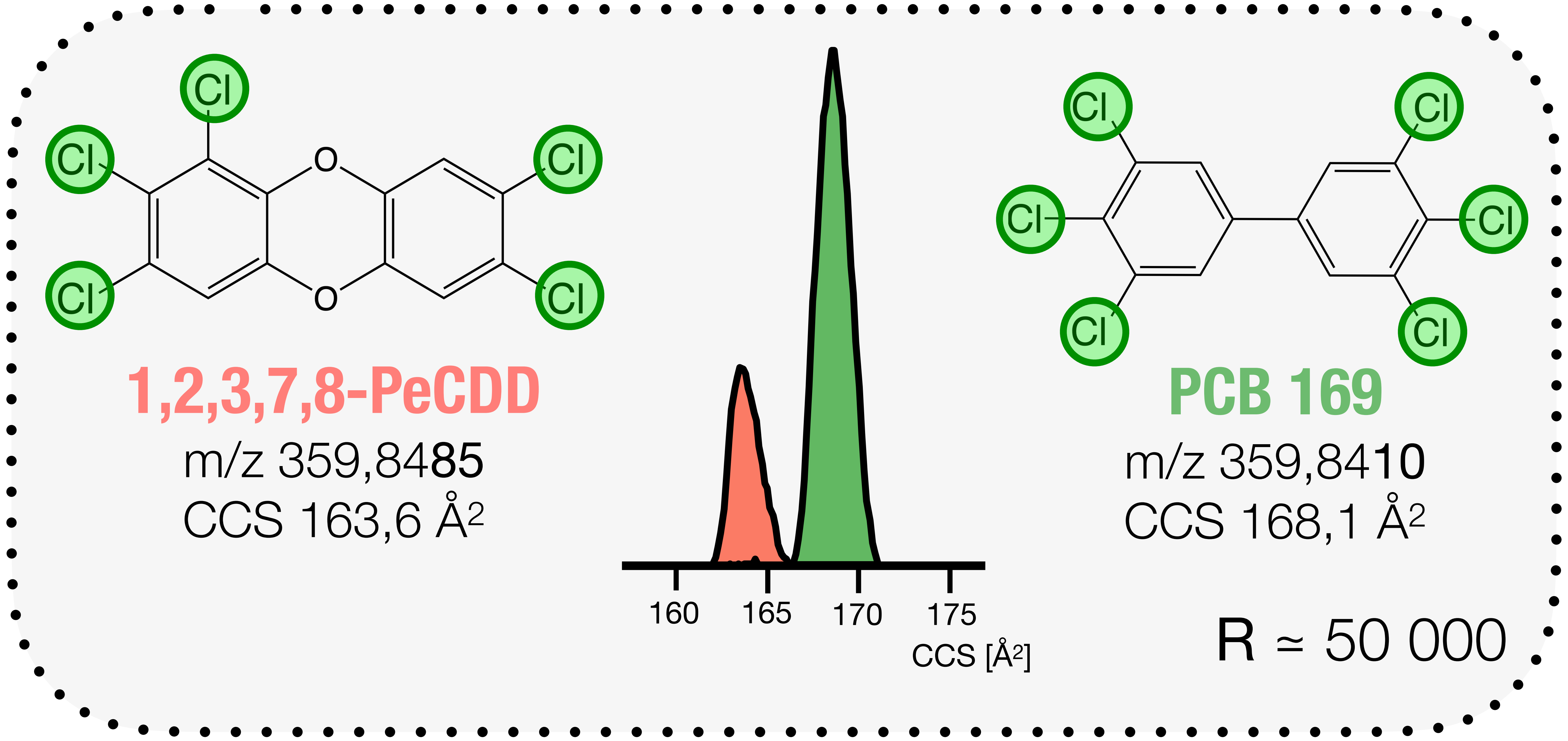
Hugo Muller et. al, "Separation of coeluting isomer and isobar compounds from complex halogenated pollutant mixtures by GC-APCI-TIMS-TOFMS", IMSC 2022

