

# Ion Mobility - Mass Spectrometry as a new approach for the screening of pesticide residues in food

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# Pesticides

= substances or mixture  
intended for preventing, destroying,  
repelling or mitigating any pest

## Challenge for the analyst:

➤ Currently, there are more than  
**1,055 pesticides** registered<sup>1</sup>

➤ **Rich in diversity**

Chemical structure, solubility, volatility...

➤ Hidden in **complex food matrices**



<sup>1</sup> U.S. Environmental Protection Agency

# Methods

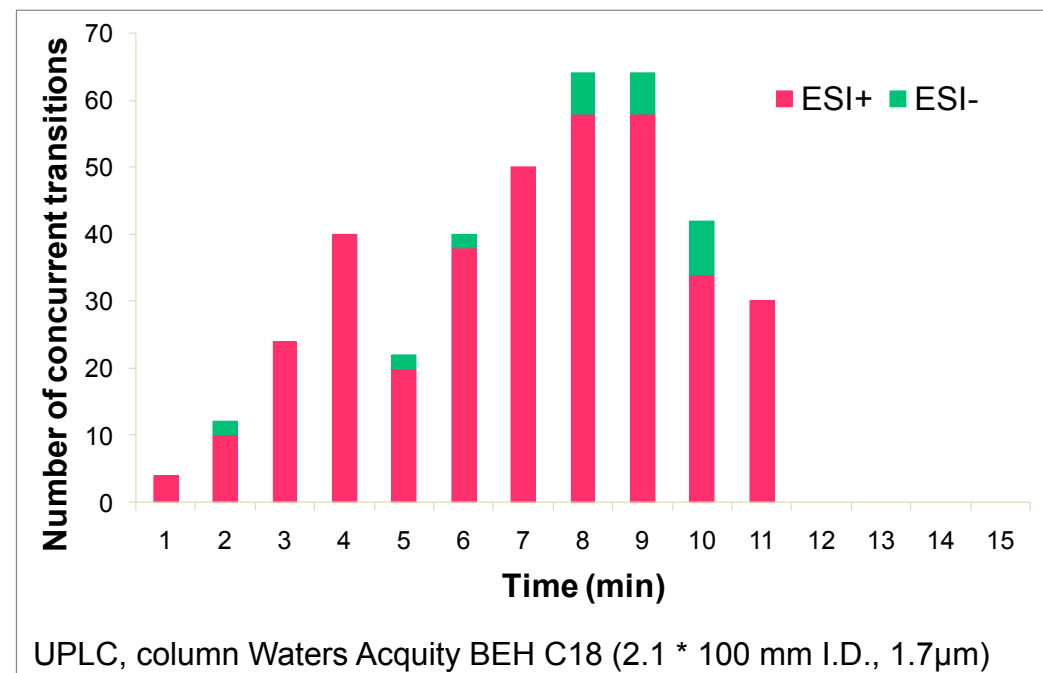
➔ Have to be viable for the lab

## Multiresidue Methods

- Generic
- Easy
- Fast

## Selected Reaction Monitoring (using triple quadrupole)

- Quantitative
- Simultaneous determination  
of a restricted number of  
compounds
- Only used with **target pesticide**



But demands for **new pesticides detection** is constantly **growing ...**

# Methods

## Screening method (ToF-MS)

- Qualitative
- Simultaneous determination of **unlimited** number of compounds
- High resolution technique and excellent sensitivity in full scan mode
- Enables to **non-target analysis** (identification of unknown peaks in the sample)

### However

- No univocal identification
- Qualitative data (present or not) requiring a high level of confidence

How can we improve screening efficiently?

By using a 3<sup>rd</sup> dimension of separation:

