DioXin 2023

10-14 SEPTEMBER **MAASTRICHT, THE NETHERLANDS**

43rd International Symposium on
Halogenated Persistent Organic Pollutants

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LIÈGE université

Assessing the performance of high resolution ion mobility-mass spectrometry for the separation of GC coeluting isomeric and isobaric halogenated persistent organic pollutants

MASS SPECTROMETRY LABORATORY

Hugo Muller
PhD student

Monday, 10 September 2023

MASS SPECTROMETRY LABORATORY

Introduction

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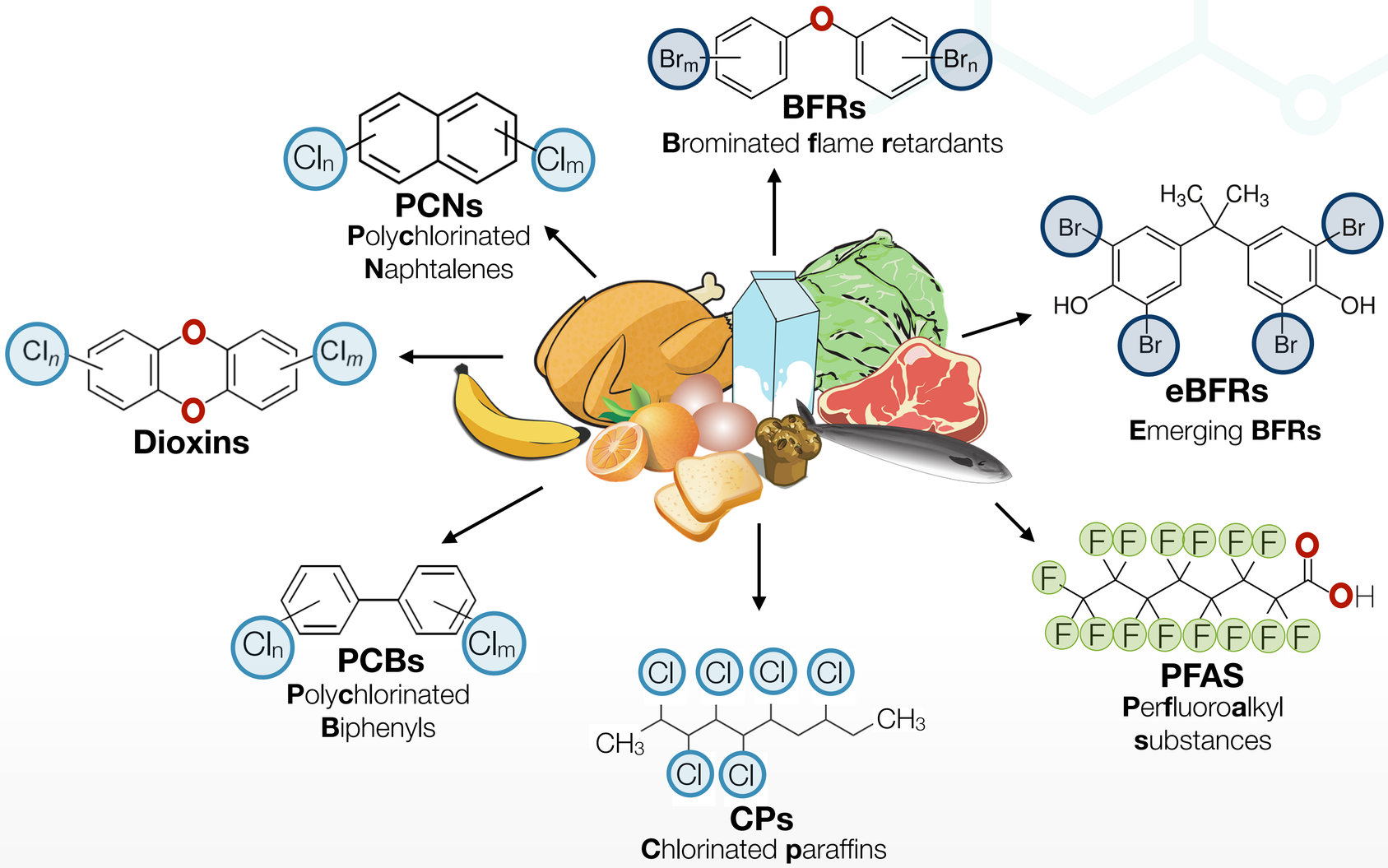
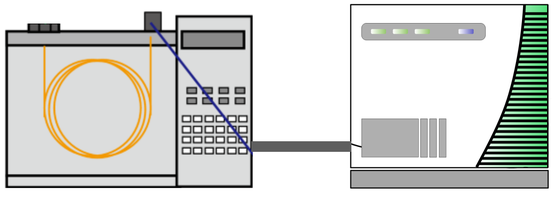
Halogenated POPs



Hugo Muller et. al, “Assessing the performance of high resolution ion mobility-mass spectrometry for the separation of GC coeluting isomeric and isobaric halogenated persistent organic pollutants ”

Analysis in food

Traditional approach



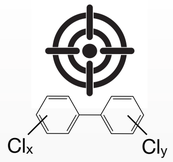
GC

Separates neutrals according to **boiling point**

MS

Separates ions according to **m/z ratio**

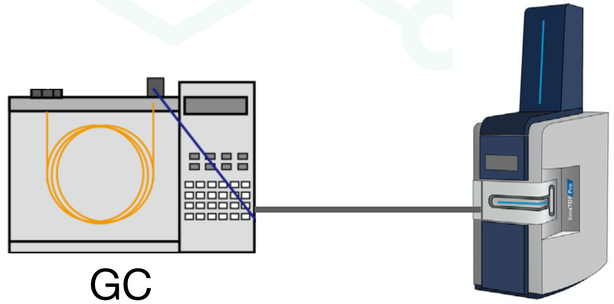
Single class targeted analysis



Selectivity

Sensitivity

Our approach



GC

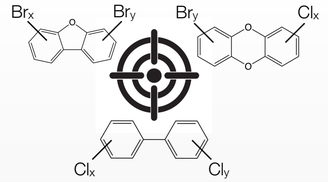
Boiling point

Ion Mobility-MS

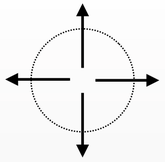
Separates ions according to **ion mobility coefficient K**

m/z ratio

Multi-class targeted analysis



Untargeted analysis



Selectivity

Hugo Muller et. al, “Assessing the performance of high resolution ion mobility-mass spectrometry for the separation of GC coeluting isomeric and isobaric halogenated persistent organic pollutants ”

Ion mobility

- → Origin: end of the 19th century
- → First commercial IM-MS instruments: mid-2000s
- → Exponential growth in the last decade

Drift speed

$$v_d = KE$$

Ion mobility constant

Fundamental low-field mobility equation

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

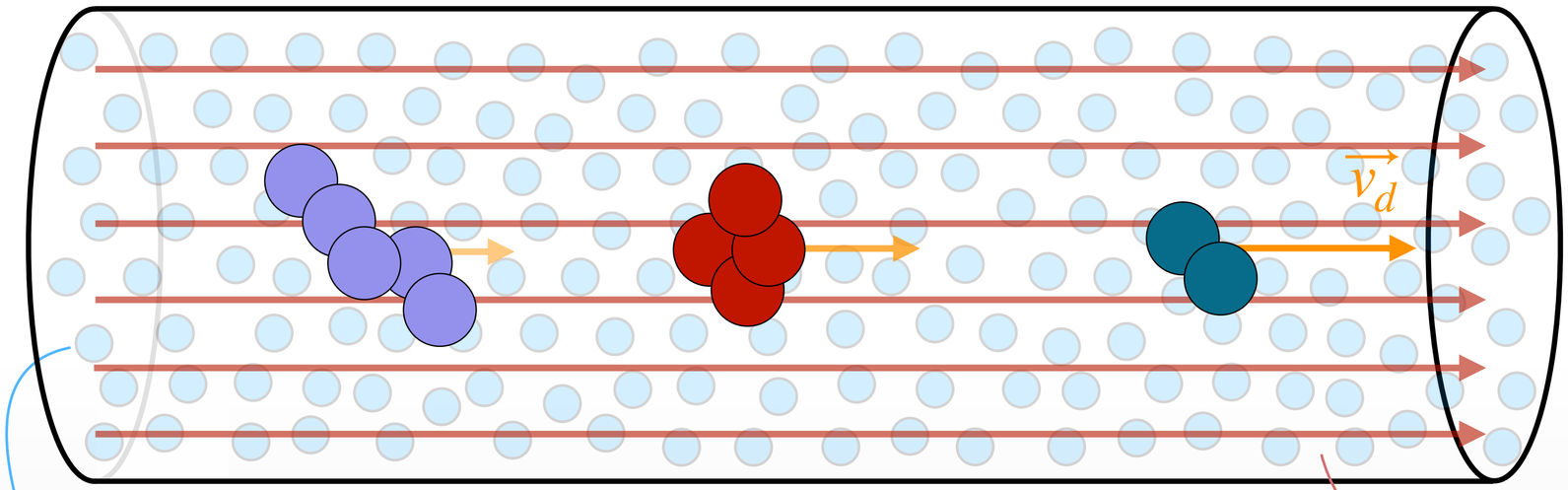
Charge

Mass

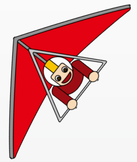
Collision **C**ross **S**ection (**CCS**)