Coeluting isobars



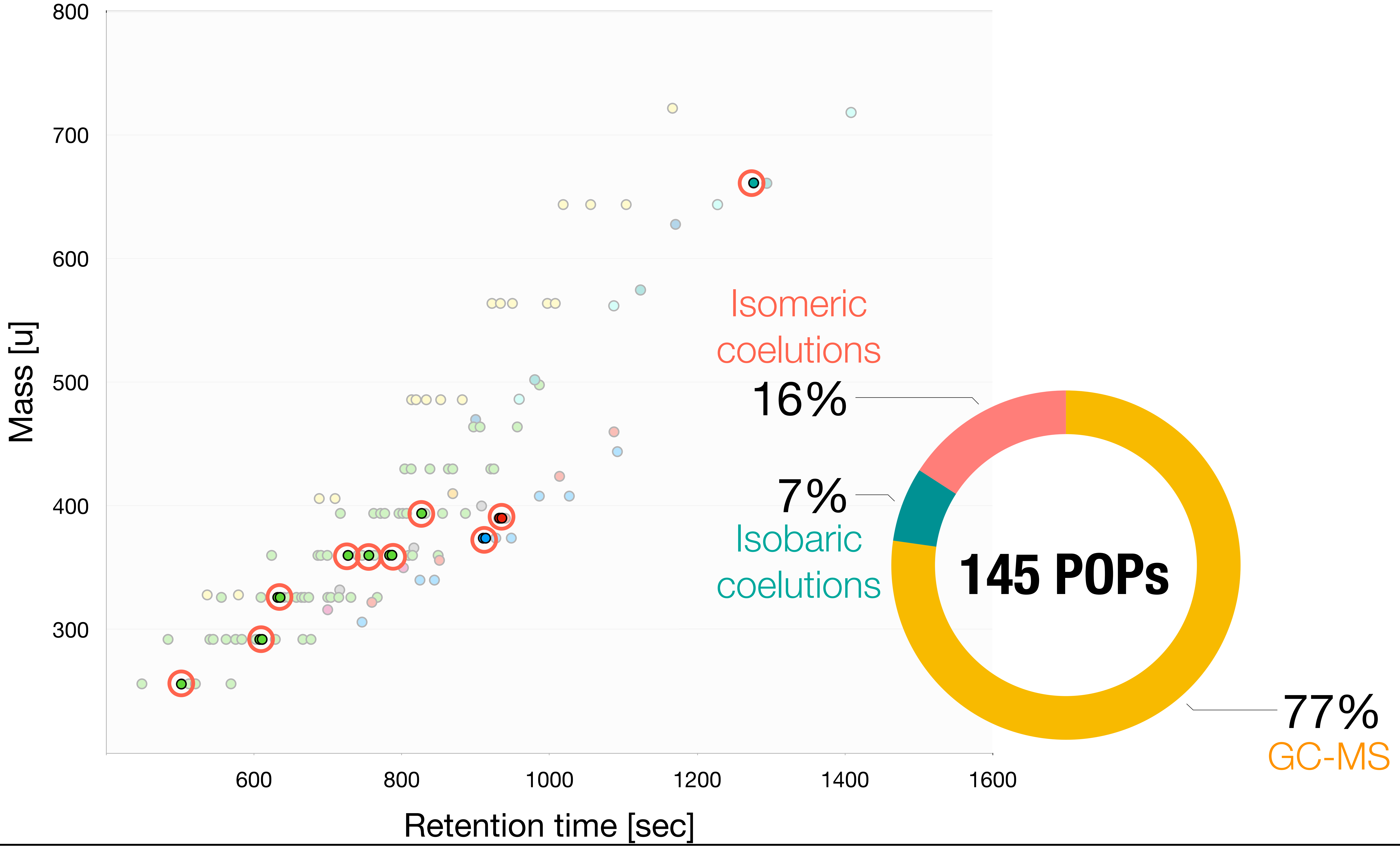






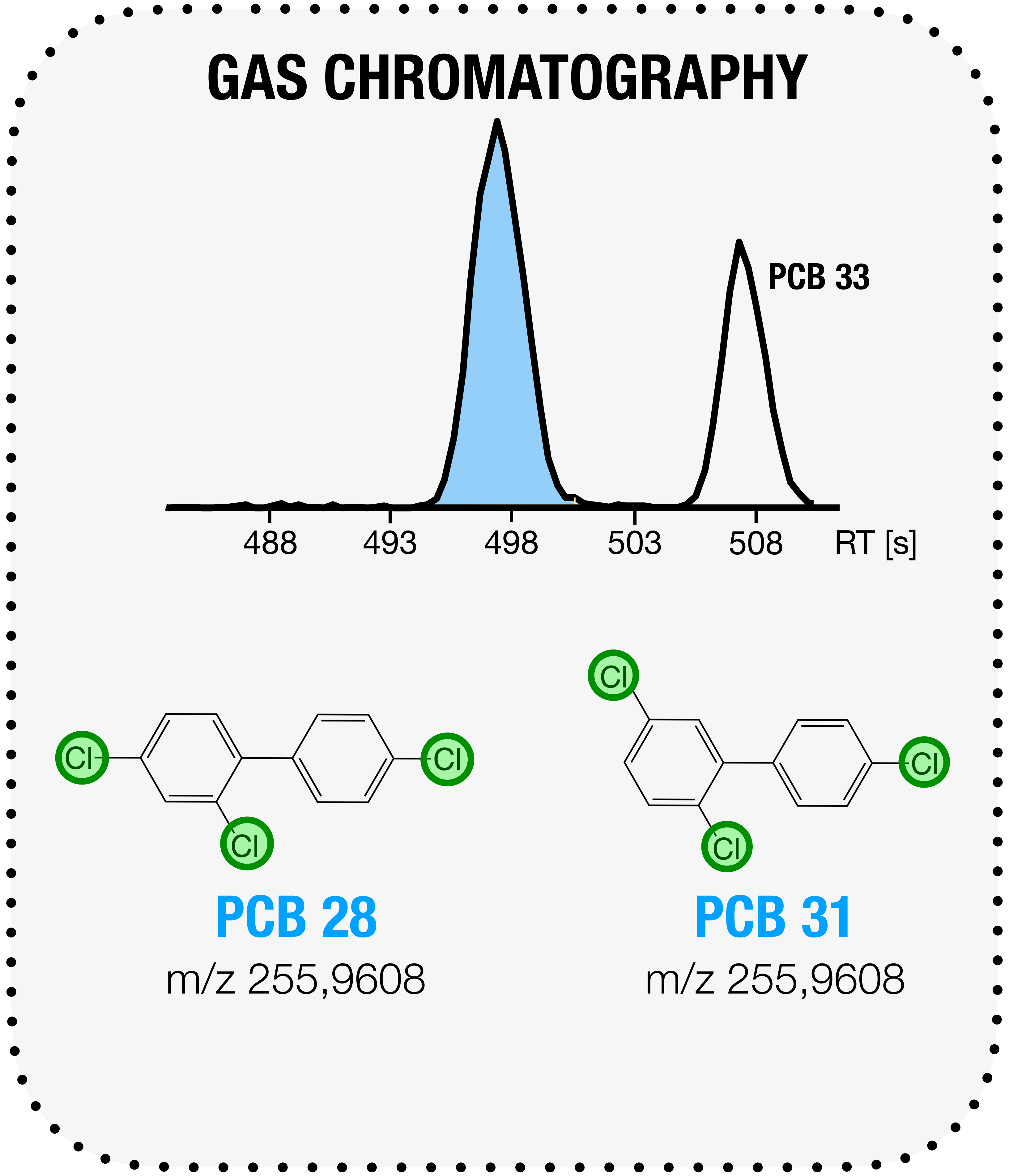
Hugo Muller et. al, “Separation of coeluting isomer and isobar compounds from complex halogenated pollutant mixtures by GC-APCI-TIMS-TOFMS”, IMSC 2022