**ION MOBILITY**

# Ion Mobility (IM)



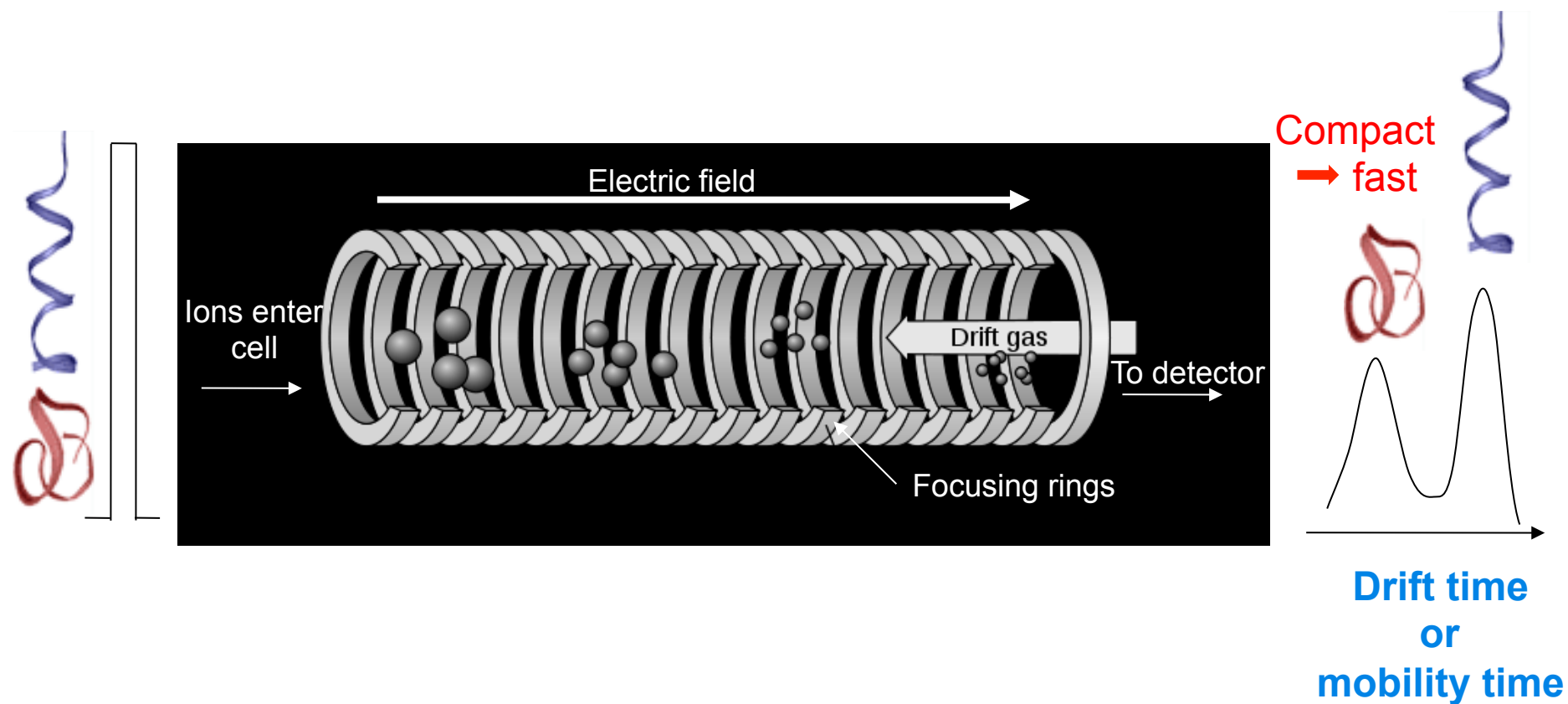
**Compact**



**Extended**

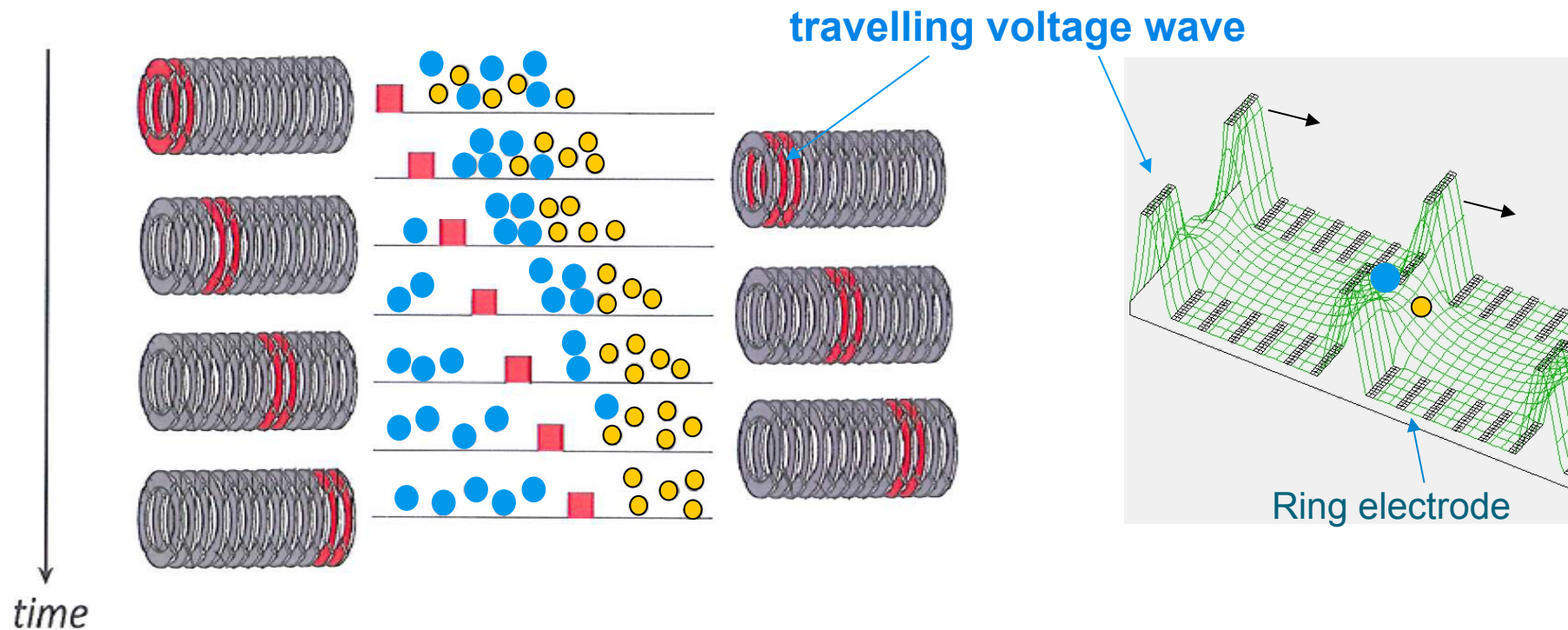
## Traditional ion mobility cell

Separation is driven by **an electric field** applied to an ion mobility cell which contains **a neutral gas** at a controlled pressure (~3.0 mbar)



