Ion Mobility-Time-of-Flight Mass Spectrometry as a new tool for the screening of pesticide residues in food

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Université de Liège

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isp wiv

Our Path today:

- Purpose
- Power
- Plackett-Burman
- Practical
- Prospect

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1

Pesticides are rich

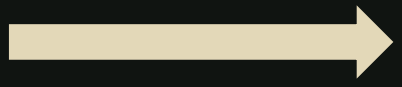
in diversity;

Chemical structure, solubility, volatility, potential for degradation…

in number;

~1200 molecules
~ 740 are allowed to be used in the EU
~ 500 compounds sought/sample
> ½ by LC

Multiresidue Methods are required tools for the determination of a great number of various compounds in one analysis



Has to be viable for the lab

Before

Specific

Complex

Time consuming

Now

No purification

Generic

Simple

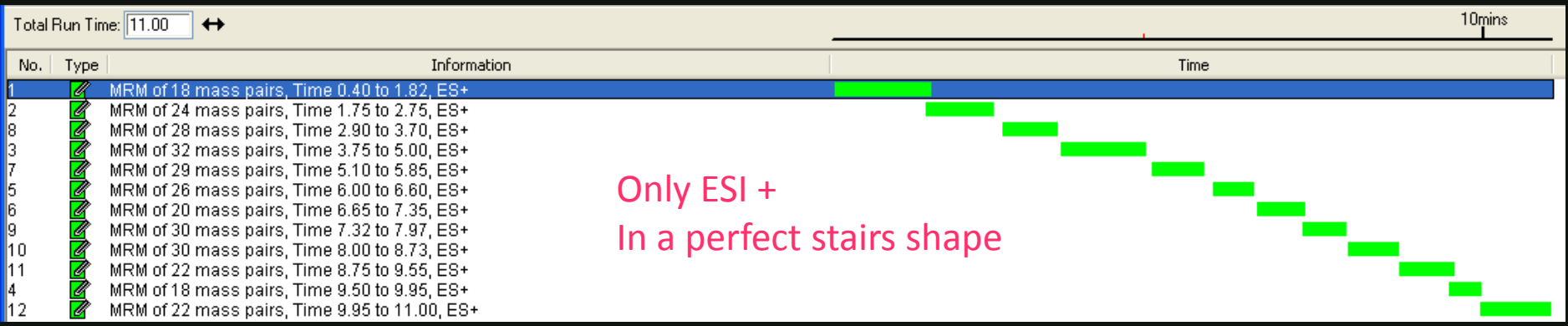
Fast

dirty samples

2

Mass spectrometry revolution

Optimize the acquisition



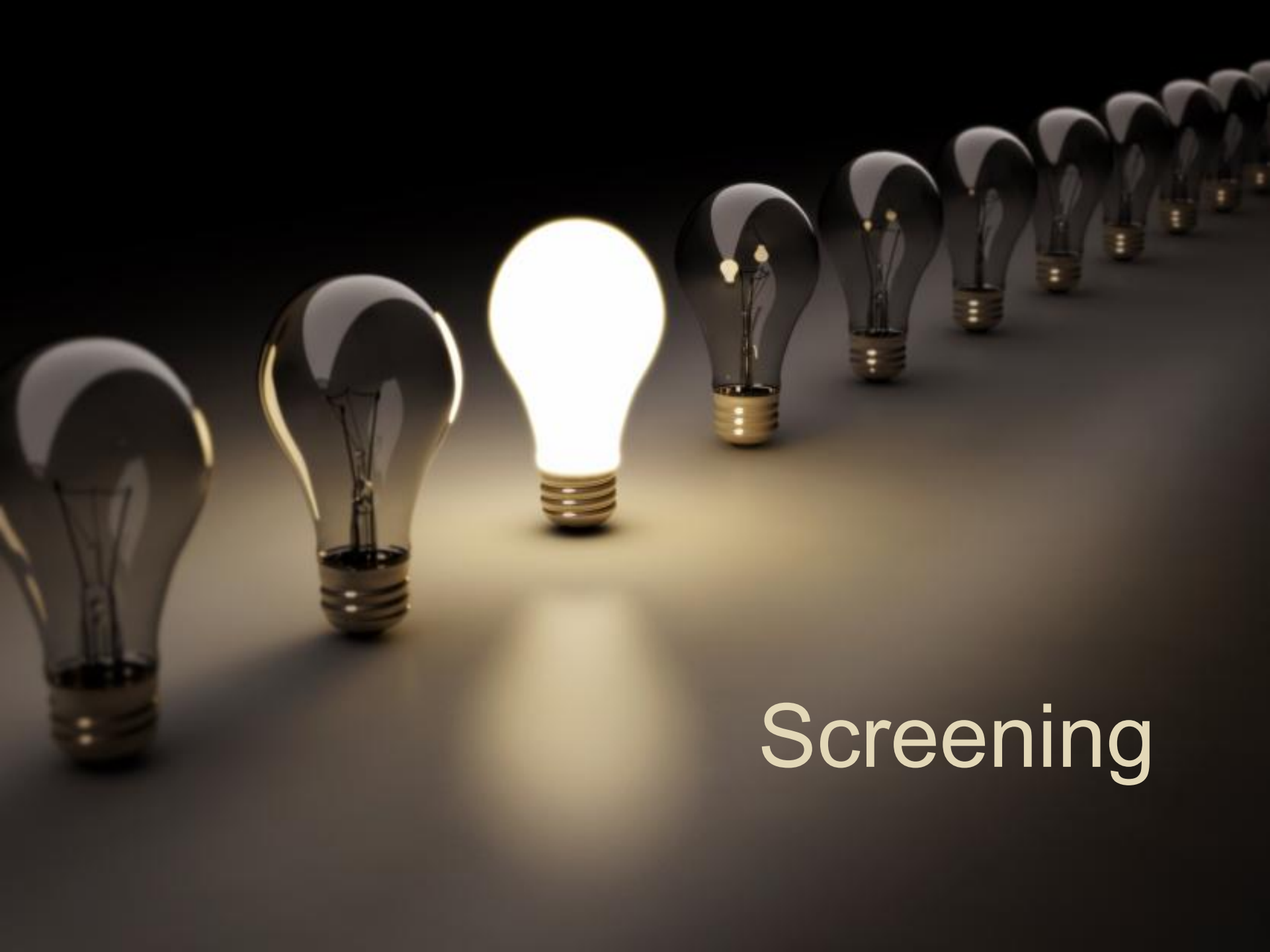
Pesticides residue analysis

Continuous challenge;