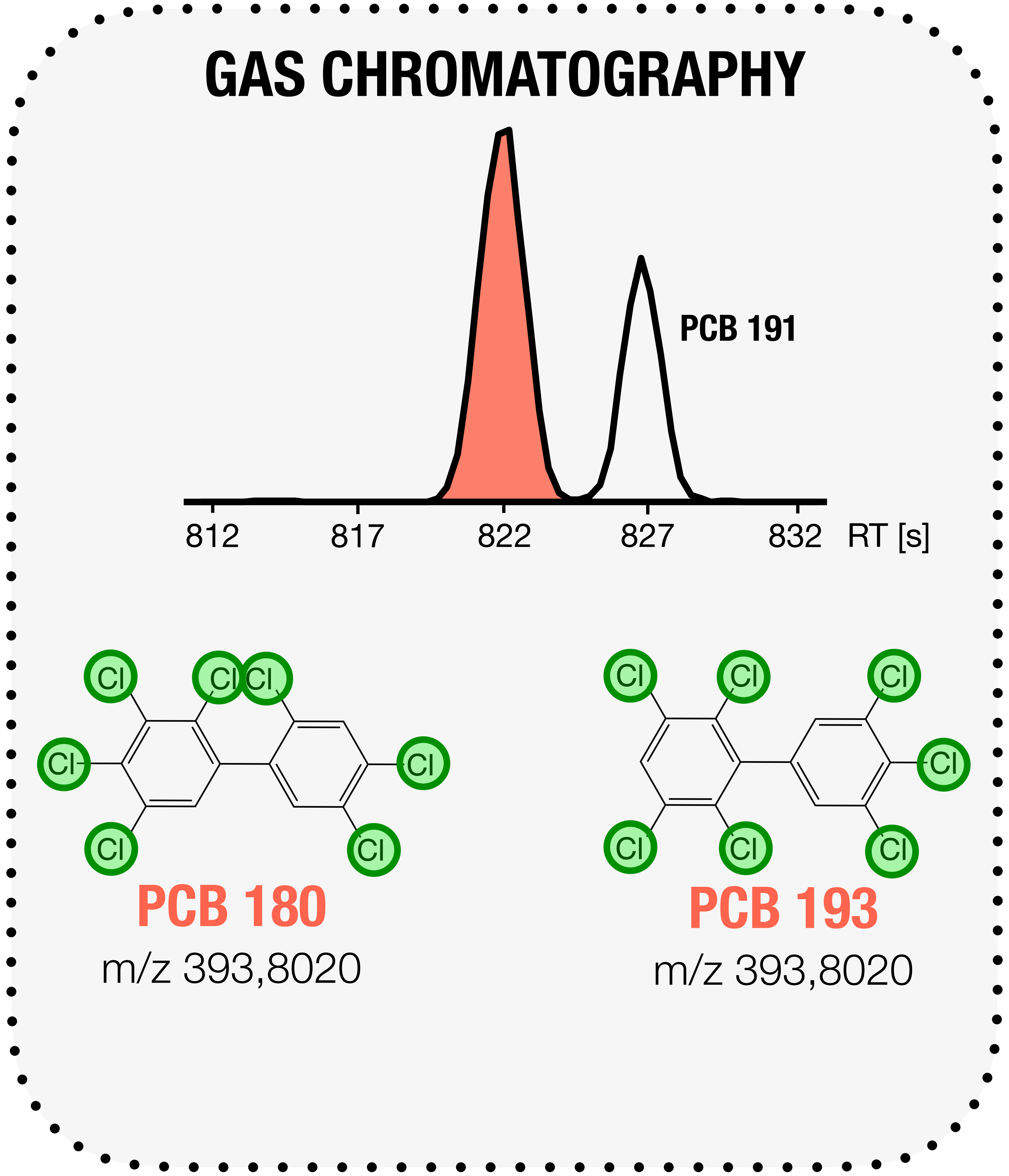
Coeluting isomers

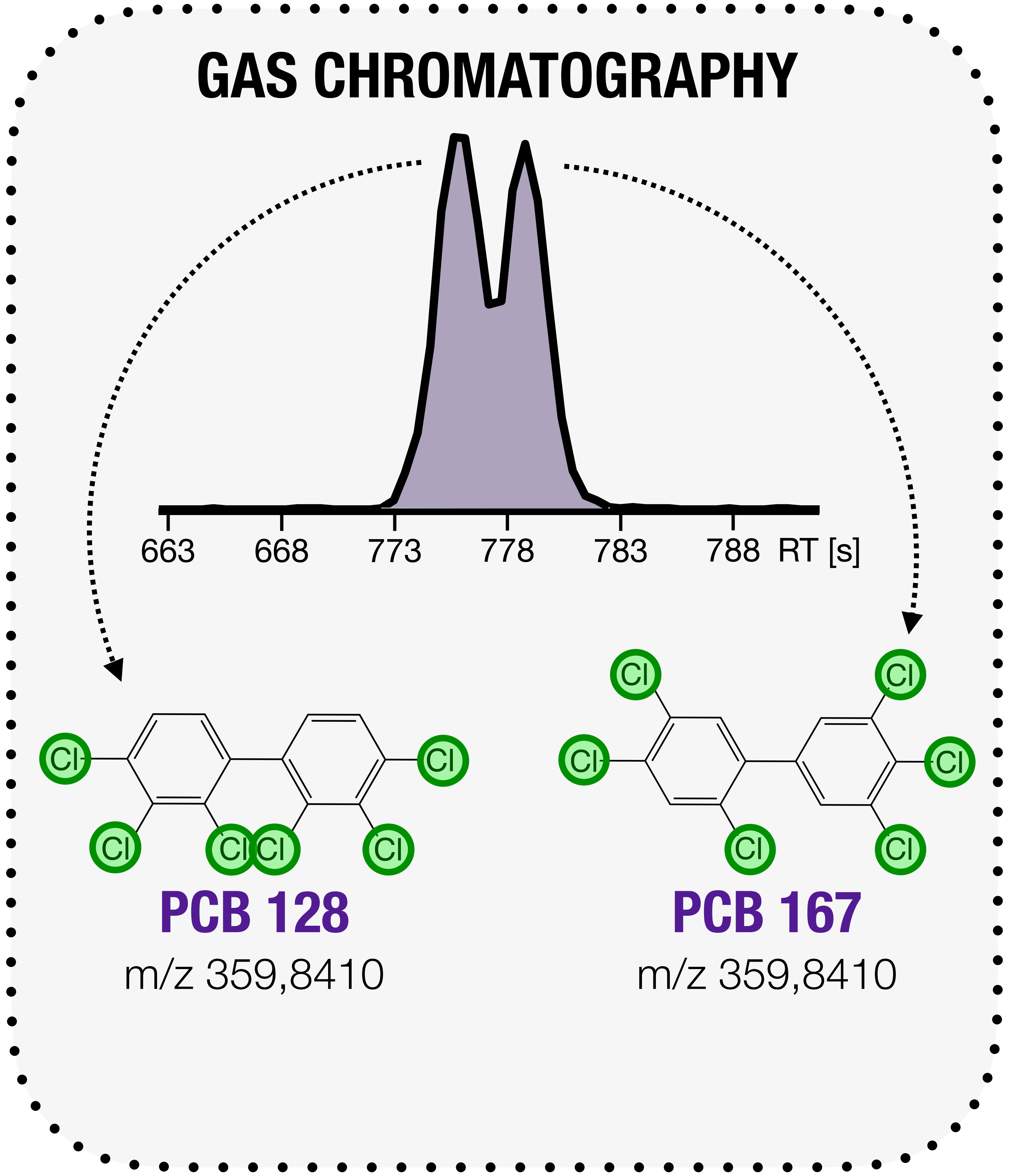


Hugo Muller et. al, “Separation of coeluting isomer and isobar compounds from complex halogenated pollutant mixtures by GC-APCI-TIMS-TOFMS”, IMSC 2022

Coeluting isomers







Hugo Muller et. al, “Separation of coeluting isomer and isobar compounds from complex halogenated pollutant mixtures by GC-APCI-TIMS-TOFMS”, IMSC 2022