# Triwave ion guide

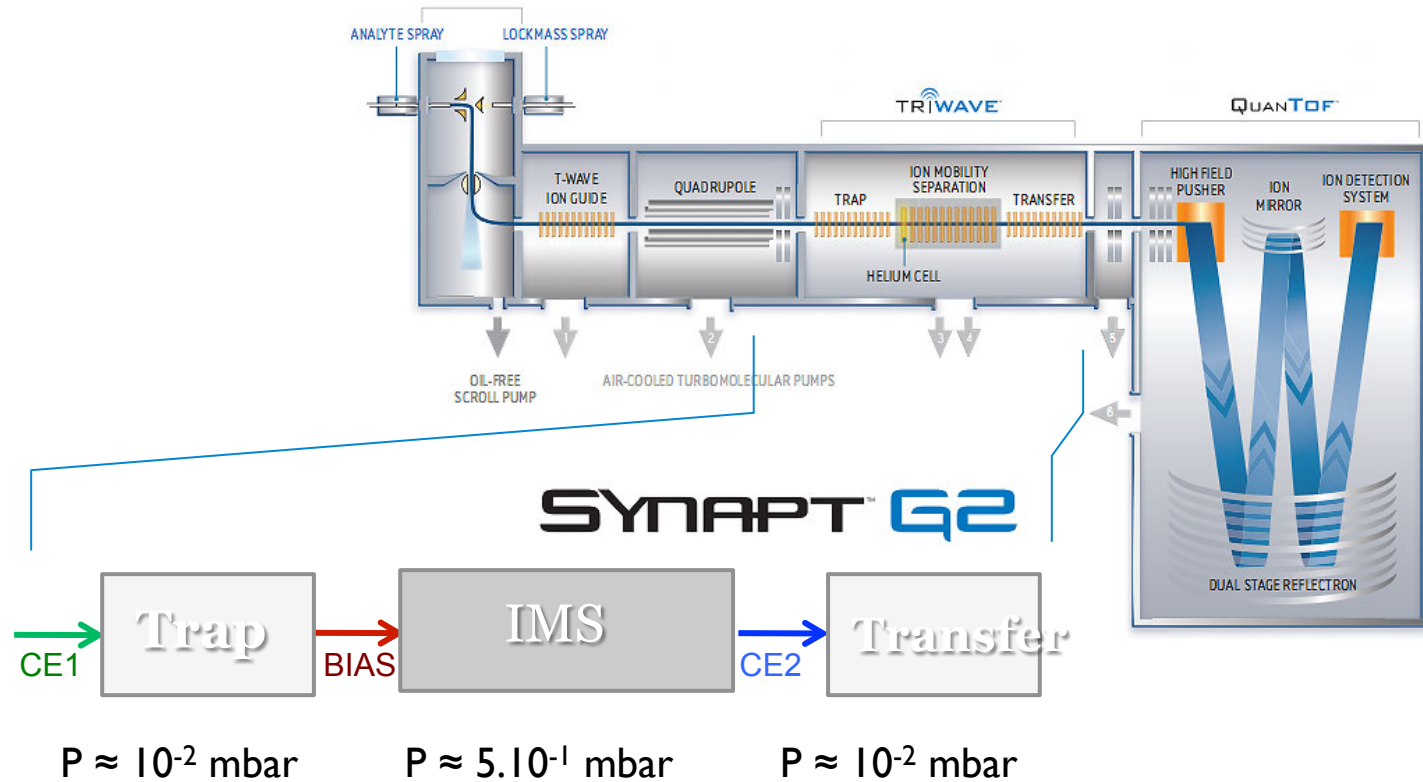
➔ **Transmission and resolution are not compromised**



**Ion propulsion** is produced by superimposing

- a **radially confining RF voltage** generate a trap along the z-axis
- a **travelling voltage wave** on which the ions can surf

# The Q-TOF type instrument (Synapt G2)

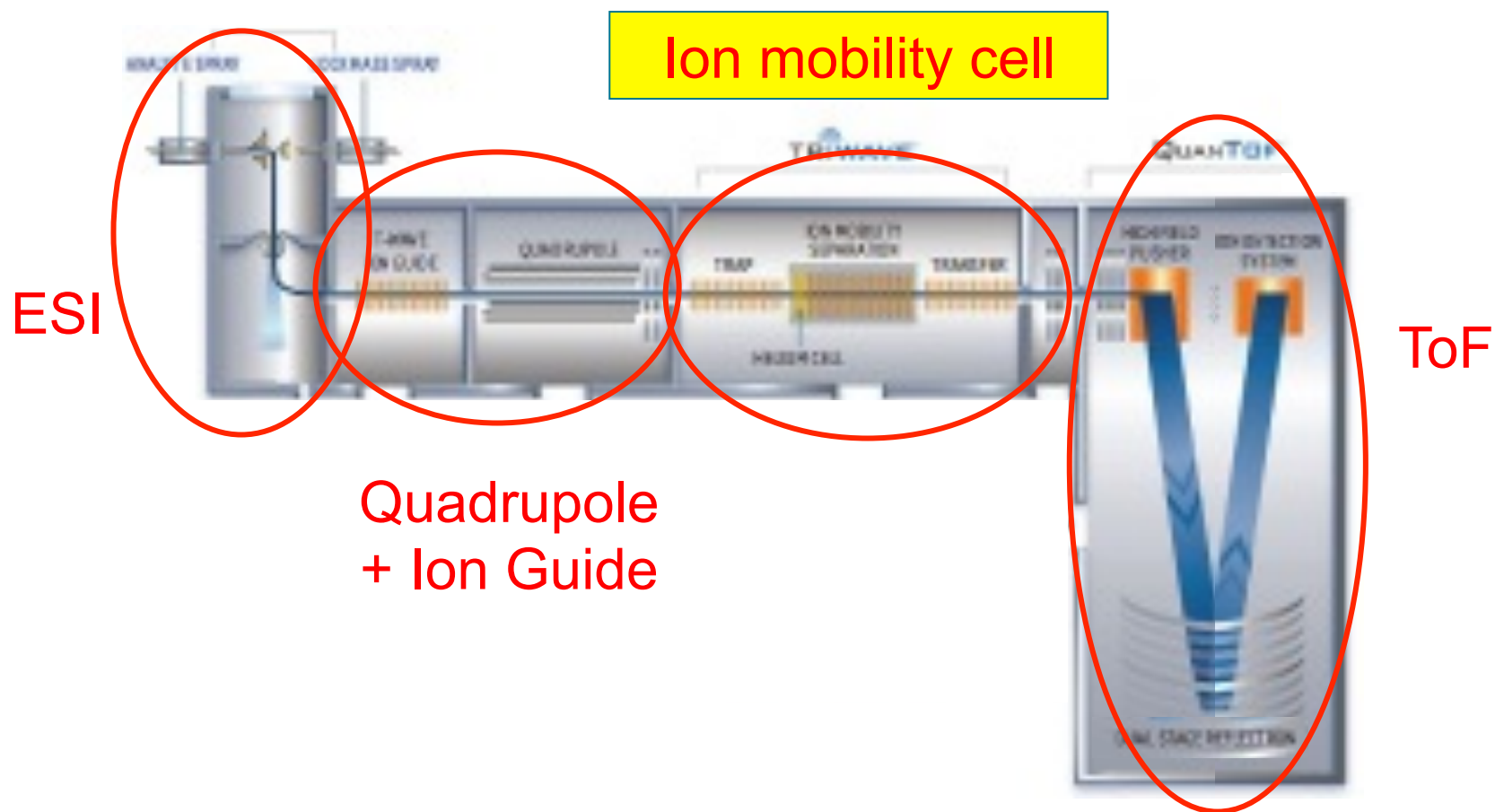


- **Potential difference CE1**
- **Potential difference Bias**
- **Potential difference CE2**