Increasing number of compounds,
at low levels,
in complex matrices


Houston,
We have a problem
Atlantis

Strategy


Screening

Screening method

Method to **detect** analyte (s)

in samples

in an easy/rapid way

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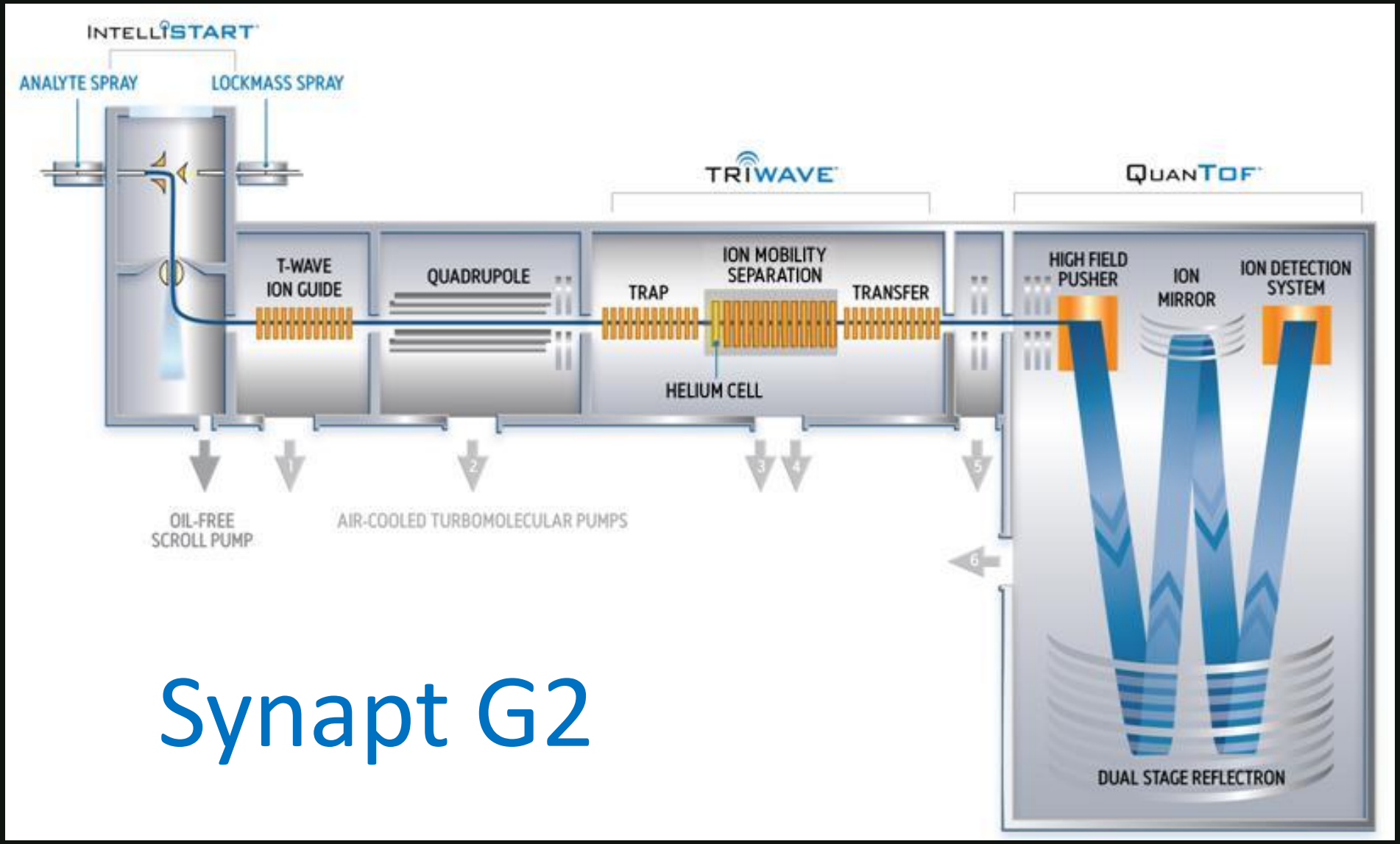
INTELLISTART
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QUANTOF
T-WAVE
ION GUIDE
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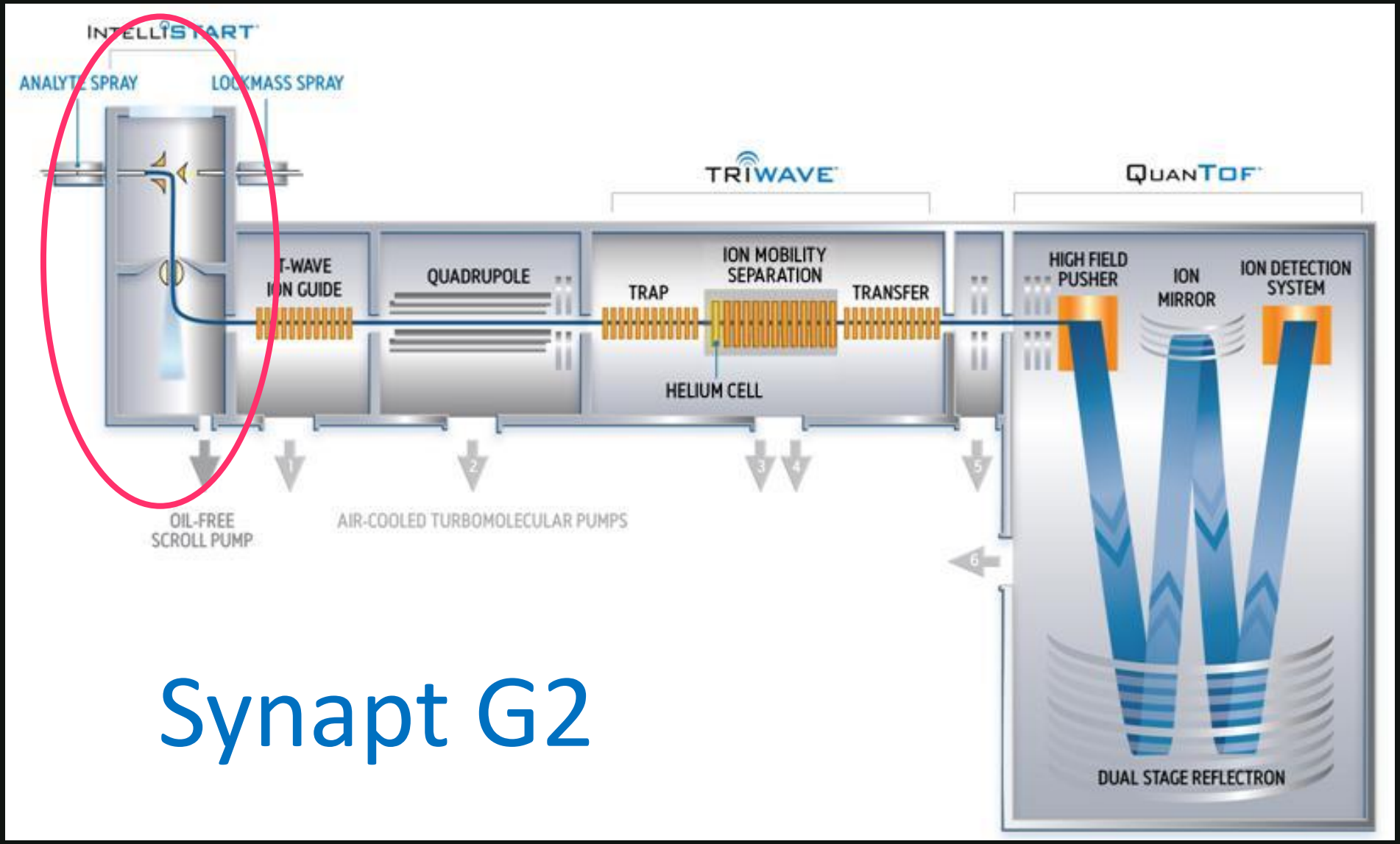
TRAP
ION MOBILITY
SEPARATION
TRANSFER
HELIUM CELL
HIGH FIELD
PUSHER
ION
MIRROR
ION DETECTION
SYSTEM
1
2
3
4
5
6
OIL-FREE
SCROLL PUMP
AIR-COOLED TURBOMOLECULAR PUMPS
DUAL STAGE REFLECTRON