Size & shape

Ion-gas interaction potential



Drift gas (N_2)



Electric field $\vec{E}$

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Ion mobility

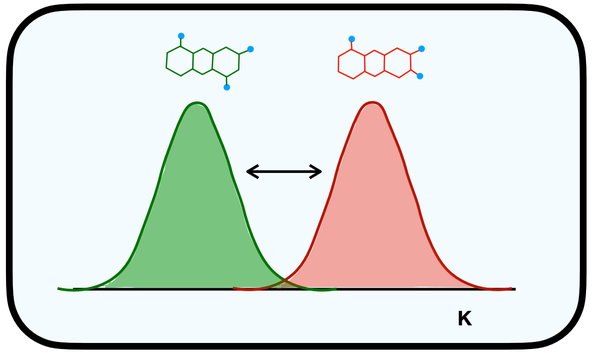
Technologies

- DTIMS
- TWIMS
- FAIMS/DMS
- TIMS

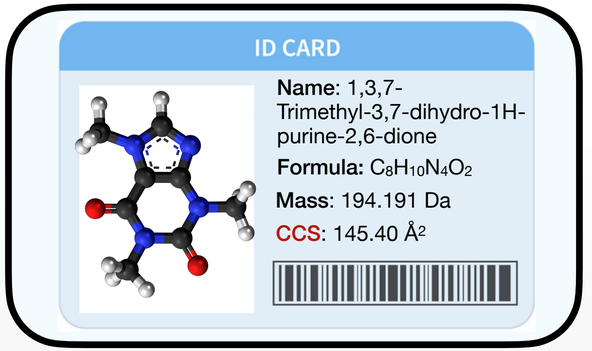
Ion mobility - mass spectrometry (IM-MS)

Advantages

- **Selectivity**
  - Isomers & Isobars
  - Interferences



- **Specificity** — CCS



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High resolution IM analysis of coeluting isobaric and isomeric POPs

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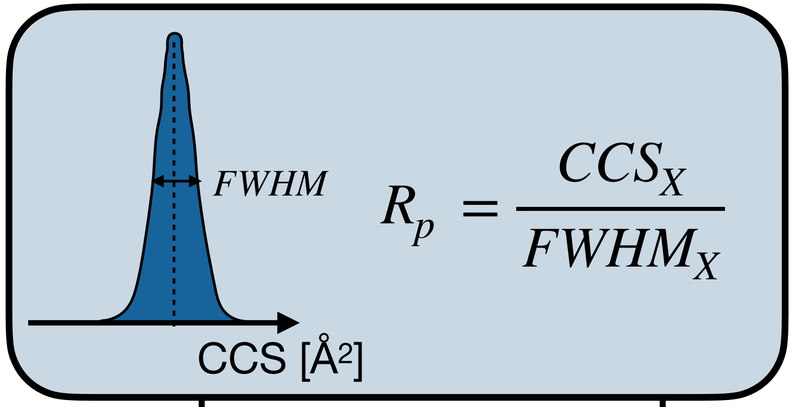
Resolving power



$$R_p = \frac{CCS_X}{FWHM_X}$$

LOW
R < 80

DTIMS
R ~ 20-40

HIGH
R ≥ 80

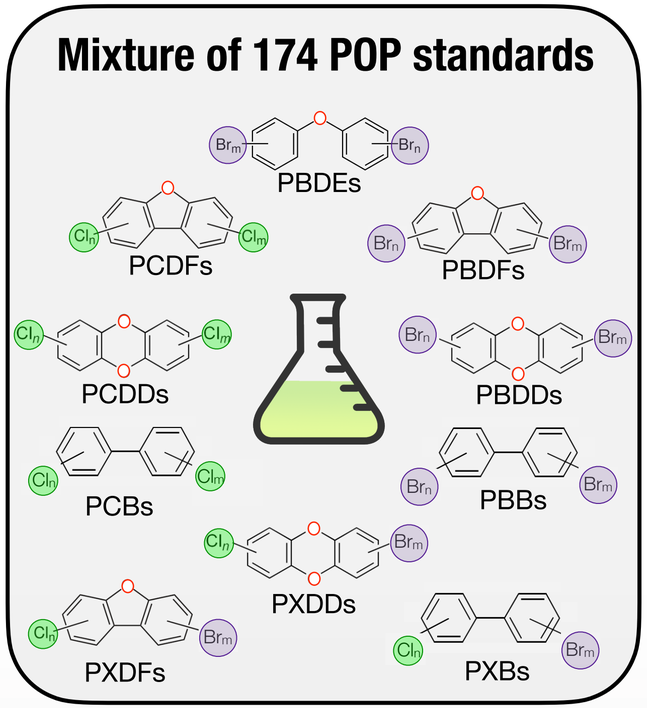
LP-DTIMS
TWIMS
TIMS

In this study: R_p ~ **140**

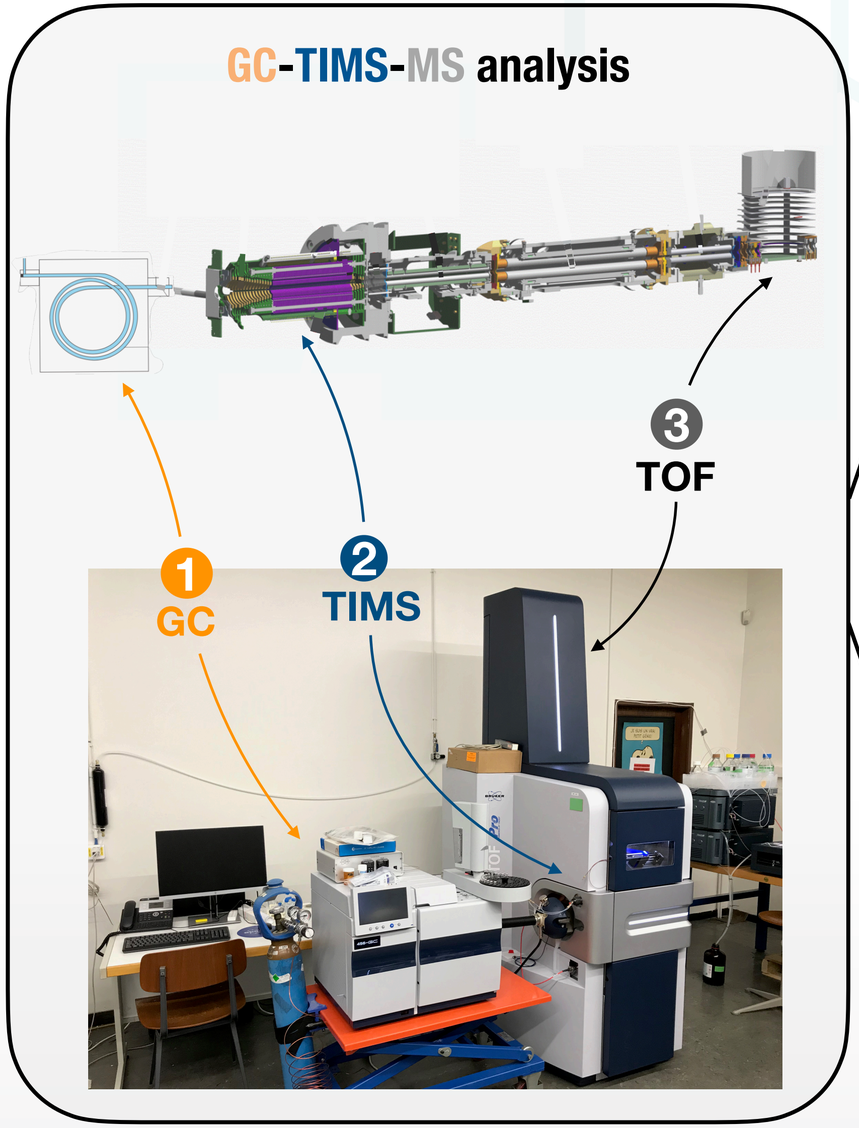
Hugo Muller et. al, "Assessing the performance of high resolution ion mobility-mass spectrometry for the separation of GC coeluting isomeric and isobaric halogenated persistent organic pollutants "

Material & method

Mixture of 174 POP standards



GC-TIMS-MS analysis



Isobars coelution

Resolvable by IMS?