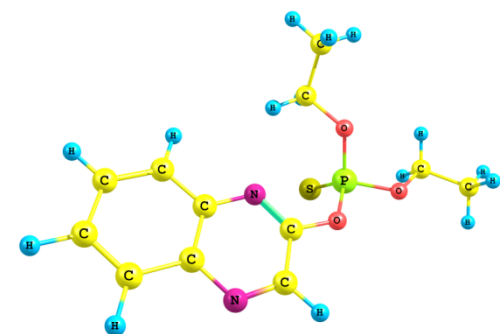
**within IM**

- Wave Amplitude
- Wave velocity
- Collision gas
- Pressure of the collision gas

# Synapt G2 HDMS @ Waters

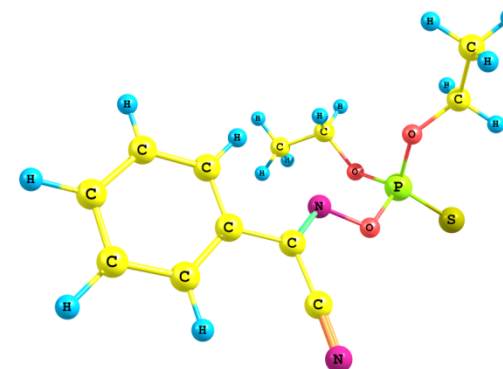


## Discrimination between isomers

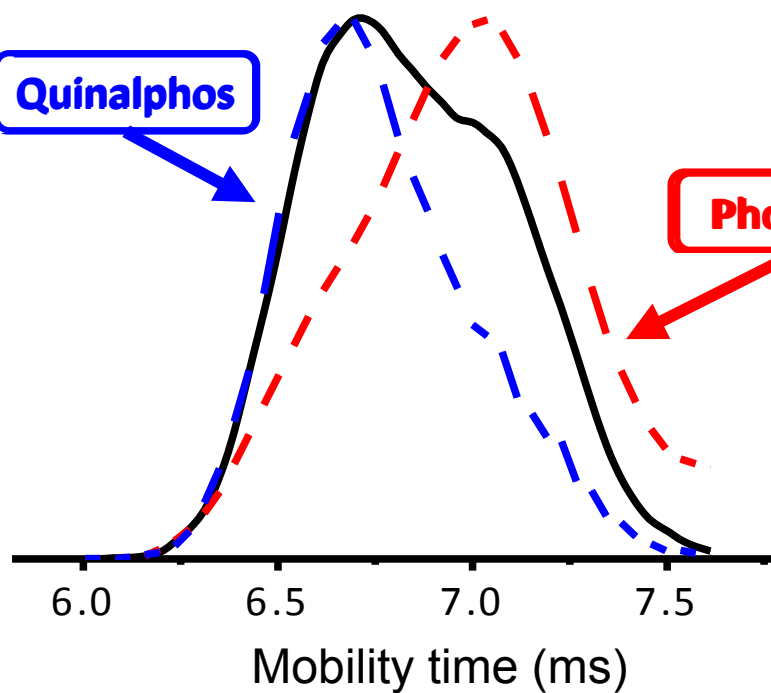
 $m/z = 299.0619$  $C_{12}H_{15}N_2O_3PS$  $\Omega = 122 \text{ \AA}^2$ 