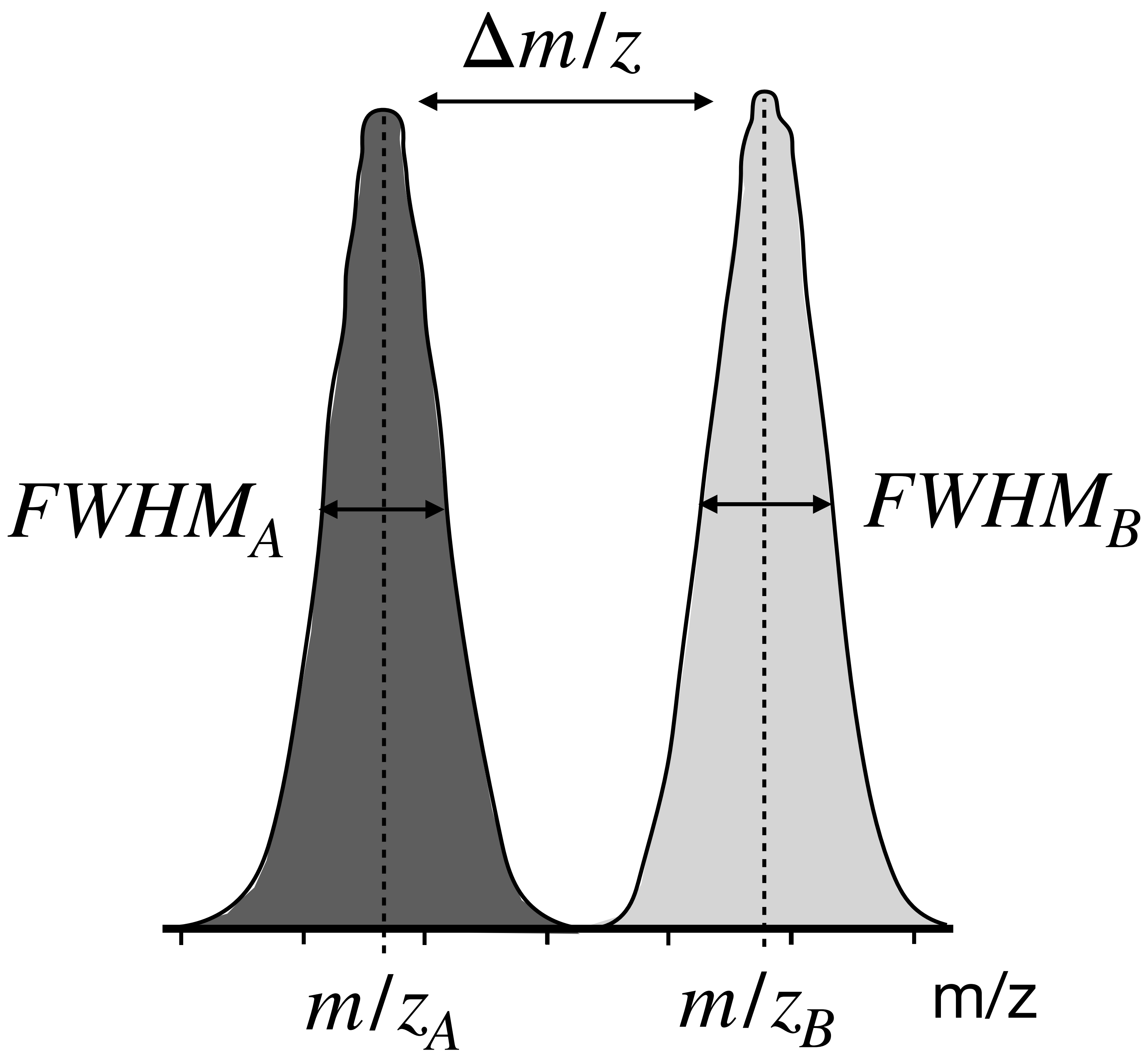
Coeluting isomers

Hugo Muller et. al, “Separation of coeluting isomer and isobar compounds from complex halogenated pollutant mixtures by GC-APCI-TIMS-TOFMS”, IMSC 2022