Isomers coelution

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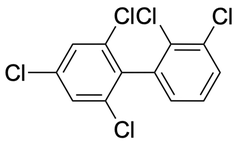
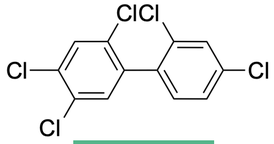
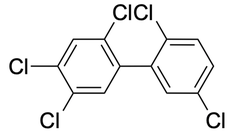
Coeluting isobars/isomers



PeCB 84

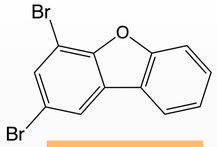


PeCB 90



PeCB 101

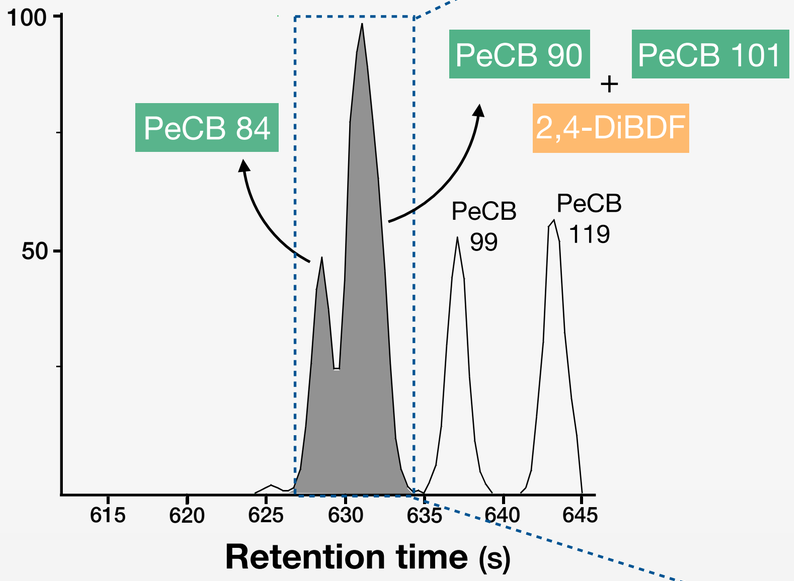
m/z 325.87**99**



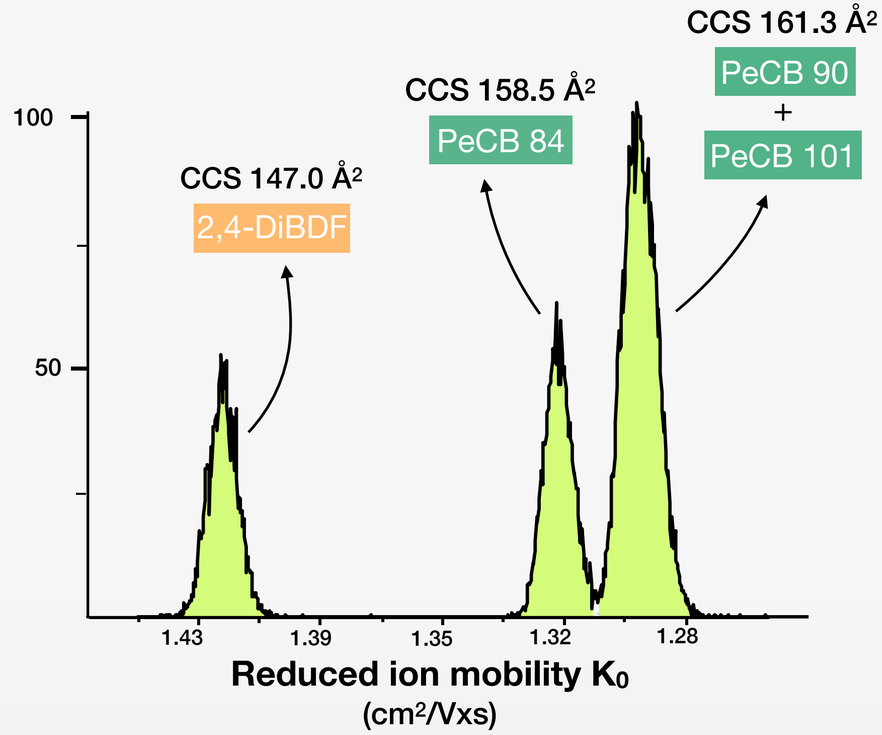
2,4-DiBDF

m/z 325.87**60**

Gas chromatography



Ion mobility



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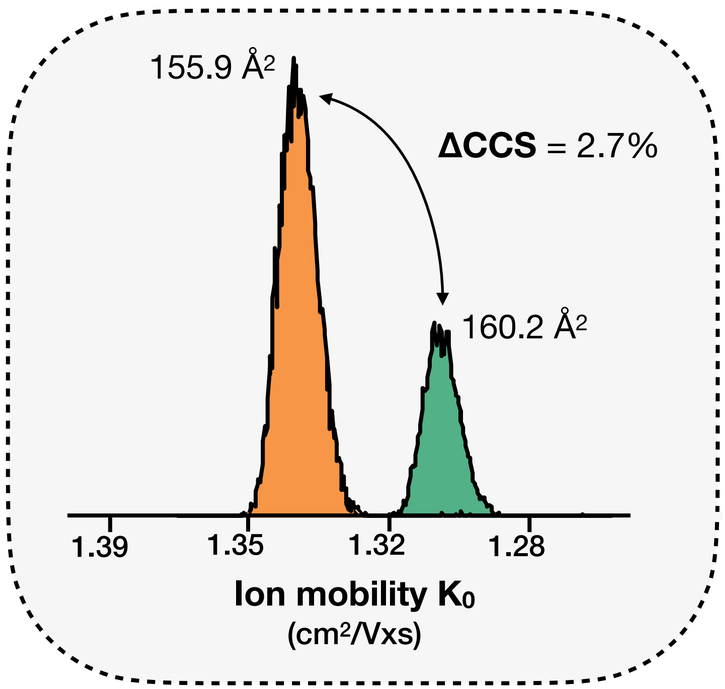
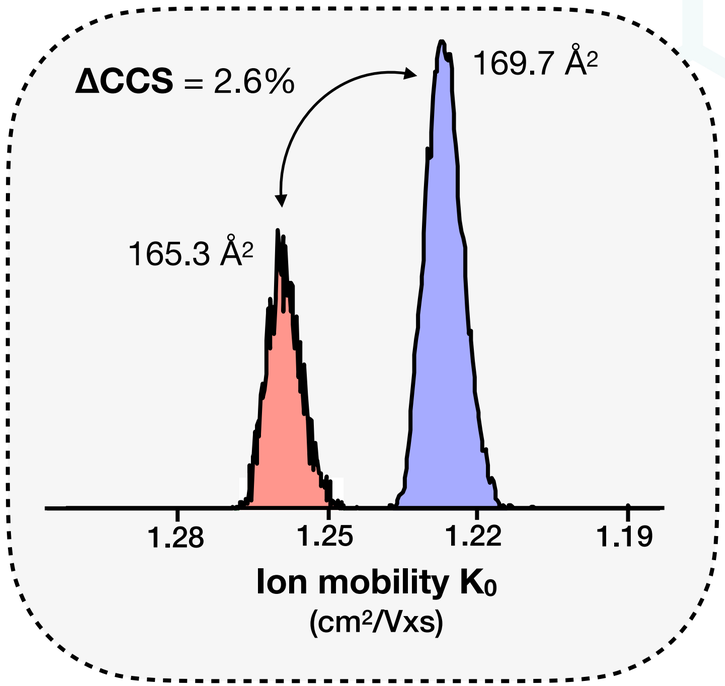
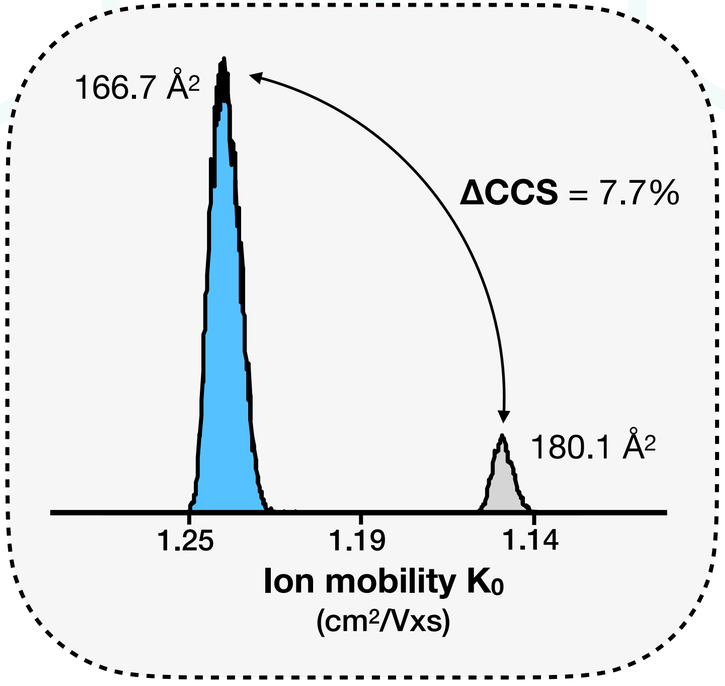
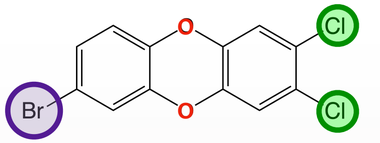
Coeluting isobars