Quinalphos

Quinalphos + Phoxim

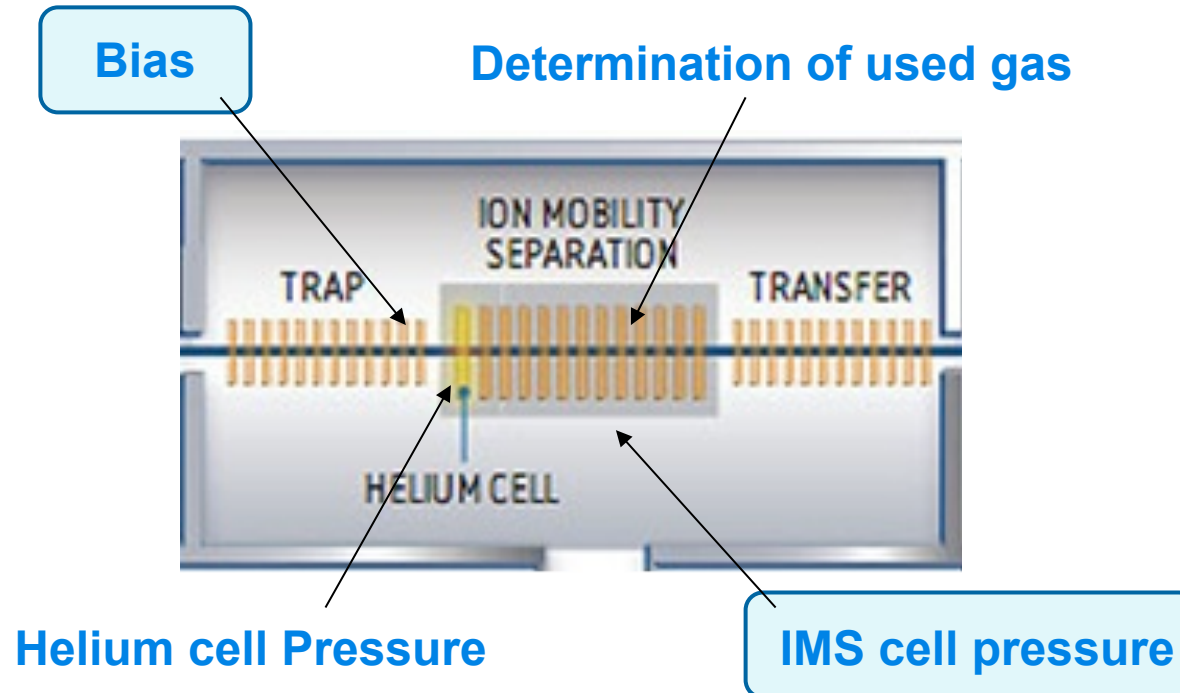
 $\Omega = 125 \text{ \AA}^2$ 

Phoxim

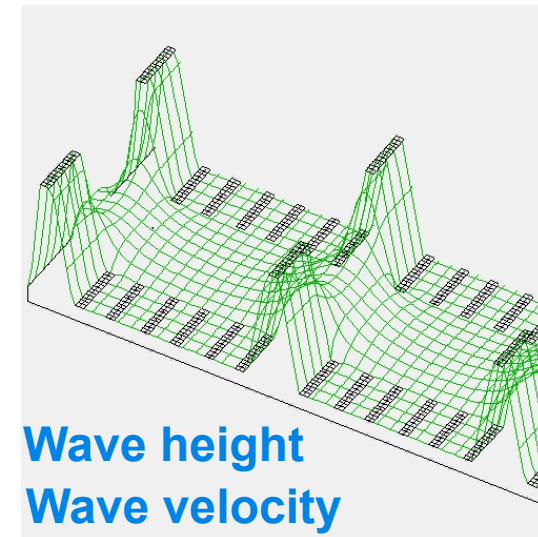


In this case parameters will be optimized to separate these 2 molecules

## Optimization of mobility cell parameters



travelling voltage wave



### Selection of 4 representative pesticides

**Plackett-Burman experimental design** followed by a **Central Composite Design** were carried out on most influential parameters

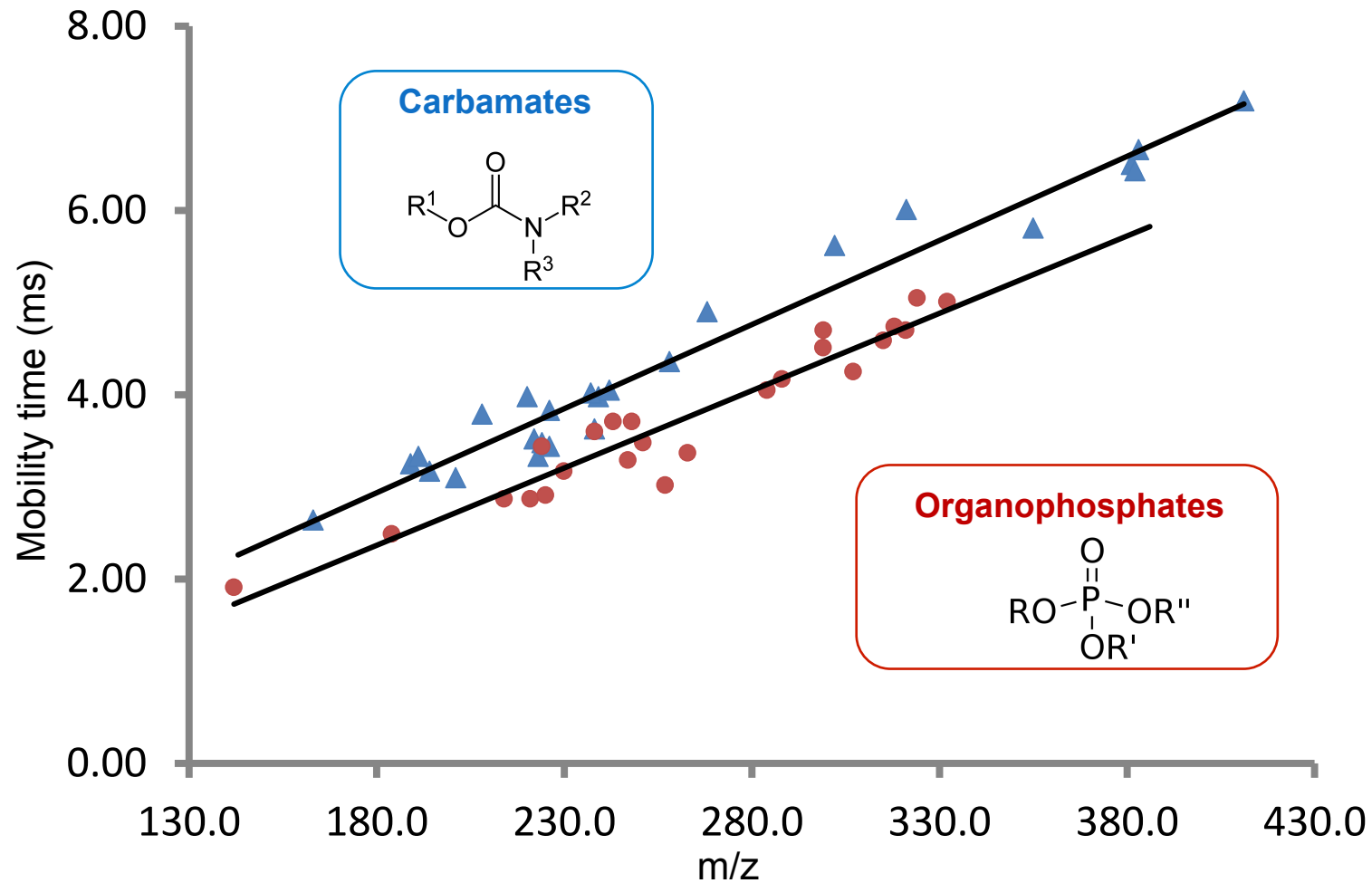
**3 responses**

**Intensity**

**Resolution**

**Relative drift time**

## Separation of 2 main pesticide classes



Two classes of pesticides were found to form characteristic mobility-mass correlation curves