Synapt G2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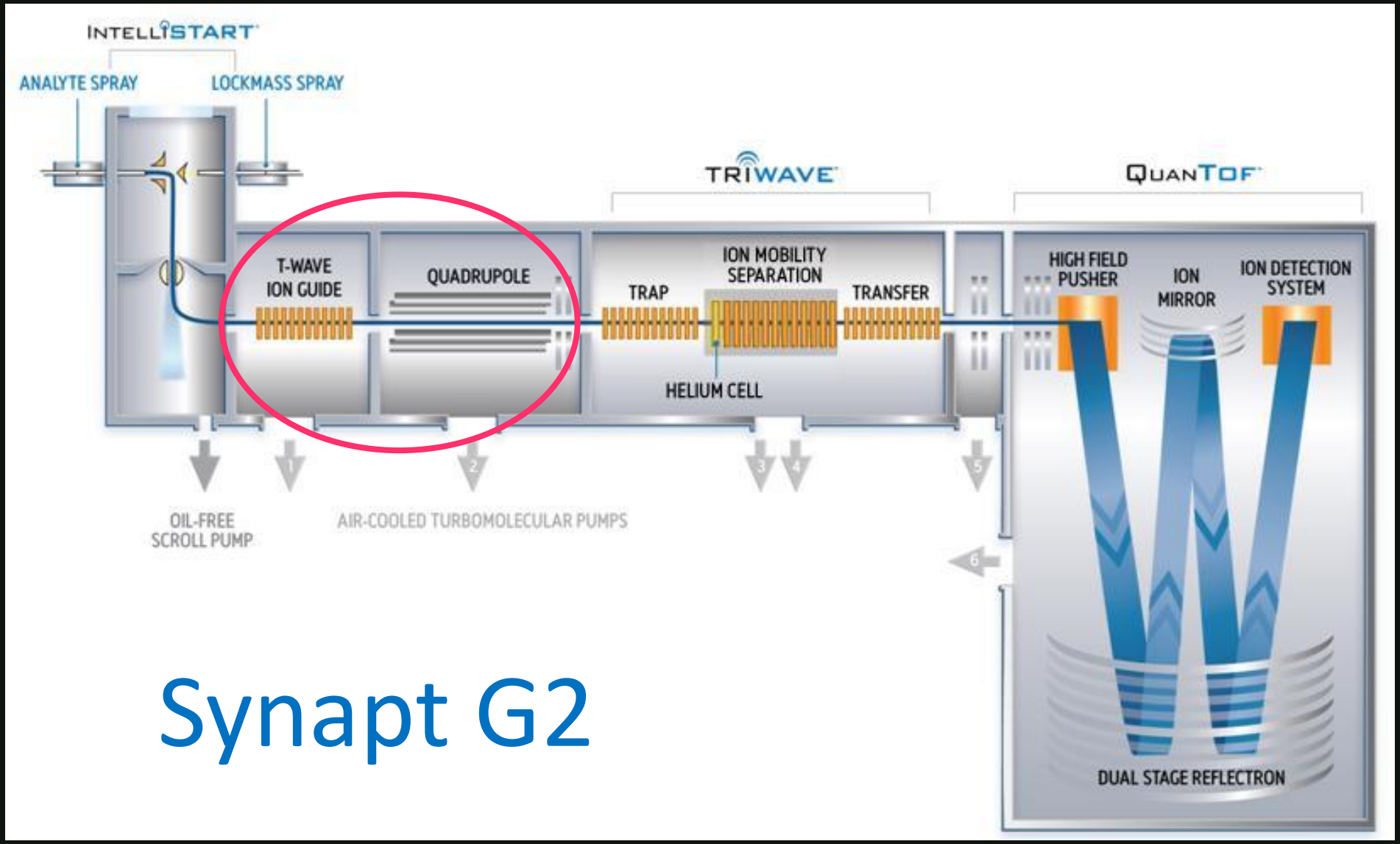
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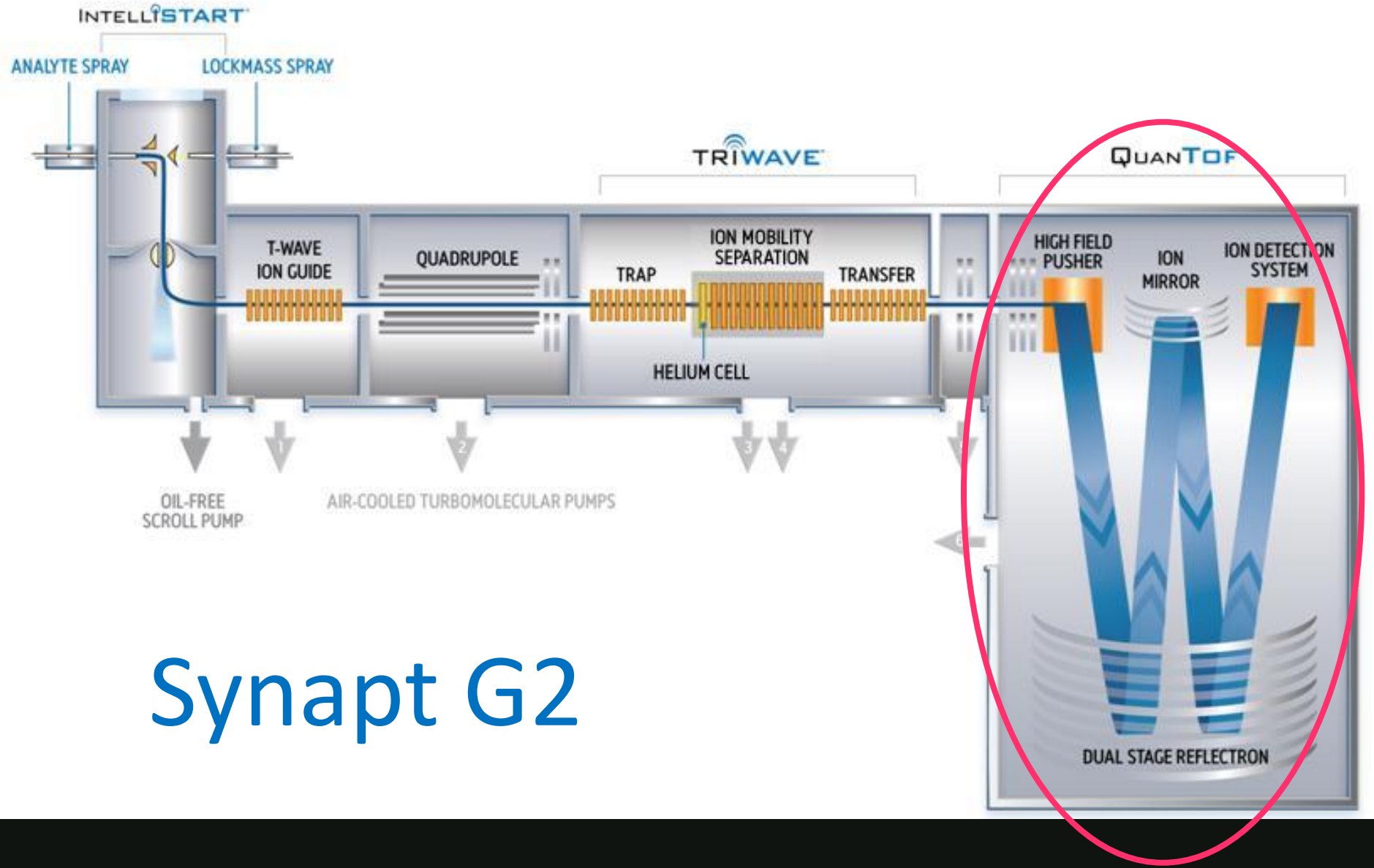