Resolving power in IM

Resolving power

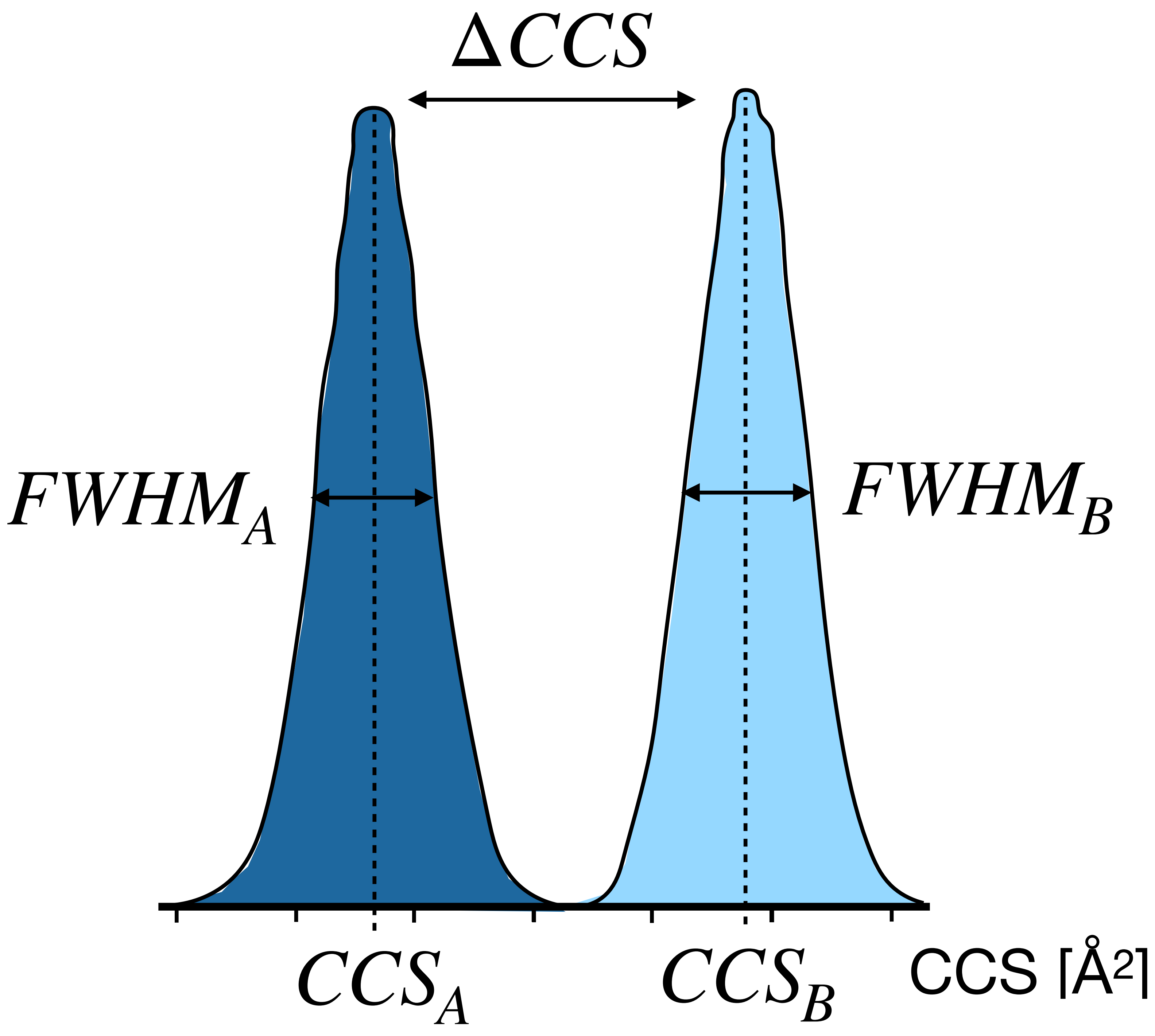
Mass spectrometry



Resolving power

$$R_p = \frac{m/z}{FWHM}$$

Ion mobility

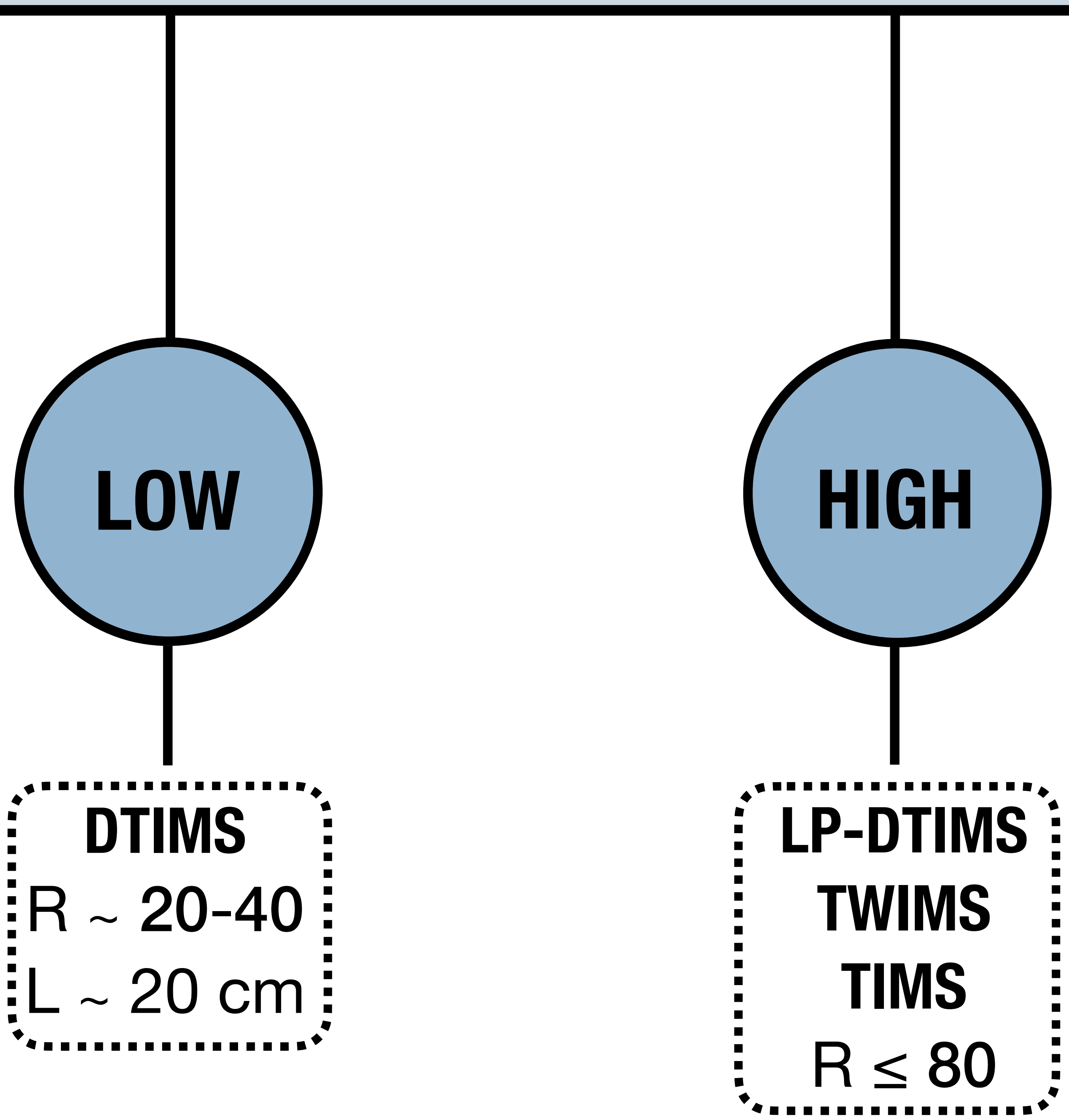


Resolving power