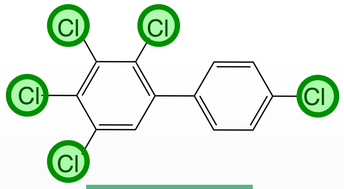






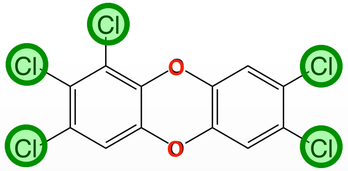
7-Bromo-2,3-dichlorodibenzo-p-dioxin

m/z 331.8715



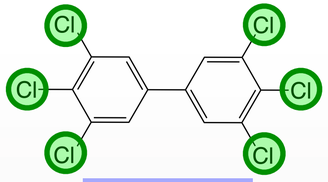
PeCB 114

m/z 331.8820



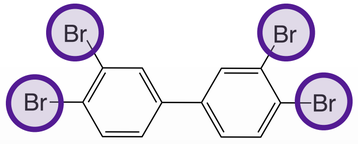
1,2,3,7,8-PeCDD

m/z 359.8485



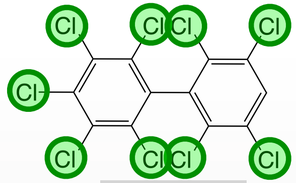
HxCB 169

m/z 359.8410



PBB 77

m/z 469.7157



PCB 208

m/z 469.7124

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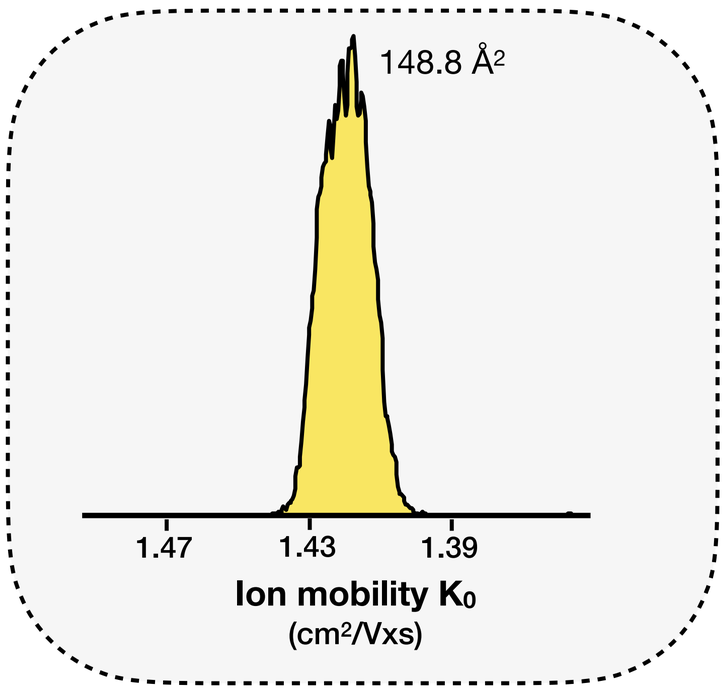
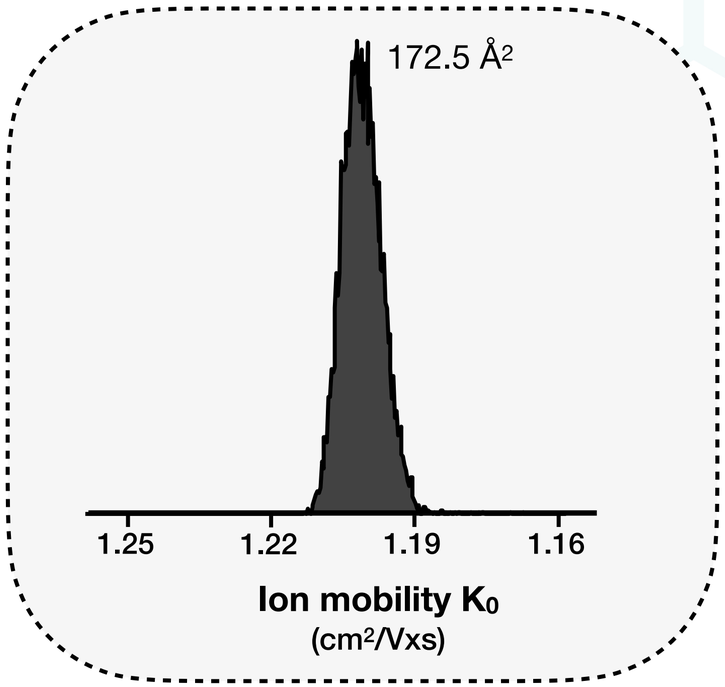
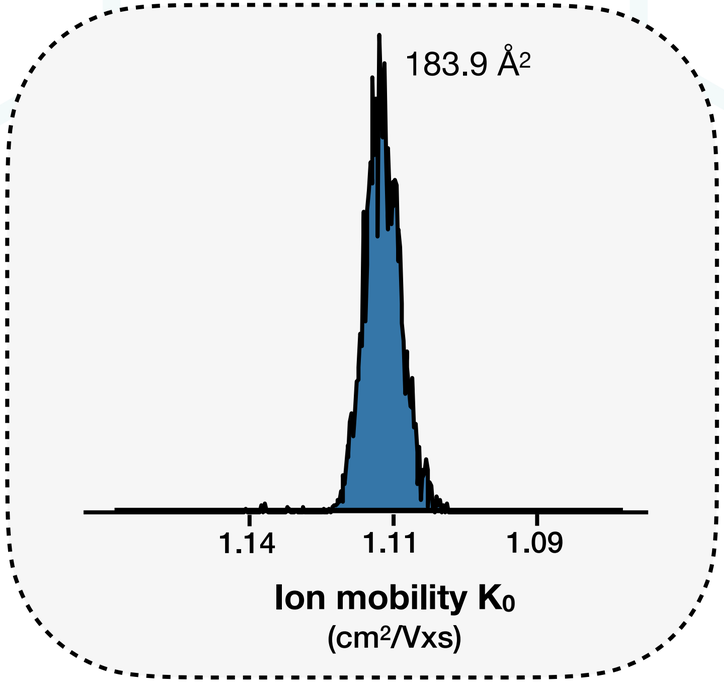
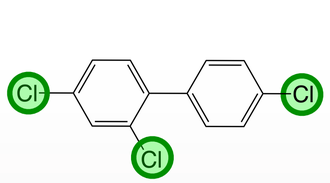
Coeluting isomers