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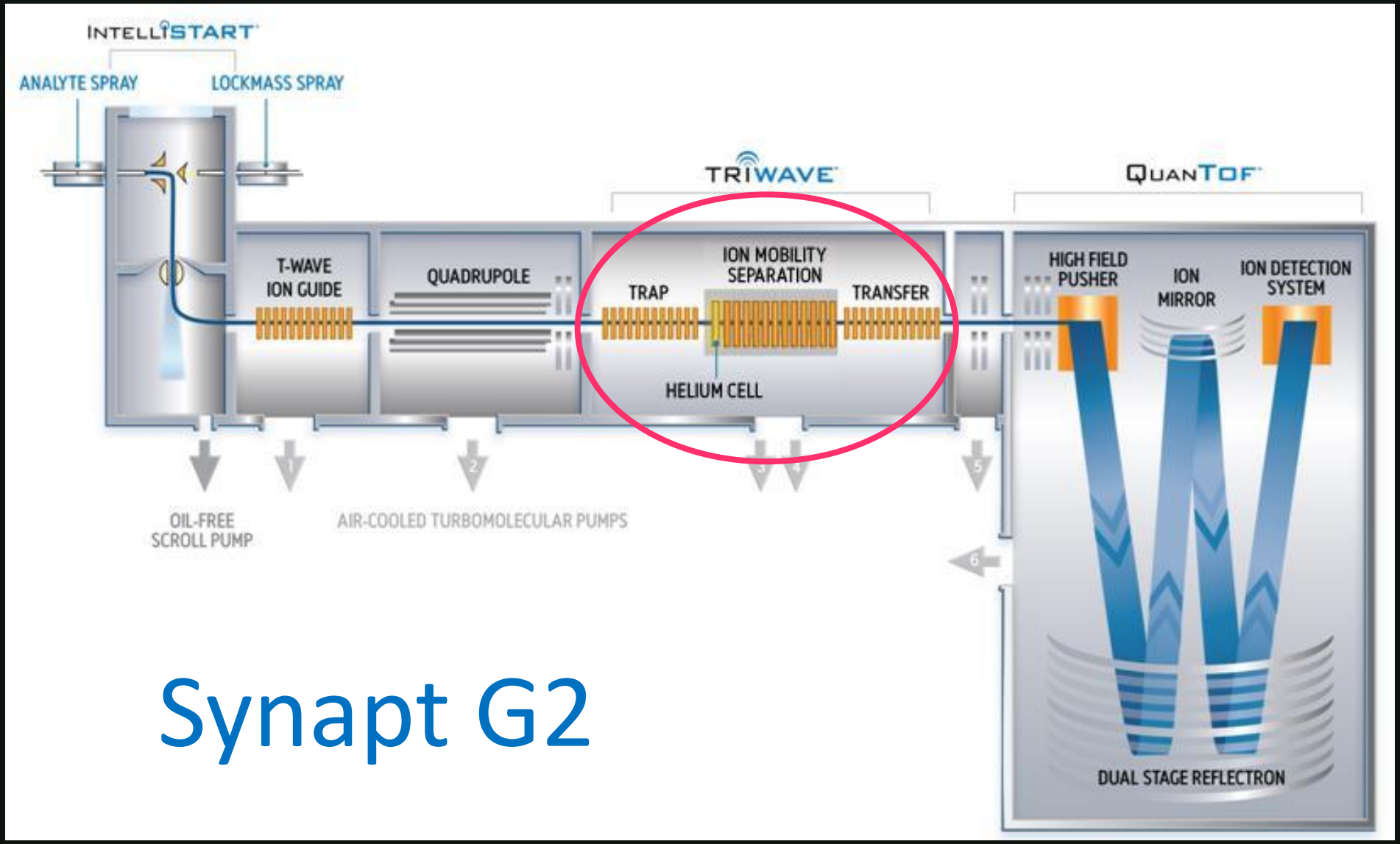
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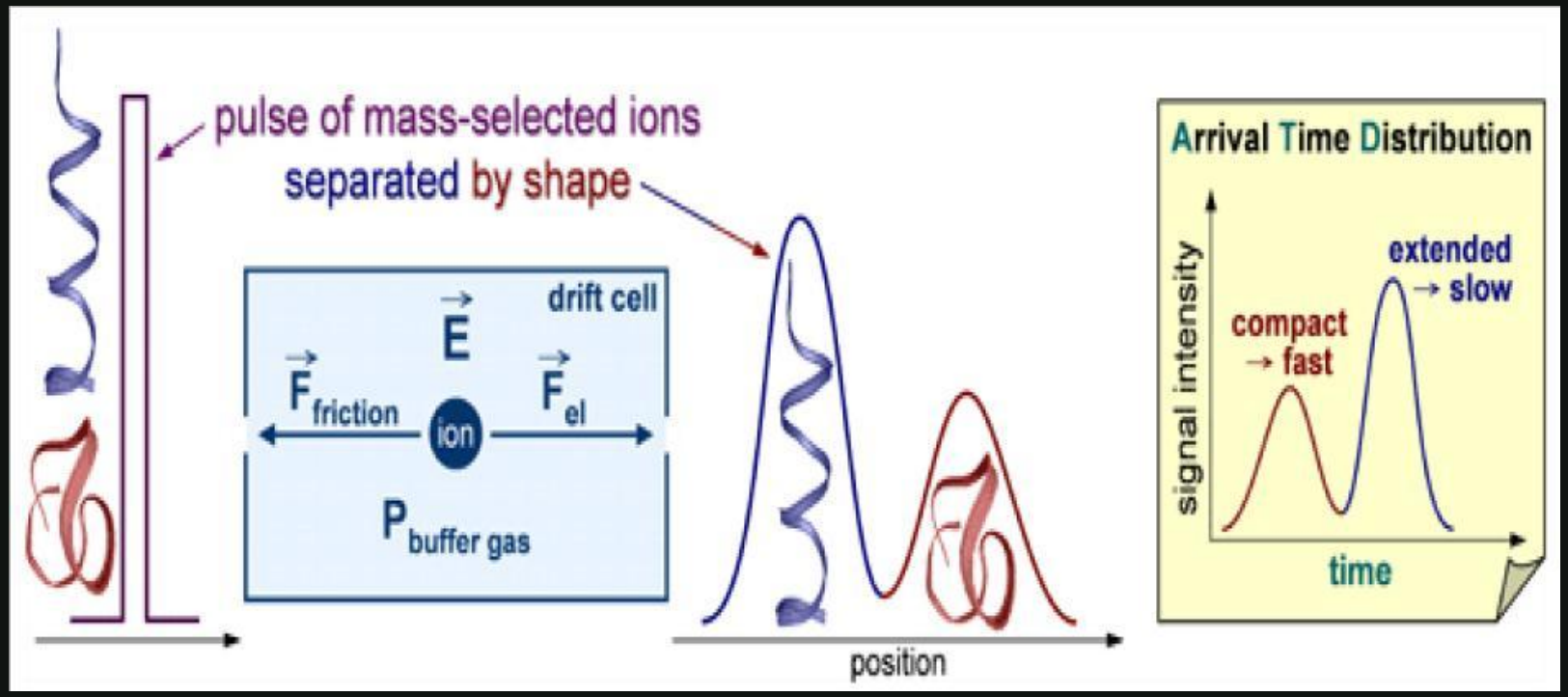
Synapt G2