## Pesticide screening



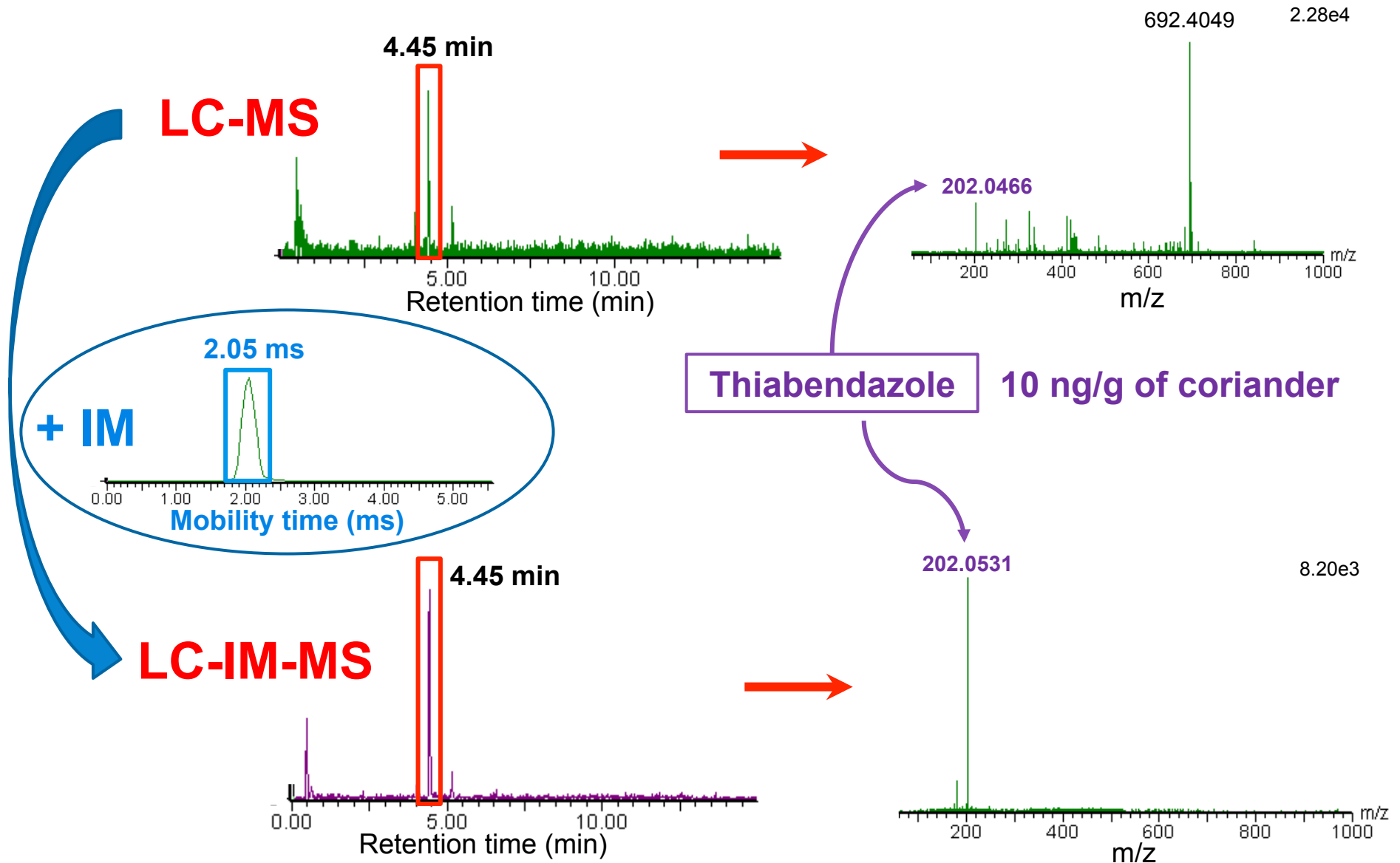
## Ion mobility



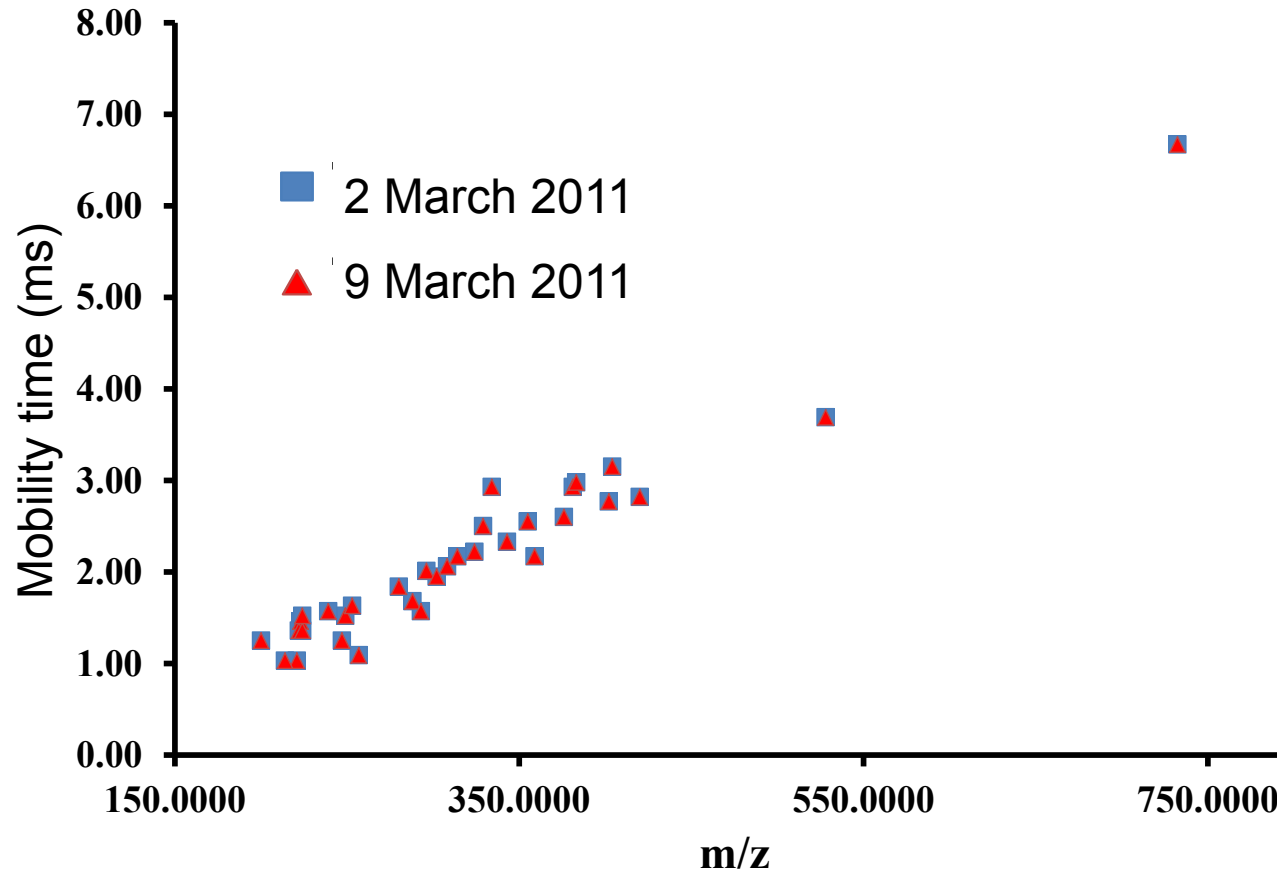
**UPLC - IM - MS**

- Does ion mobility have the potential **to separate target ions from matrix interferences?**