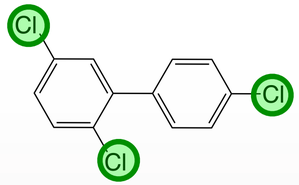






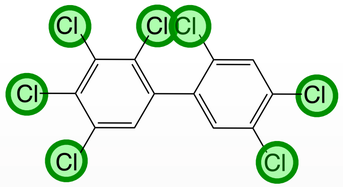
TriCB 28

m/z 255.9608



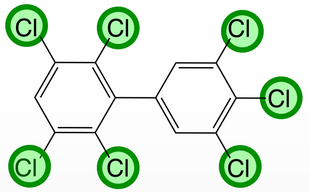
TriCB 31

m/z 255.9608



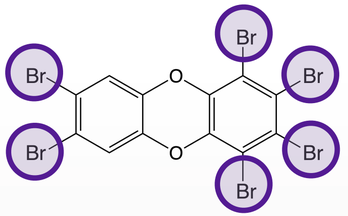
HpCB 180

m/z 393.8020



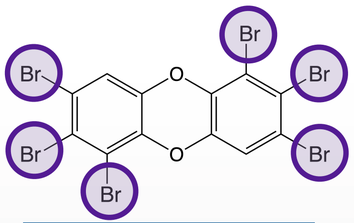
HpCB 193

m/z 393.8020



1,2,3,4,7,8-HxBDD

m/z 657.5089



1,2,3,6,7,8-HxBDD

m/z 657.5089

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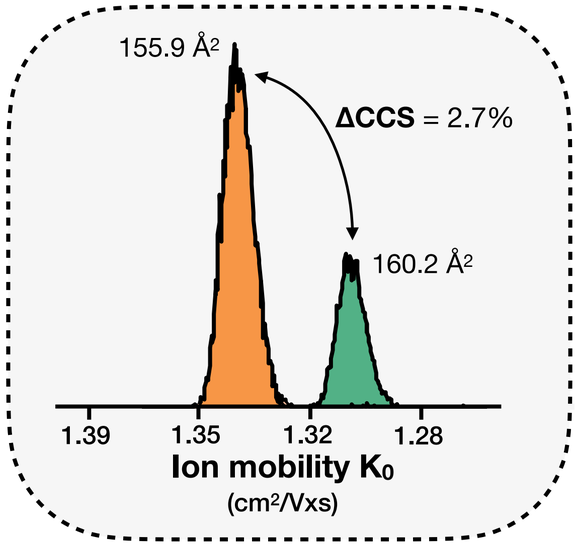
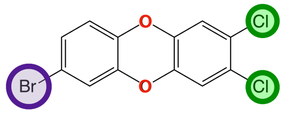
First summary

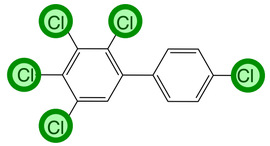
Coeluting isobars





7-Bromo-2,3-dichlorodibenzo-p-dioxin

m/z 331.8715



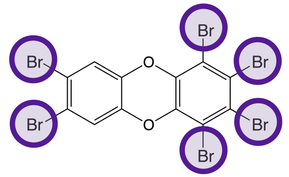
PeCB 114

m/z 331.8820

→ **Baseline** separation in IM (9/9 → 100%)

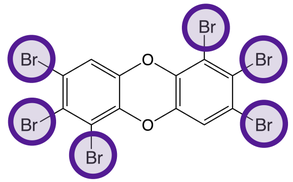
→ Structurally **different** (ΔCCS 2-8%):
- Aromatic backbone
- Number/type of halogen substituents

Coeluting isomers



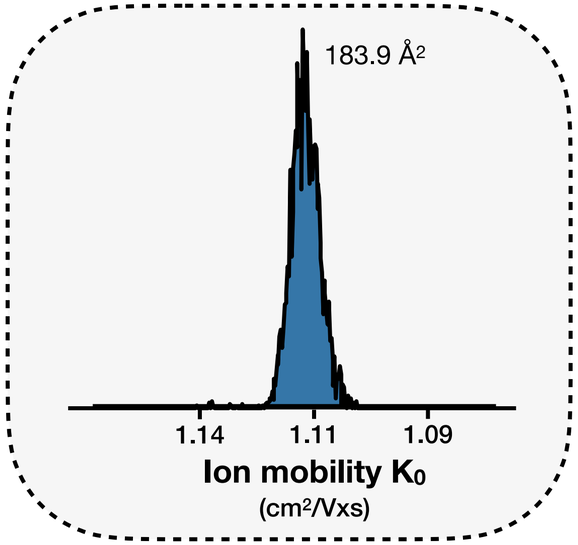
1,2,3,4,7,8-HxBDD

m/z 657.5089



1,2,3,6,7,8-HxBDD

m/z 657.5089



→ **No** separation in IM (2/13 → ~15%)

→ Structurally **similar**:
- Positional isomers

➪ Separation at higher R_p?

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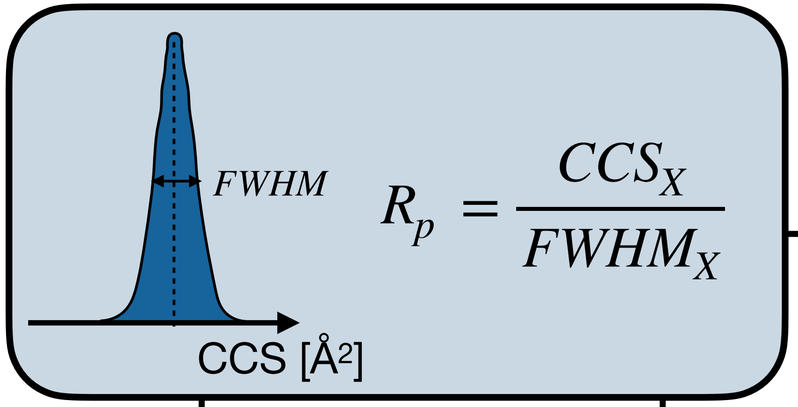
Resolving power



$$R_p = \frac{CCS_X}{FWHM_X}$$

LOW
R < 80

DTIMS
R ~ 20-40

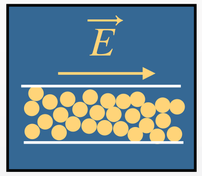
HIGH
R ≥ 80

LP-DTIMS
TWIMS
TIMS

In this study: R_p ~ **140**

ULTRA HIGH
R ≥ 200

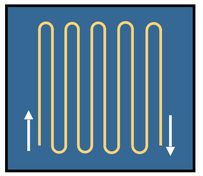
AP-DTIMS
R_{max} ~ 250



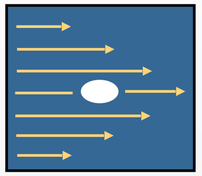
Cyclic DTIMS
R_{max} ~ 1000

Cyclic TWIMS
R_{max} ~ 800

SLIM TWIMS
R_{max} ~ 1800



TIMS
R_{max} ~ 400



⚠ Targeted ⚠
analytes ↔ Resolving power

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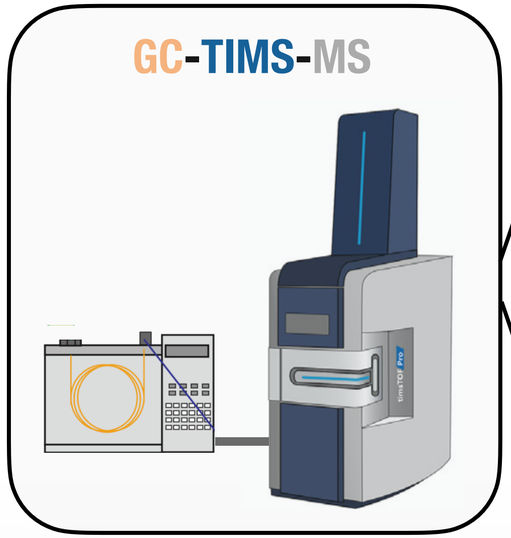
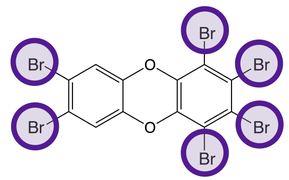
UHR TIMS