Ion Mobility

Small, compact

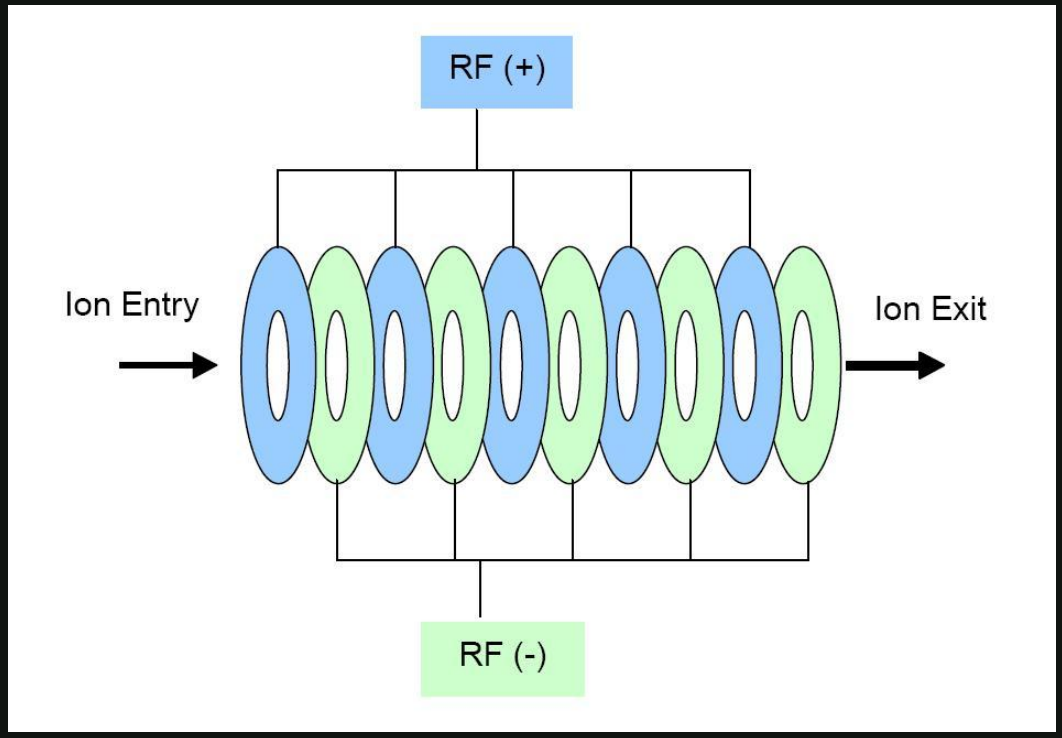
Large extended



- A 80 years old concept (C.F. Powell, 1932)
- The idea: ions «race»; the most mobile reach the detector first
- Separation is driven by electric fields not under vacuum

Traditional IMS

Travelling Wave Ion Guides



Introduced by Waters with the range of Premier MS:

Eliminates crosstalk problems ➡ faster ion transit

T-Wave and IM separation

High electric field applied SEQUENTIALLY throug the IM cell

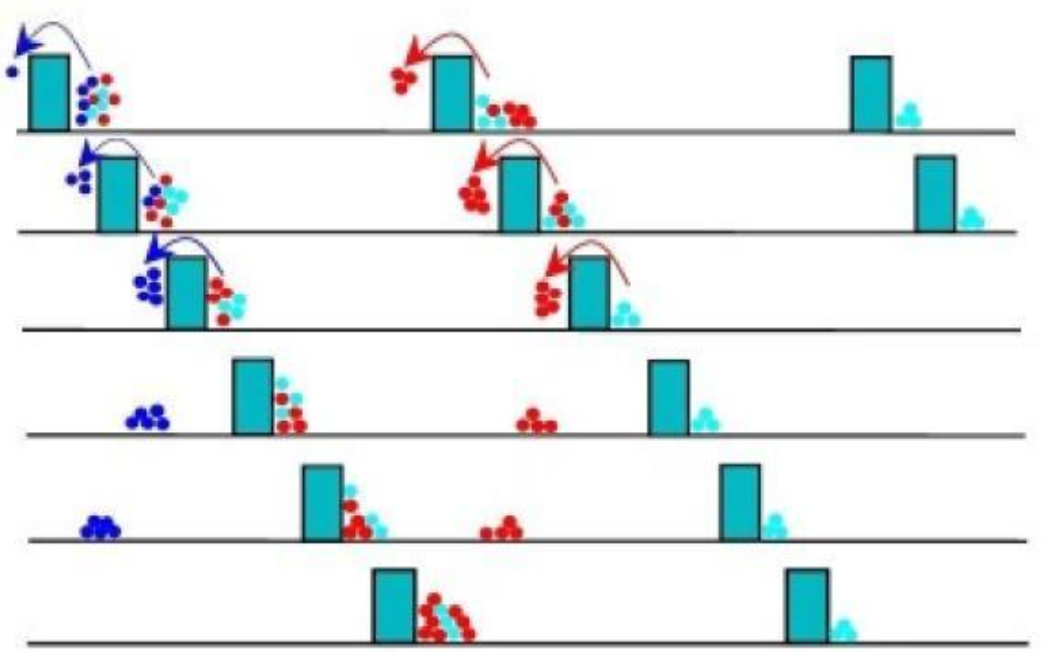
Ions are moved through the IM cell in PULSES as WAVES

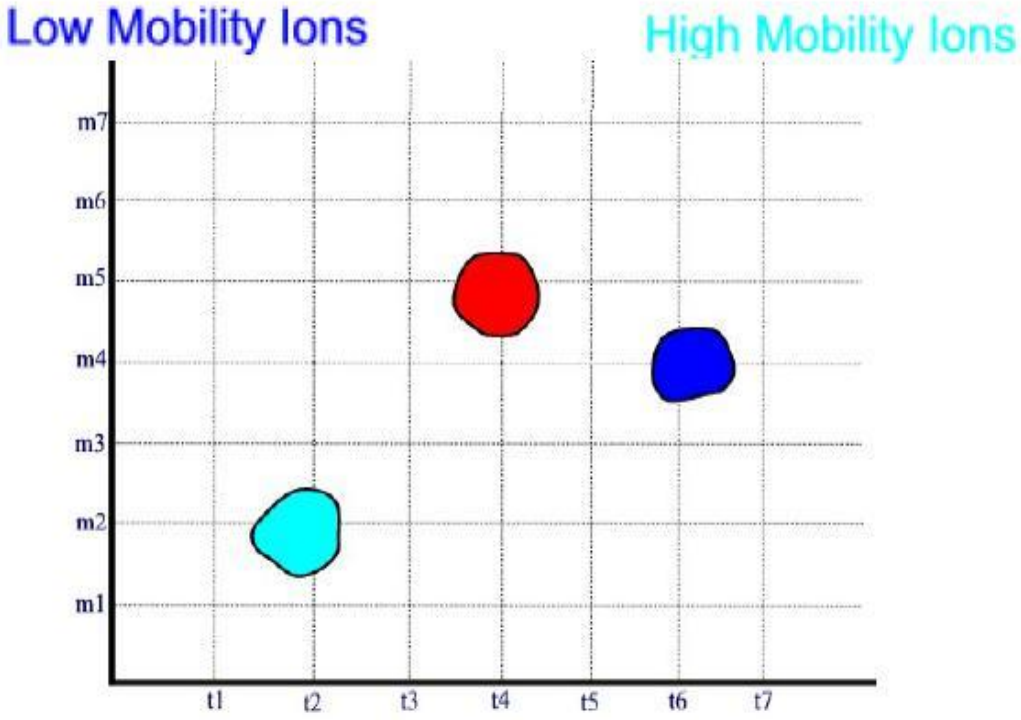
↓

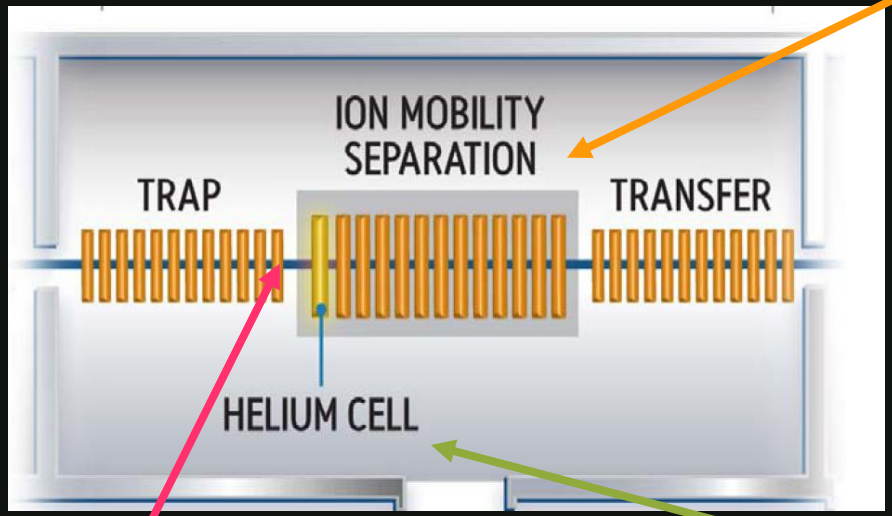
faster IMS duty cycles

↓

MS sensitivity is not compromized







Nature of the gas : N_2

IMS T-Wave velocity (m/sec)