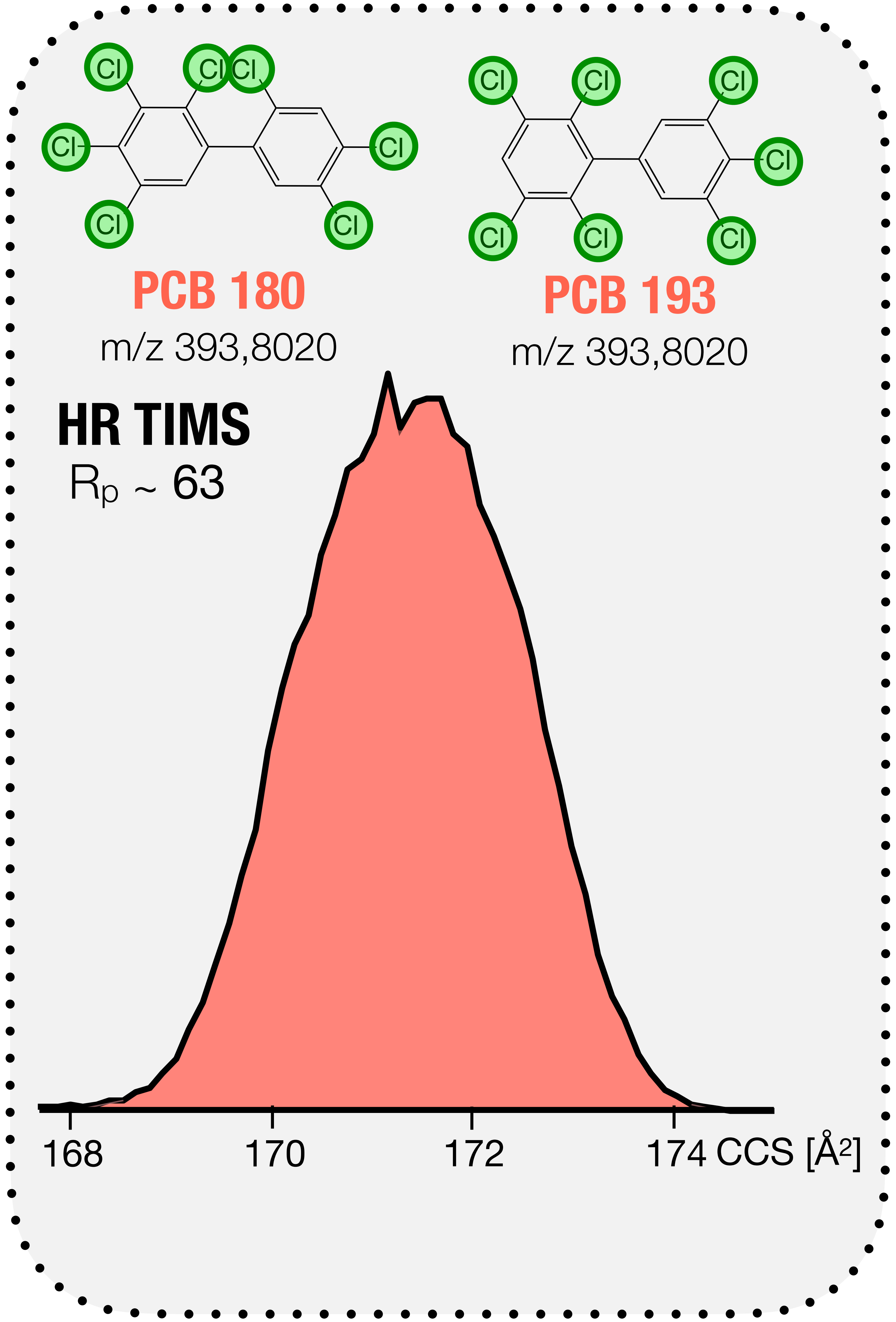
$$R_p = \frac{CCS}{FWHM}$$

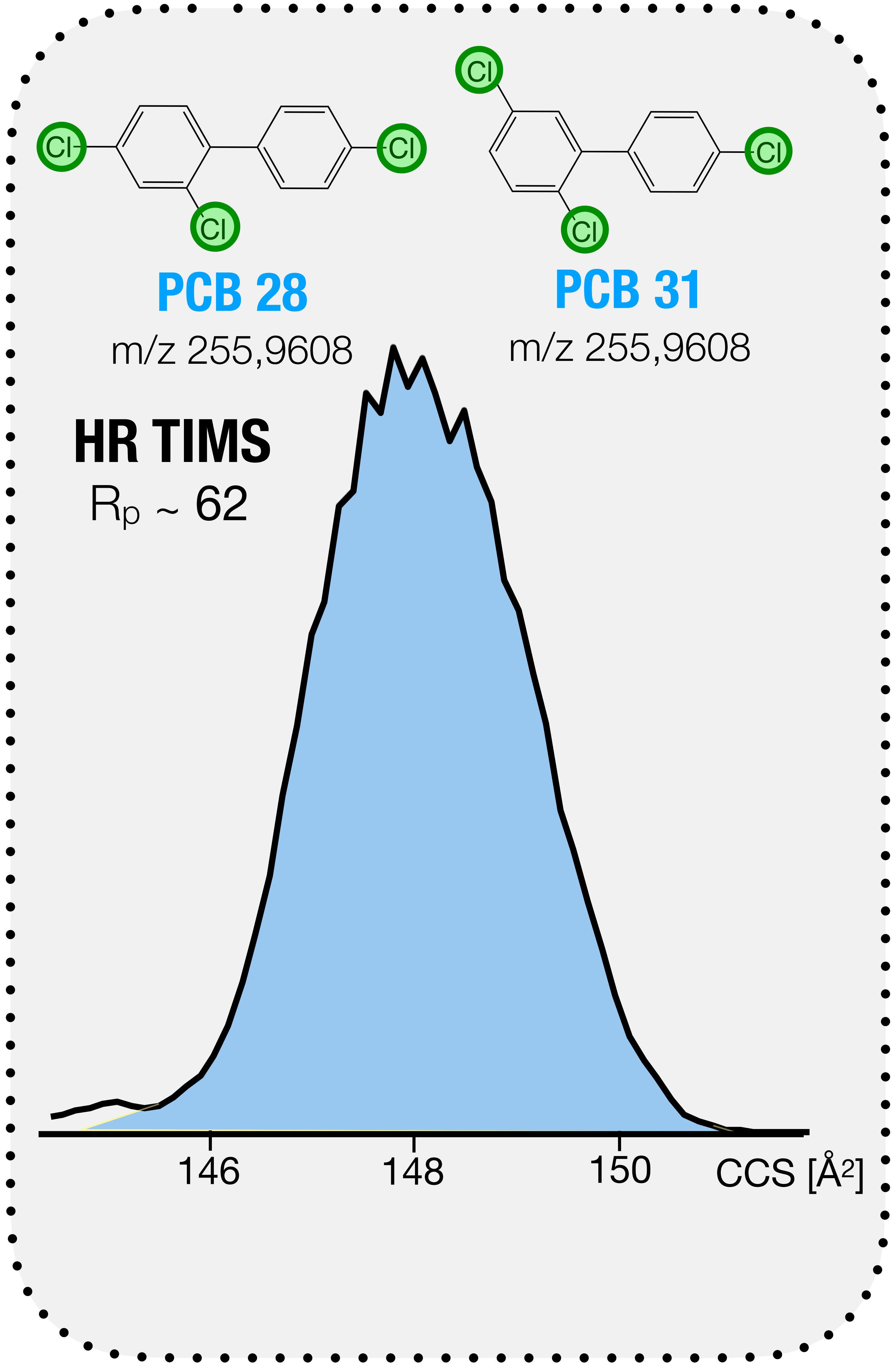
Resolving power

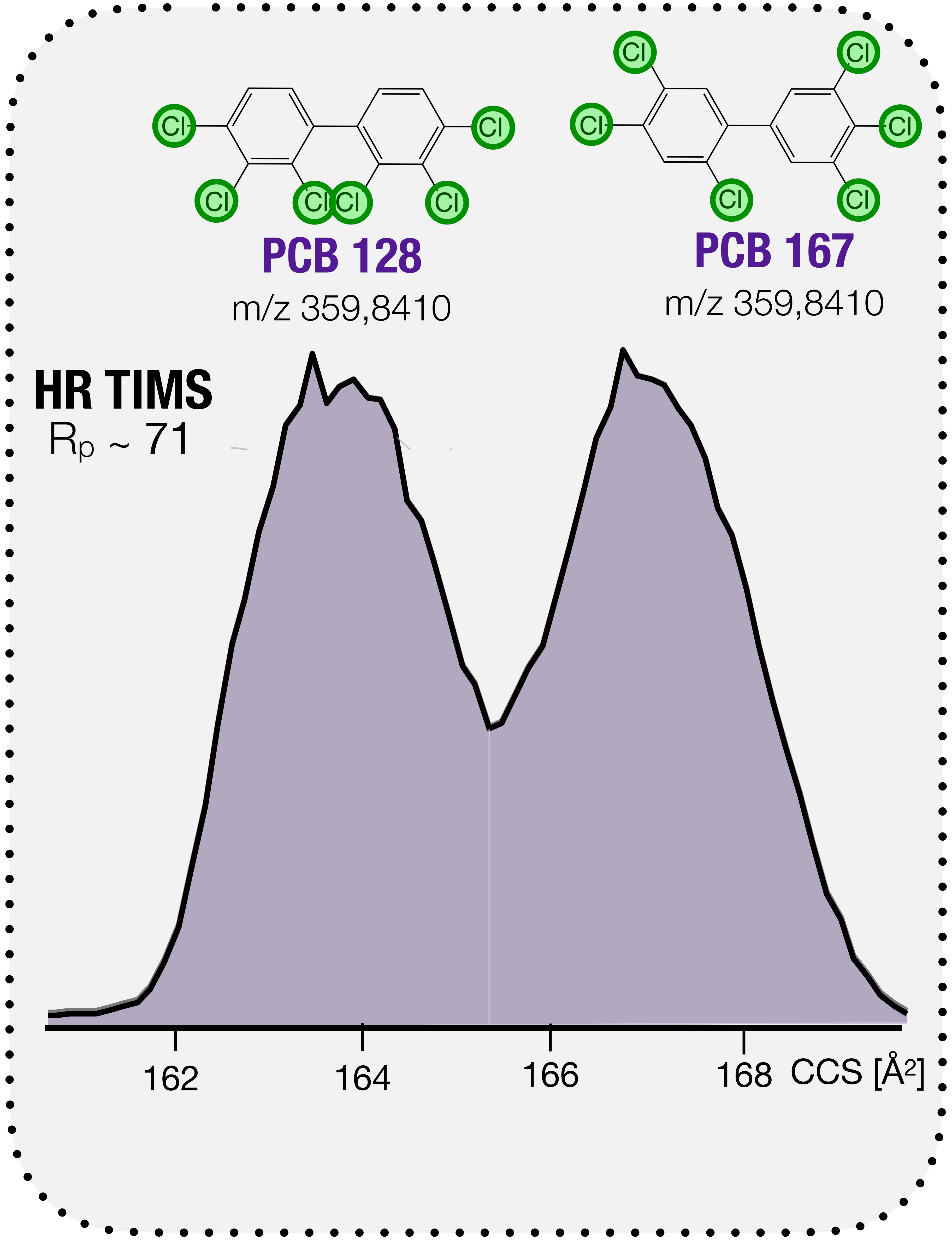
$$R_p = \sqrt{\frac{1}{16\ ln2\ k_b} \times \frac{q}{T} \times E\ L}$$