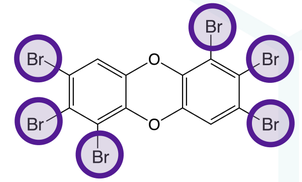
HR TIMS
R_p ~ **140**

UHR TIMS
R_p ~ **200**



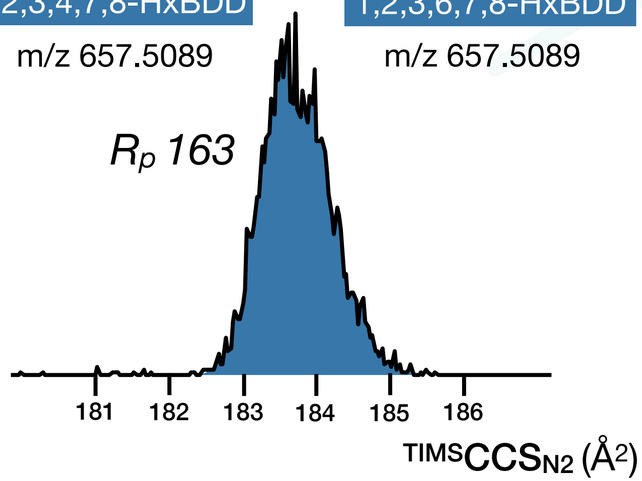
1,2,3,4,7,8-HxBDD

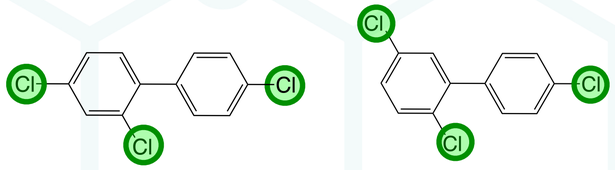
m/z 657.5089



1,2,3,6,7,8-HxBDD

m/z 657.5089



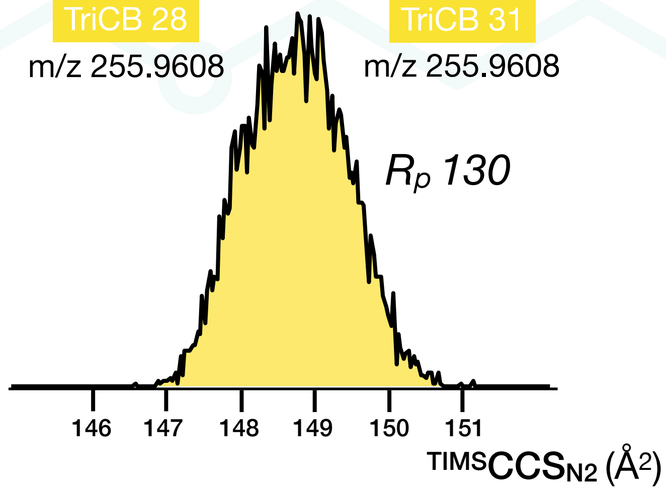


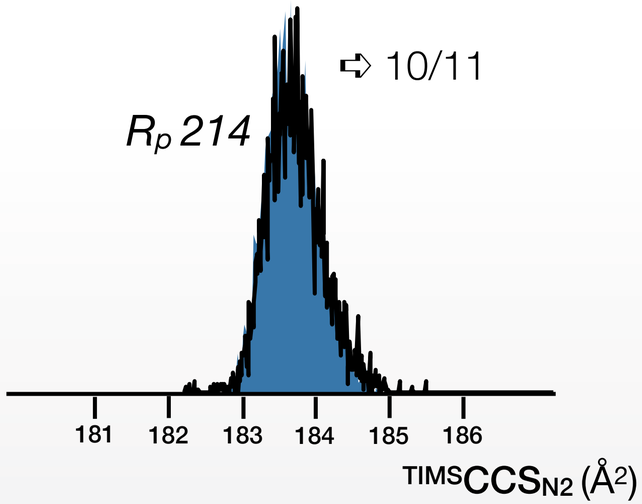
TriCB 28

m/z 255.9608

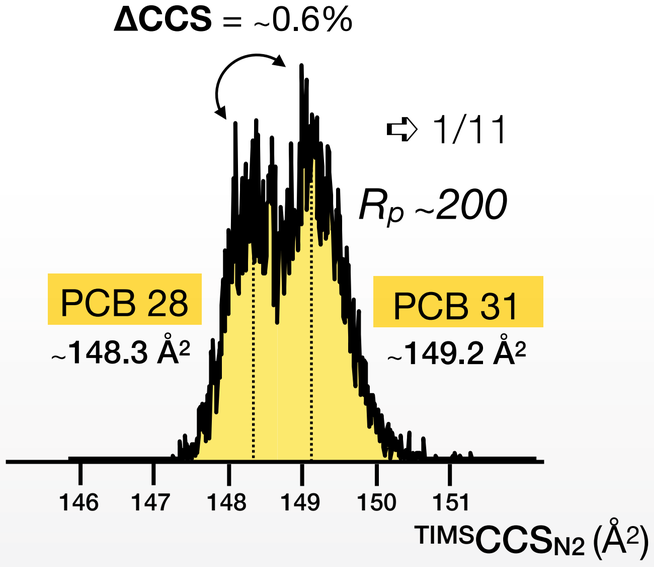
TriCB 31

m/z 255.9608



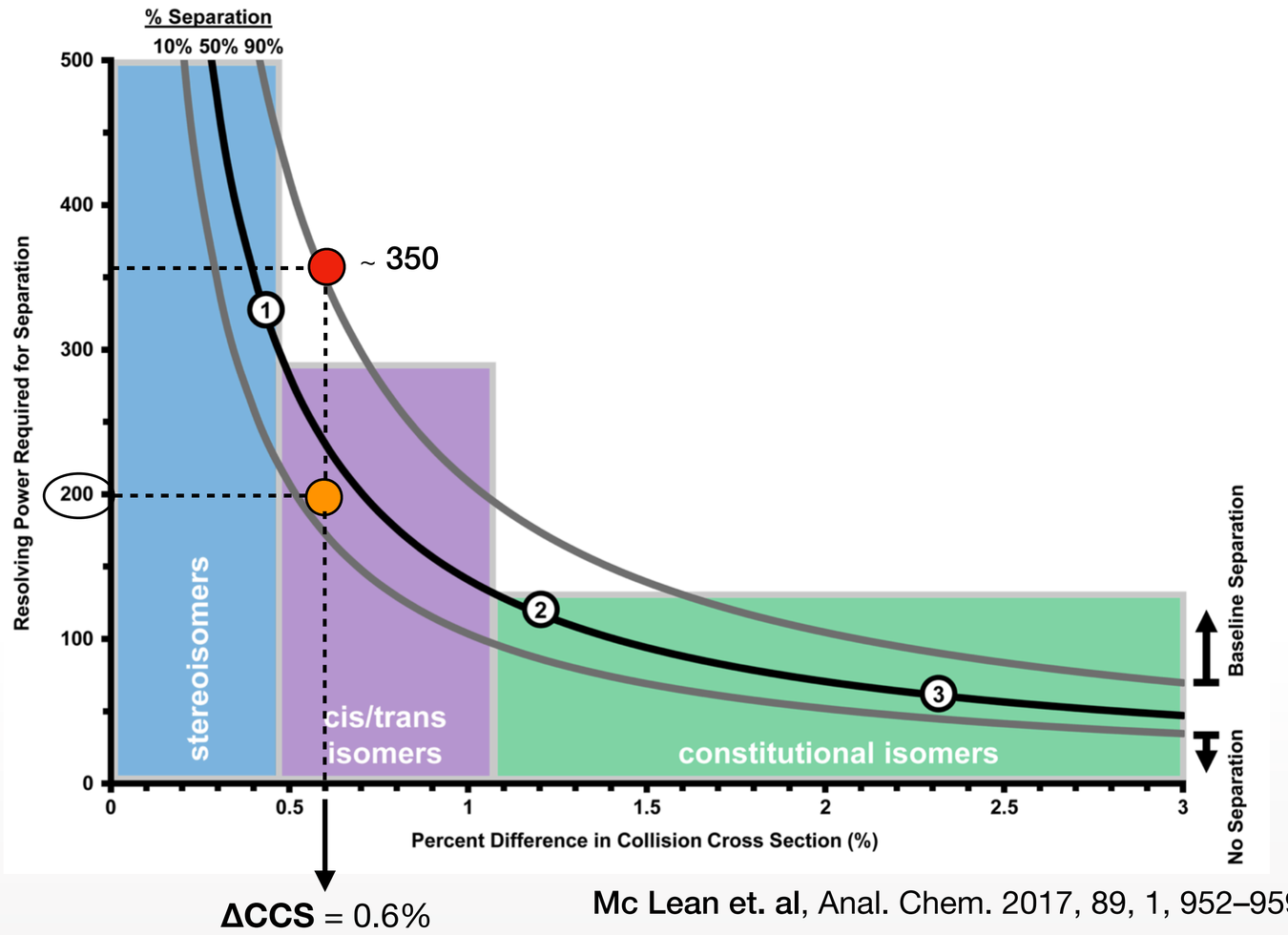


ΔCCS = ~0.6%

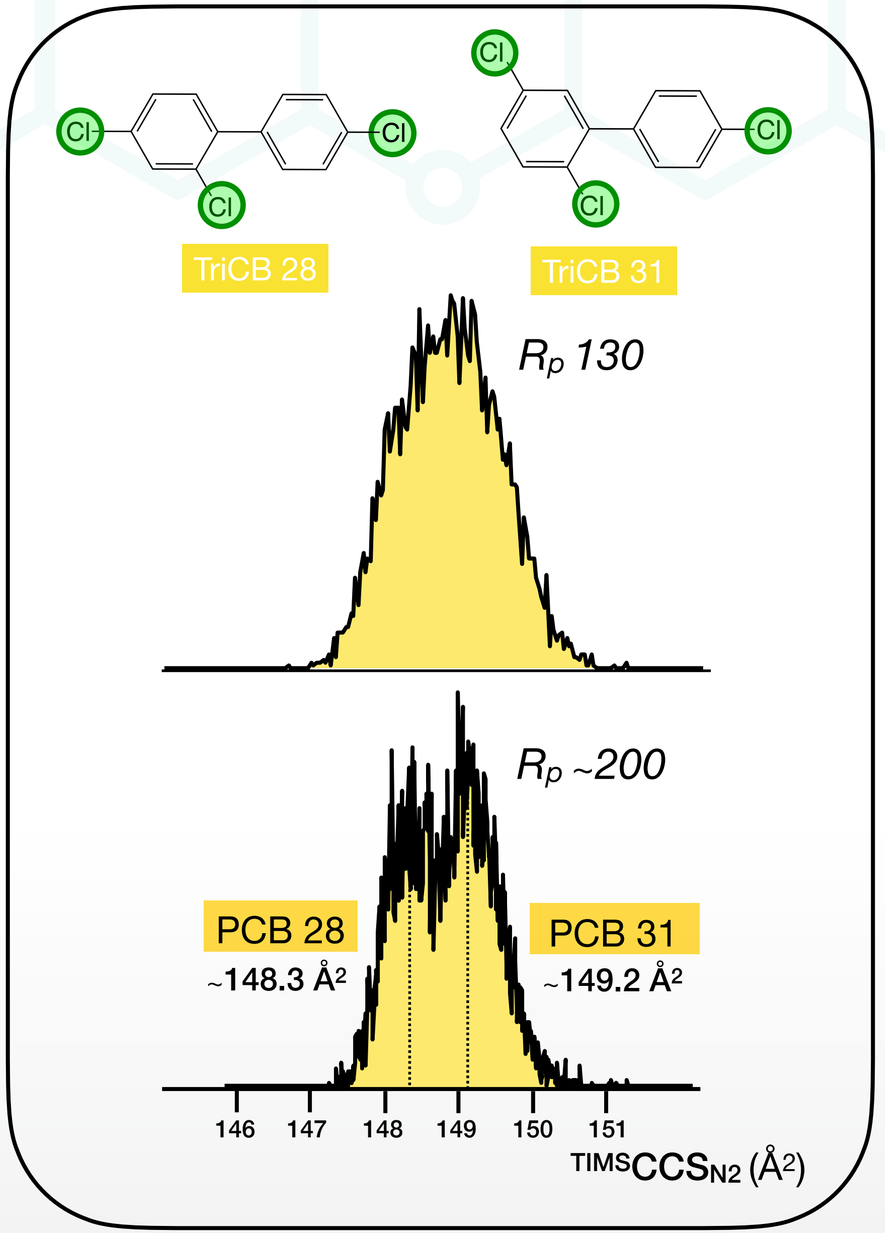