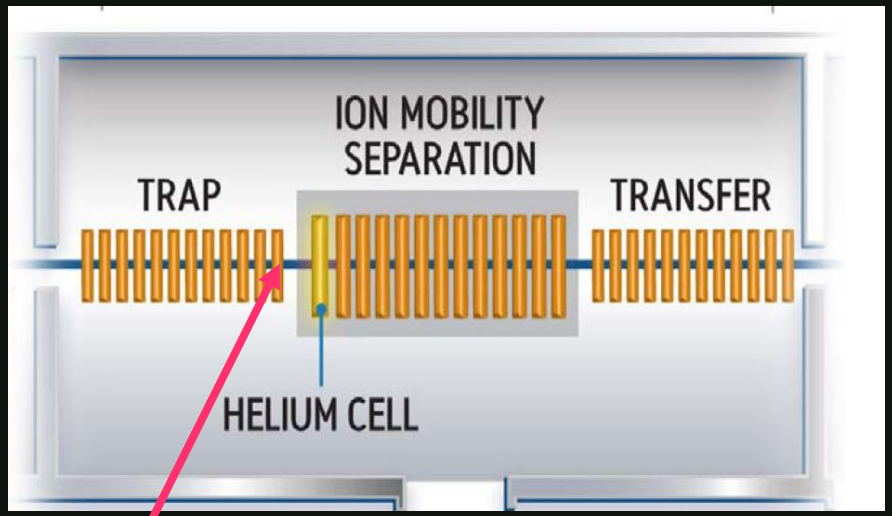
IMS T-Wave Height (V)

Gas Pressure (mbar)

Biais (V)

Helium Cell Pressure

Last voltage before the IM cell



Biais (V)