- Can we consider mobility time as **an additional information point?**

a. Does IMS have the potential to separate target ions from matrix interferences?

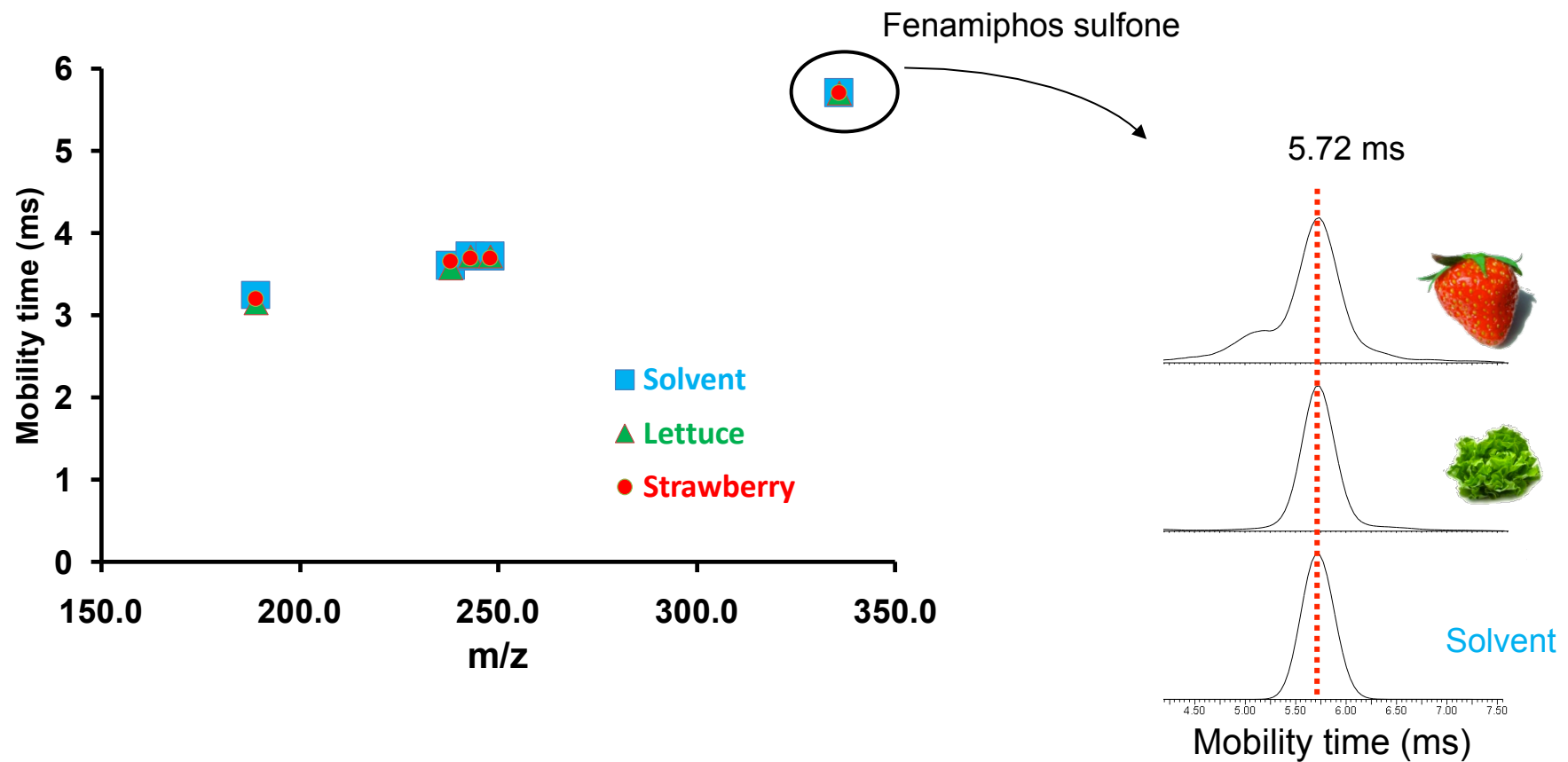


b. Can we consider mobility time as an additional information point?