Hugo Muller et. al, “Assessing the performance of high resolution ion mobility-mass spectrometry for the separation of GC coeluting isomeric and isobaric halogenated persistent organic pollutants ”

UHR TIMS

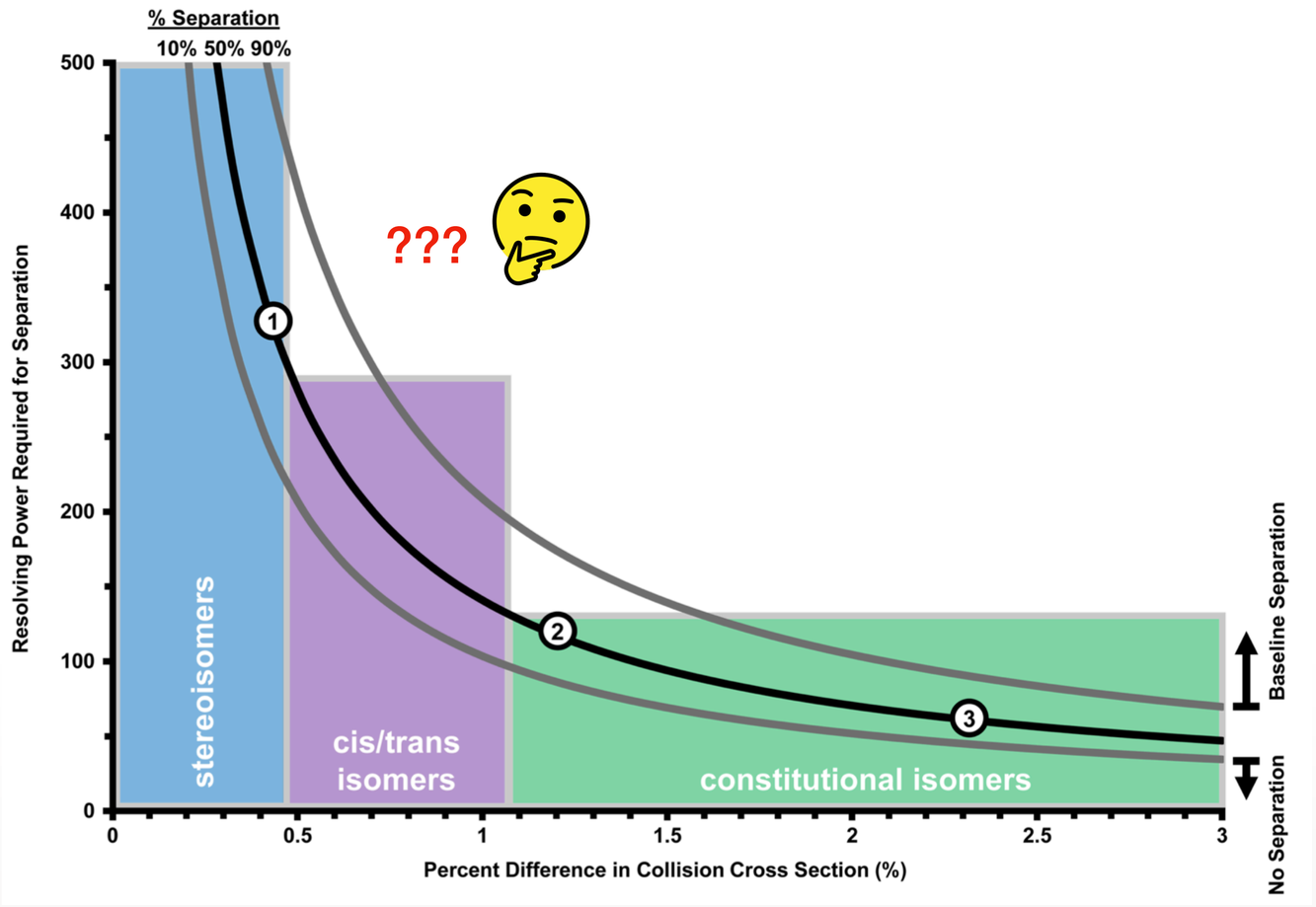


Mc Lean et. al, Anal. Chem. 2017, 89, 1, 952–959

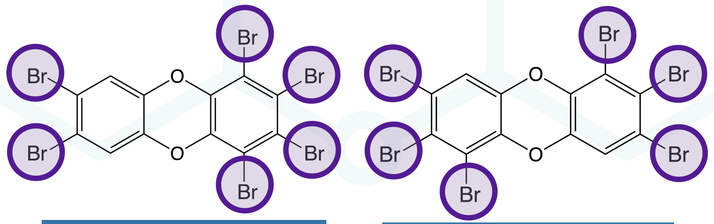


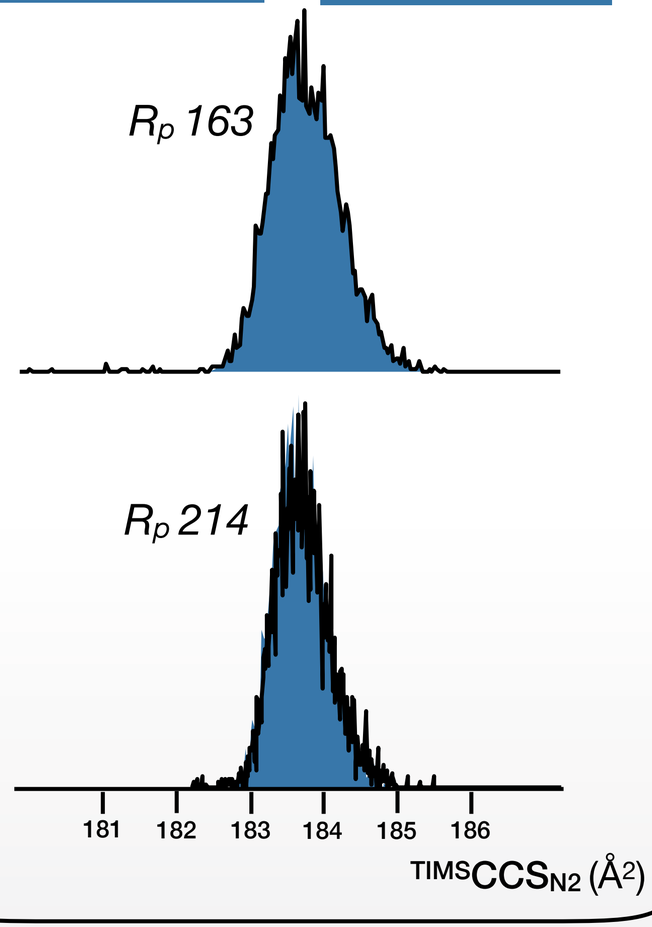
Hugo Muller et. al, "Assessing the performance of high resolution ion mobility-mass spectrometry for the separation of GC coeluting isomeric and isobaric halogenated persistent organic pollutants "