Coeluting isomers



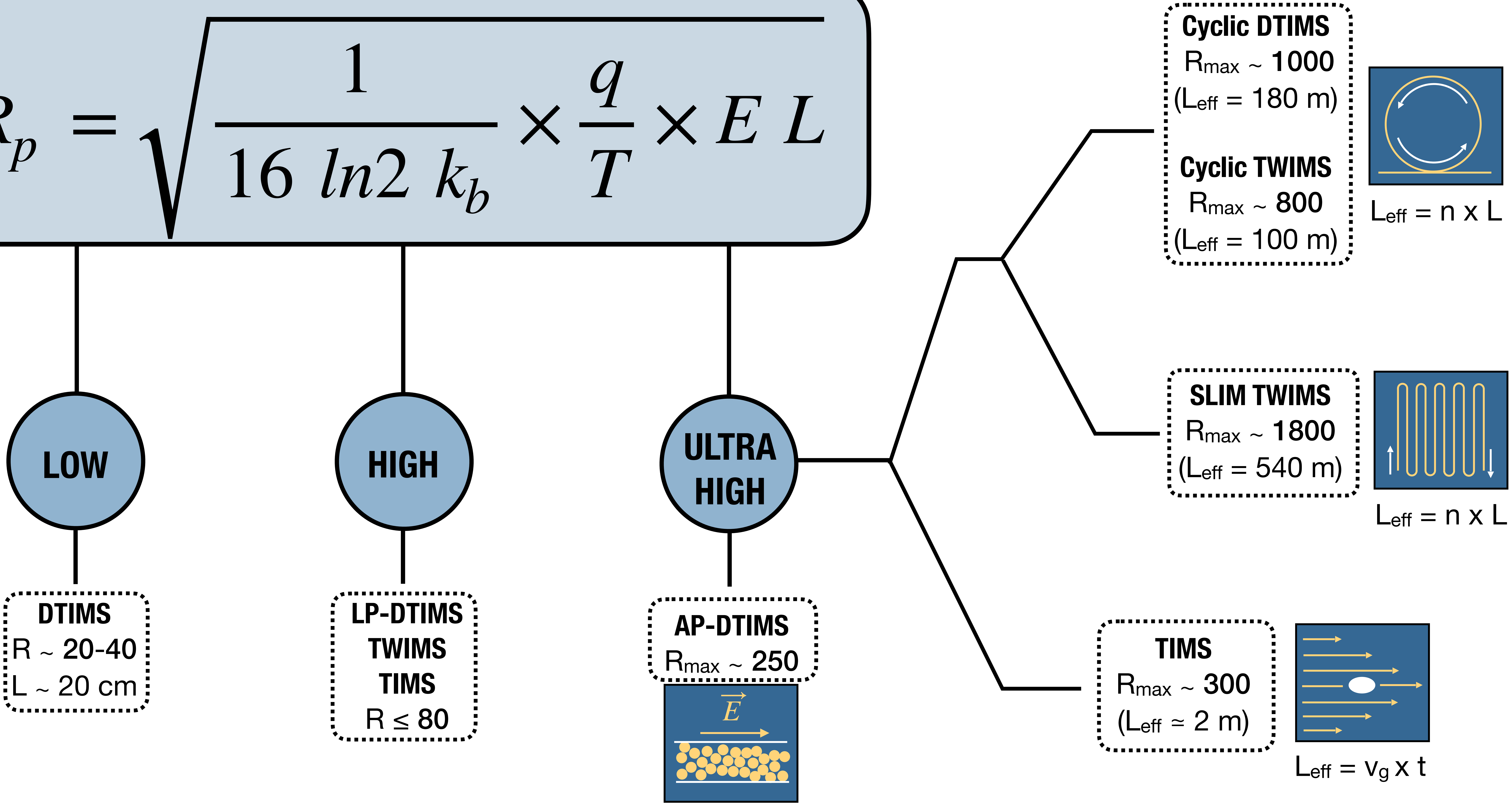




Hugo Muller et. al, “Separation of coeluting isomer and isobar compounds from complex halogenated pollutant mixtures by GC-APCI-TIMS-TOFMS”, IMSC 2022

Resolving power

$$R_p = \sqrt{\frac{1}{16\ ln2\ k_b} \times \frac{q}{T} \times E\ L}$$



Coeluting isomers

Hugo Muller et. al, "Separation of coeluting isomer and isobar compounds from complex halogenated pollutant mixtures by GC-APCI-TIMS-TOFMS", IMSC 2022