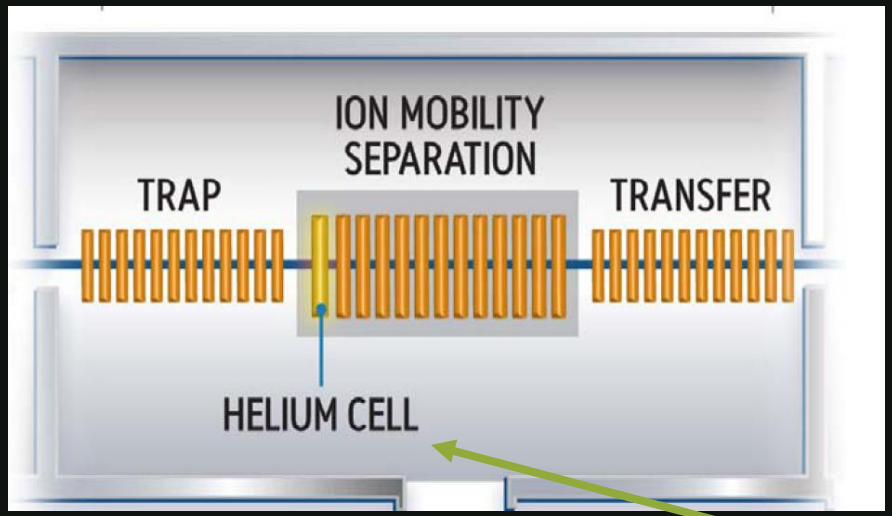
Too low

bad transmission

Too high

Ion fragmentation

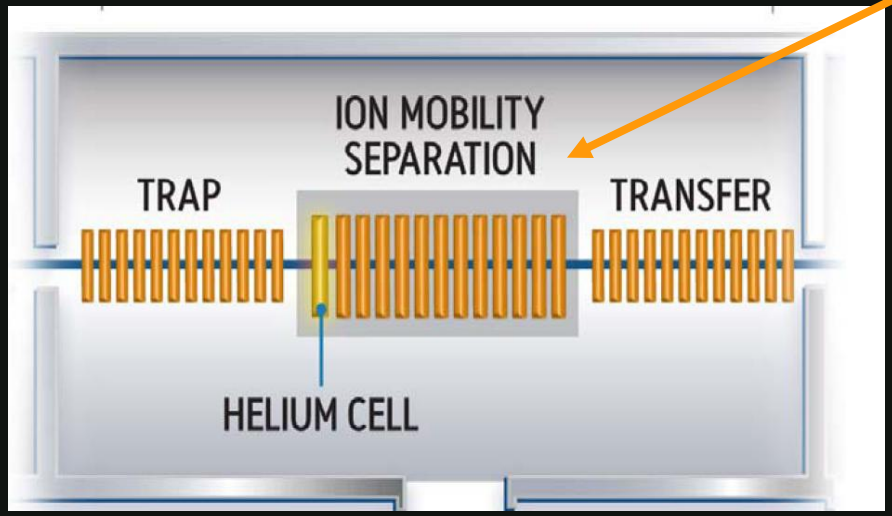
Buffer gas: softly reduces ion velocity



Maximises transmission of ions on entry into the IM cell

Helium Cell Pressure

IMS T-Wave velocity

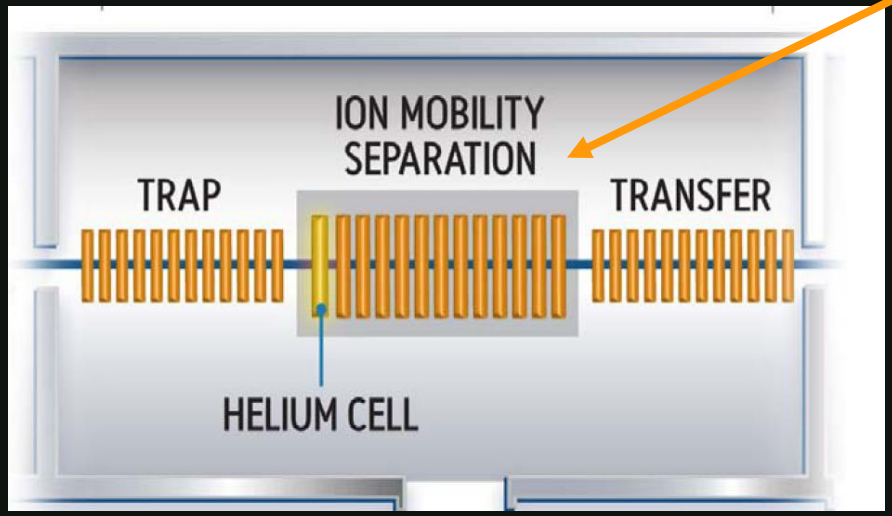


Fast

Ions roll over the wave

Better the separation

IMS T-Wave Height



High field

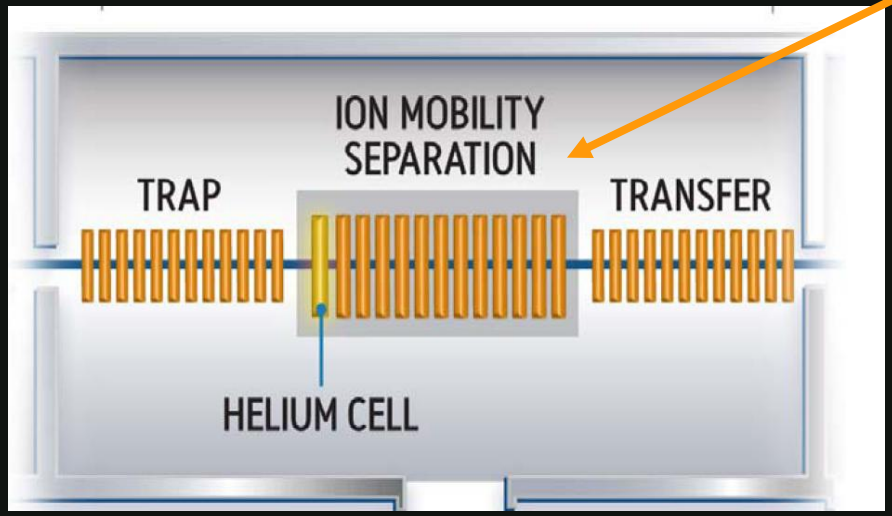
↓

High pulses

↓

Better separation selectivity

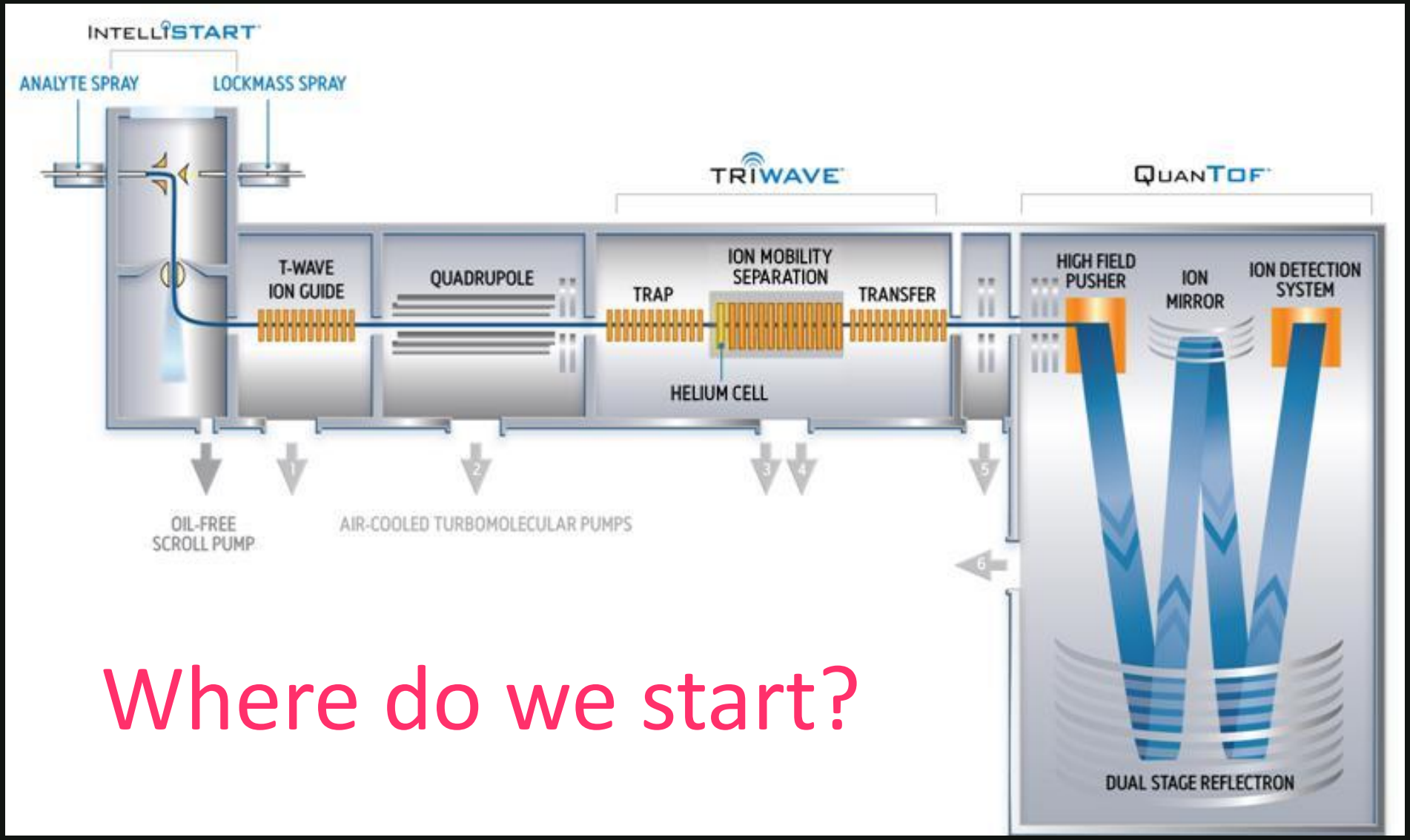
Gas Pressure



Higher

Better the resolving power


Stike the optimum



Where do we start?

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Plackett-Burman design

So called « Screening Designs »

Finds influencing factors with a limited number of experiments

Plackett-Burman design

5 parameters

IMS T-Wave velocity

IMS T-Wave Height

Gas Pressure

Helium Cell Pressure

Biais (V)

3 responses

Intensity

Resolution

Relative drift time

The construction of the design is done with 15 runs

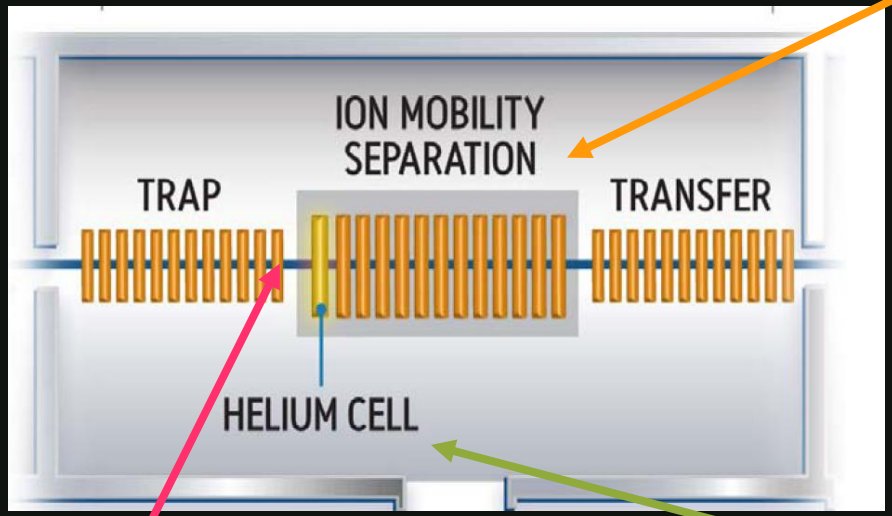
Most influencing factors

Nature of the gas

IMS T-Wave velocity (m/sec)

IMS T-Wave Height (V)