UHR TIMS



Mc Lean et. al, Anal. Chem. 2017, 89, 1, 952–959





Hugo Muller et. al, “Assessing the performance of high resolution ion mobility-mass spectrometry for the separation of GC coeluting isomeric and isobaric halogenated persistent organic pollutants ”

MASS LABORATORY SPECTROMETRY

Conclusion

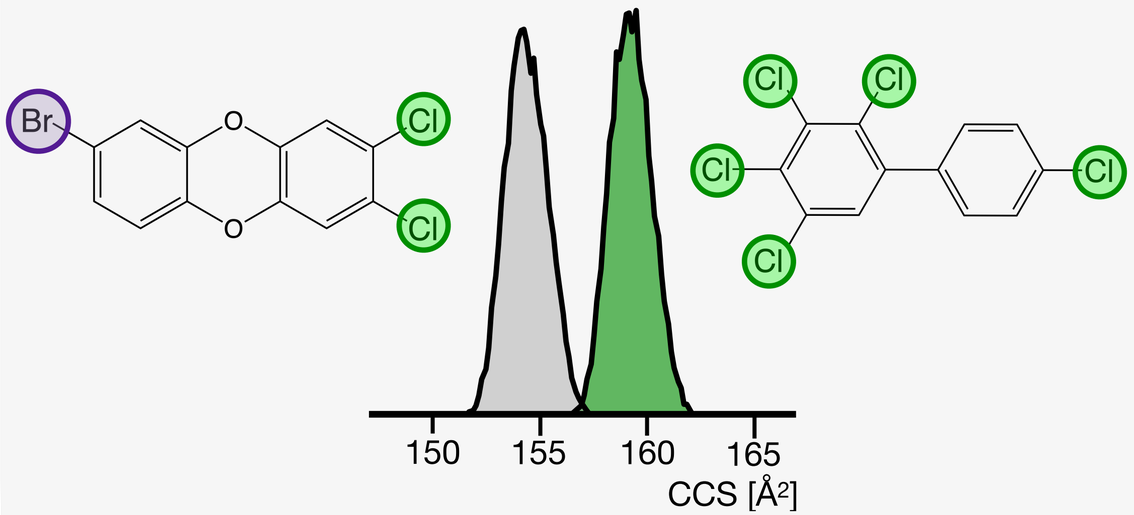
LIÈGE université

Summary

GC-IM-MS

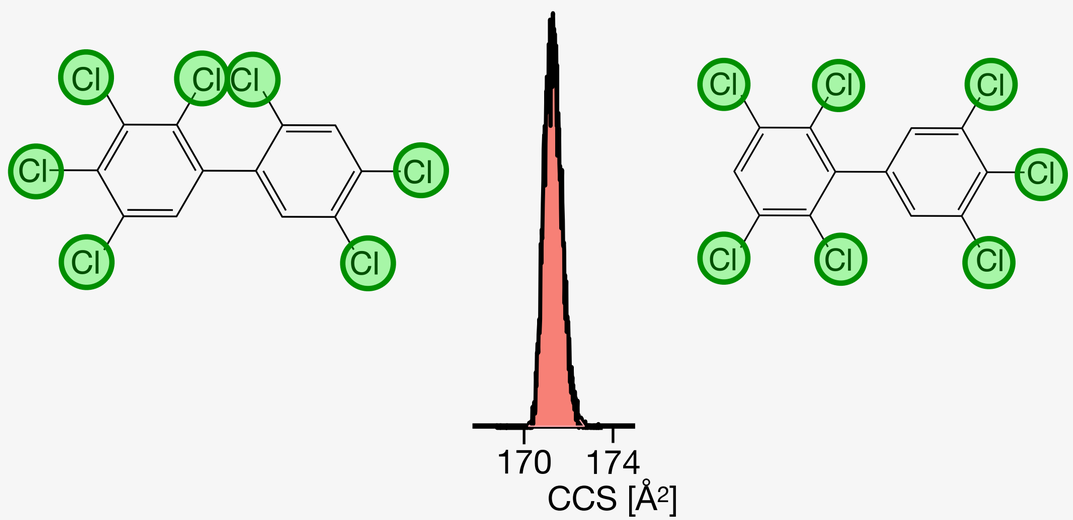
Results published in anal. chem.
https://doi.org/10.1021/acs.analchem.3c03039

Coeluting isobars

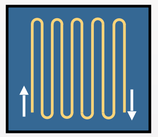


→ Baseline separation (R_p ~ 140)

Coeluting isomers



→ No separation (R_p ~ 200)

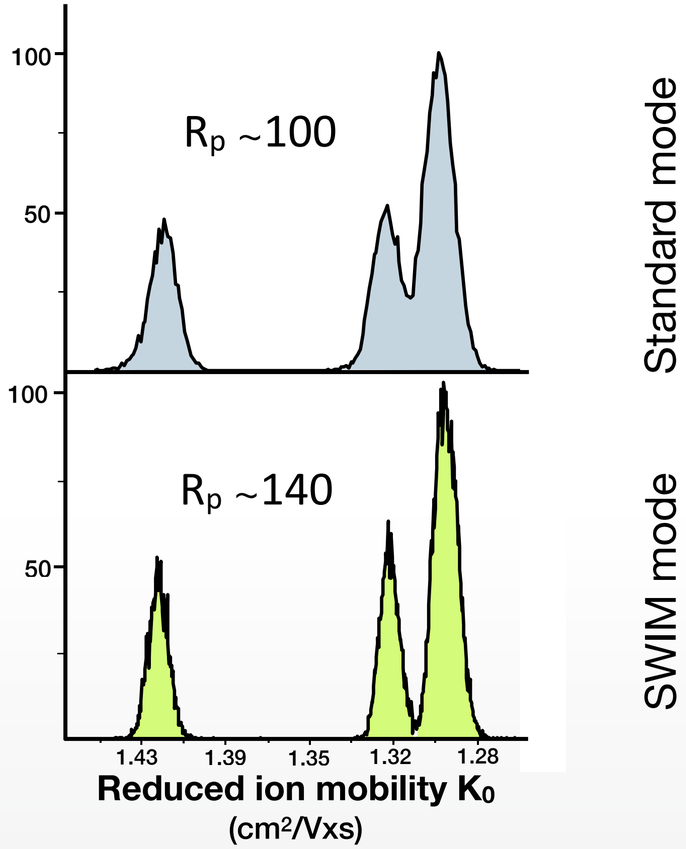
?  Cyclic/SLIM TWIMS  ?

Hugo Muller et. al, “Assessing the performance of high resolution ion mobility-mass spectrometry for the separation of GC coeluting isomeric and isobaric halogenated persistent organic pollutants ”

Announcements

Oral *MON-PM2-D2* (4 pm ; room 0.4)

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



Bruker seminar (Prof. Gauthier Eppe, 12.15 pm)

"Novel approach in addressing the challenges of monitoring multi-classes of Halogenated POPs in food and feed"

VENDOR PRESENTATION

BAMS seminar: Monday 11th September, 12h15 – 13h15 (after the scientific session, during the lunch break)

BRUKER

- Room name: 0.5 Paris
- Date: Monday 11 September
- Timing: 12:15 to 13:15

Gauthier Eppe, Professor, Université de Liège

LIÈGE université Sciences

Novel approach in addressing the challenges of monitoring multi-classes of Halogenated POPs in food and feed

Hugo Muller et. al, "Assessing the performance of high resolution ion mobility-mass spectrometry for the separation of GC coeluting isomeric and isobaric halogenated persistent organic pollutants "

MSSV LABORATORY
SPECTROMETRY

LIÈGE université

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

fnrs
FREEDOM TO RESEARCH

Thank you

Hugo Muller et. al, “Assessing the performance of high resolution ion mobility-mass spectrometry for the s… …ric and isobaric halogen… …nic pollutants ”