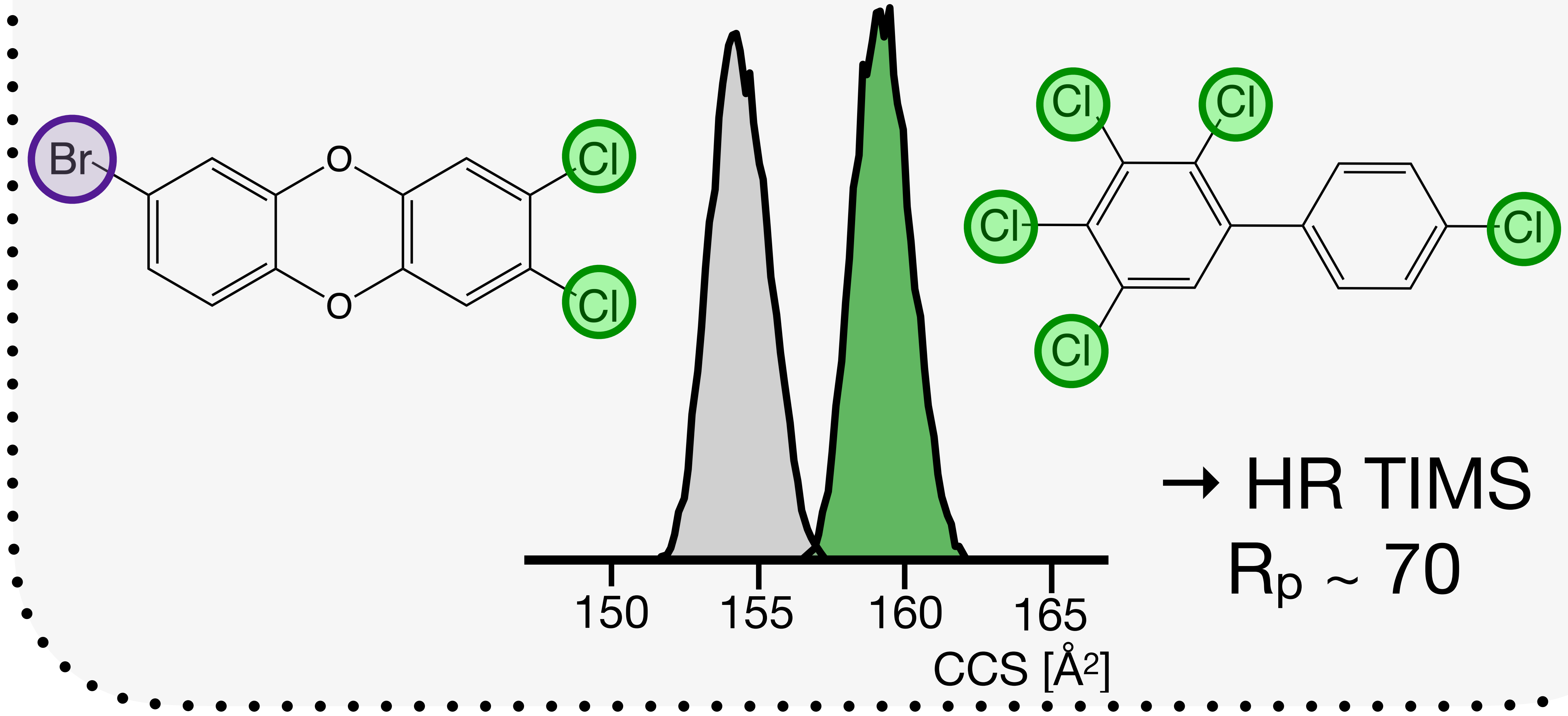
Conclusion

Summary

GC-TIMS-MS

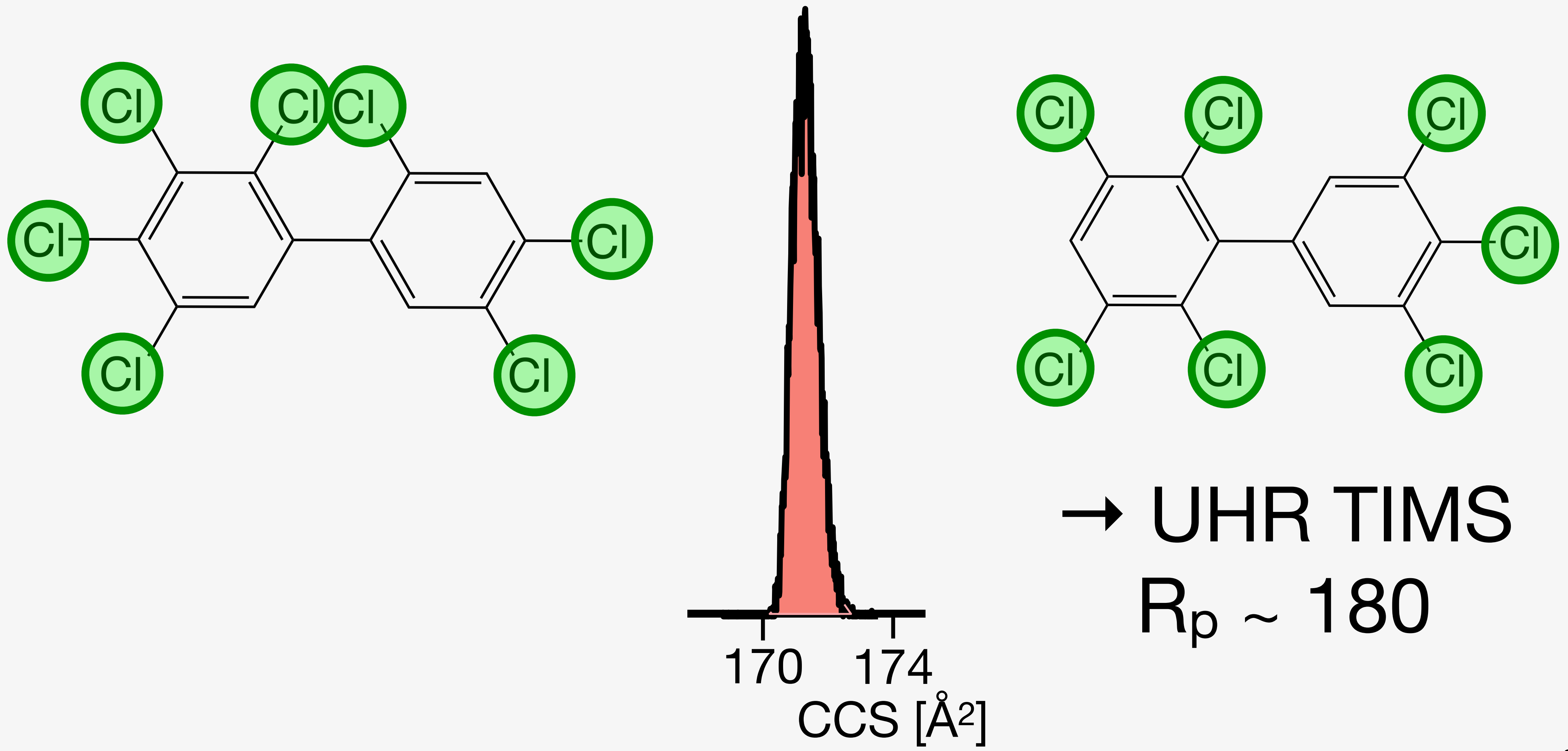
Coeluting isobars

Baseline separation



Coeluting isomers

No separation



Hugo Muller et. al, “Separation of coeluting isomer and isobar compounds from complex halogenated pollutant mixtures by GC-APCI-TIMS-TOFMS”, IMSC 2022

Publication

analytical chemistry

pubs.acs.org/ac Article

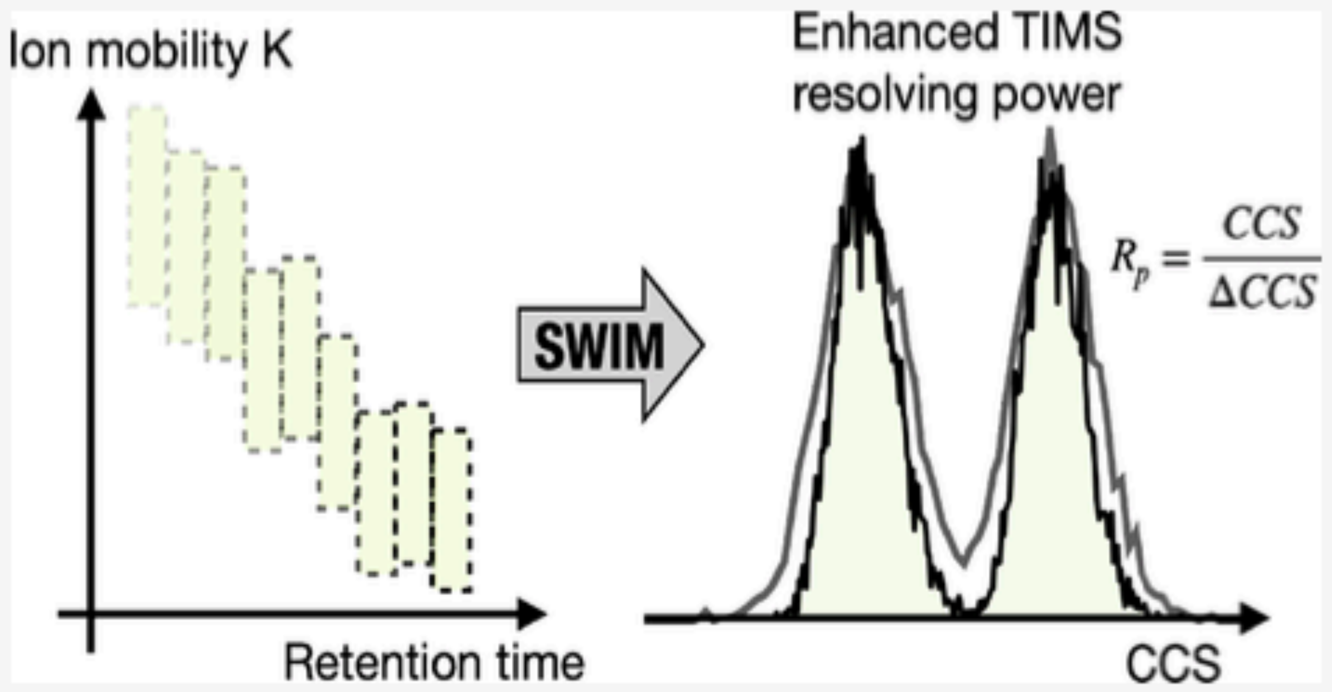
Sliding Windows in Ion Mobility (SWIM): A New Approach to Increase the Resolving Power in Trapped Ion Mobility-Mass Spectrometry Hyphenated with Chromatography

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

Cite This: *Anal. Chem.* 2023, 95, 17586–17594 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Over the past decade, the separation efficiency achieved by linear IMS instruments has increased substantially, with state-of-the-art IM technologies, such as the trapped ion mobility (TIMS), the cyclic traveling wave ion mobility (cTWIMS), and the structure for lossless ion manipulation (SLIM) platforms commonly demonstrating resolving powers in excess of 200. However, for complex sample analysis that require front end separation, the achievement of such high resolving power in TIMS is significantly hampered, since the ion mobility range must be broad enough to analyze all the classes of compounds of interest, whereas the IM analysis time must be short enough to cope with the time scale of the preseparation technique employed.



In this paper, we introduce the concept of sliding windows in ion mobility (SWIM) for chromatography hyphenated TIMS applications that bypasses the need to use a wide and fixed IM range by using instead narrow and mobile ion mobility windows that adapt to the analytes' ion mobility during chromatographic separation. GC-TIMS-MS analysis of a mixture of 174 standards from several halogenated persistent organic pollutant (POP) classes, including chlorinated and brominated dioxins, biphenyls, and PBDEs, demonstrated that the average IM resolving power could be increased up to 40% when the SWIM mode was used, thereby greatly increasing the method selectivity for the analysis of complex samples.

https://doi.org/10.1021/acs.analchem.3c03039

Hugo Muller et. al, "Separation of coeluting isomer and isobar compounds from complex halogenated pollutant mixtures by GC-APCI-TIMS-TOFMS", IMSC 2022

MS LABORATORY
SPECTROMETRY

- Pr Gauthier Eppe
- Edwin de Pauw
- Georges Scholl
- Johann Far
- Aurore Schneiders

LIÈGE université

fnrs
FREEDOM TO RESEARCH

Thank you