Mobility times are **reproducible**

b. Can we consider mobility time as an additional information point?



**No matrix effect** on mobility time

## To sum it up

### **ION MOBILITY is a powerful tool to**

#### ➤ **Separate**

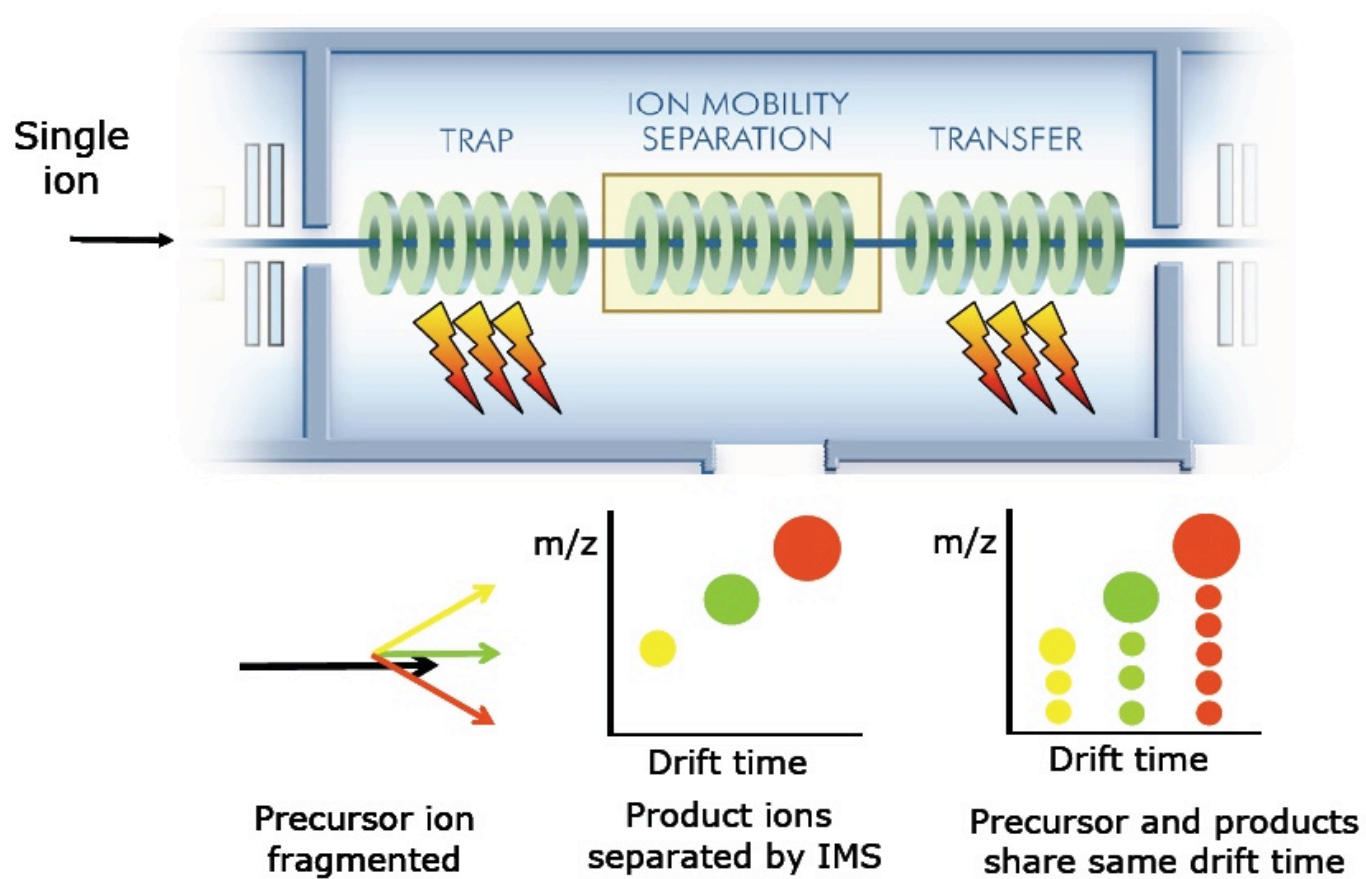
- Compounds with the same mass
- Target ions from matrix interferences

#### ➤ **Identify**

- mobility time could be considered as an additional IP  
according to SANCO/10684 requirements
- UPLC IM MS should reduce the rate of false positive and  
false negative samples







## Identification pesticides (Guidance criteria SANCO/10684)

79. Different types and modes of mass spectrometric detectors provide different degrees of selectivity, which relates to the confidence in identification. The requirements for identification are given in Table 3. They should be regarded as guidance criteria for identification, not as absolute criteria to prove presence or absence of a compound.

**Table 3** Identification requirements for different types of mass spectrometers

MS mode:	Single MS (standard mass resolution)	Single MS (high resolution/high mass accuracy)	MS/MS
Typical systems (examples)	quadrupole, ion trap, time-of-flight (TOF)	TOF, Orbitrap, FTMS, magnetic sector	Triple quadrupole ion trap, hybride MS (e.g. Q-TOF, Q-trap)
Acquisition:	Full scan, Limited m/z range, Selected ion monitoring (SIM)	Full scan, Limited m/z range, Selected ion monitoring (SIM)	Selected/multiple reaction monitoring (SRM/MRM), full scan product-ion spectra
Requirements for identification:	≥ 3 diagnostic ions, (preferably including quasi molecular ion)	≥ 2 diagnostic ions (preferably including the quasi molecular ion). Mass accuracy < 5 ppm. At least one fragment ion.	≥ 2 product ions
Ion ratio(s):	according to Table 4		