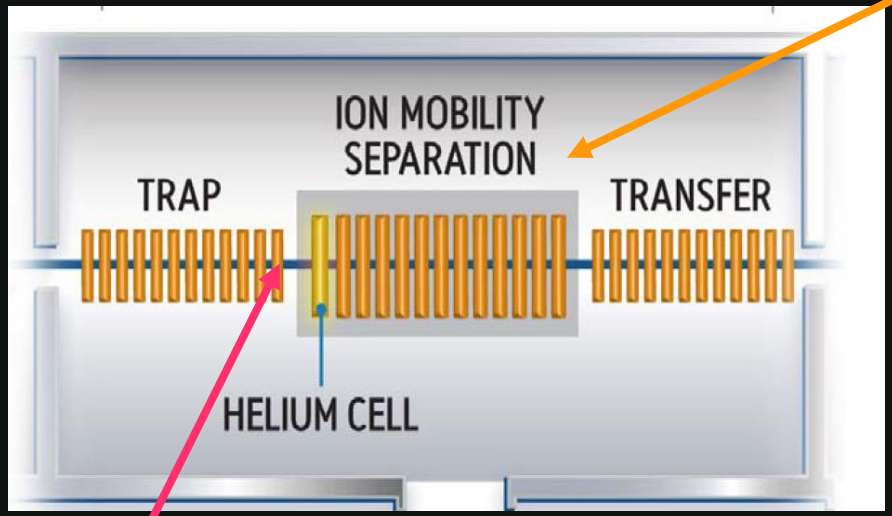
Gas Pressure (mbar)



Biais (V)

Helium Cell Pressure

Most influencing factors



Gas Pressure (mbar)

Biais (V)

Optimization of 2 parameters!

Central Composite Design

The 3 less influencing parameters are set to the values of maximum separation

Then the CCD will be perofrmed with the 2 most influencing parameters

2 parameters

Gas Pressure

Biais (V)

3 responses

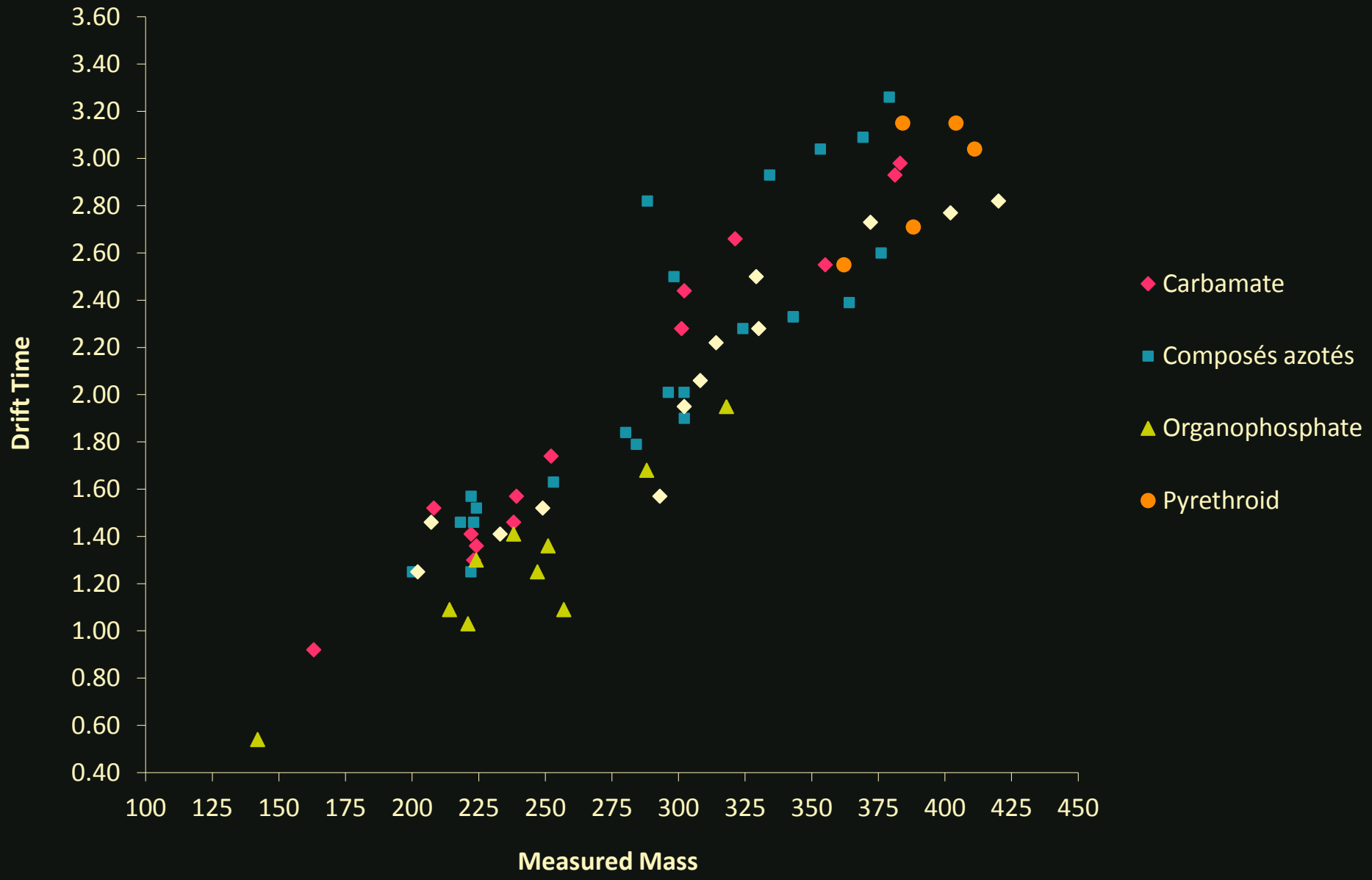
Intensity

Resolution

Relative drift time

The construction of the design is done with 13 runs (5 with centered values)

Ion Mobility of 5 classes of pesticide



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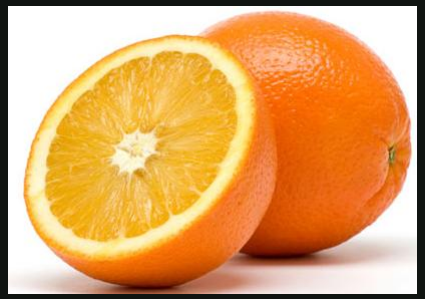
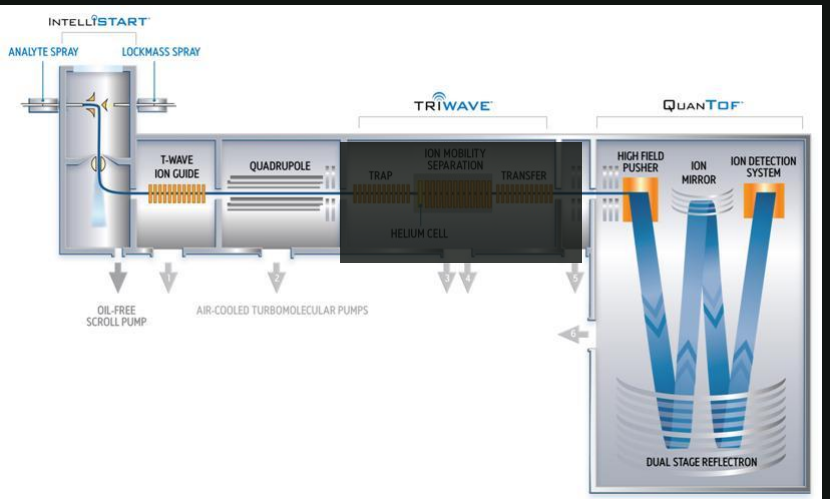
How can we help the Detection ?




Extraction

MS

IM-MS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ION DETECTION SYSTEM
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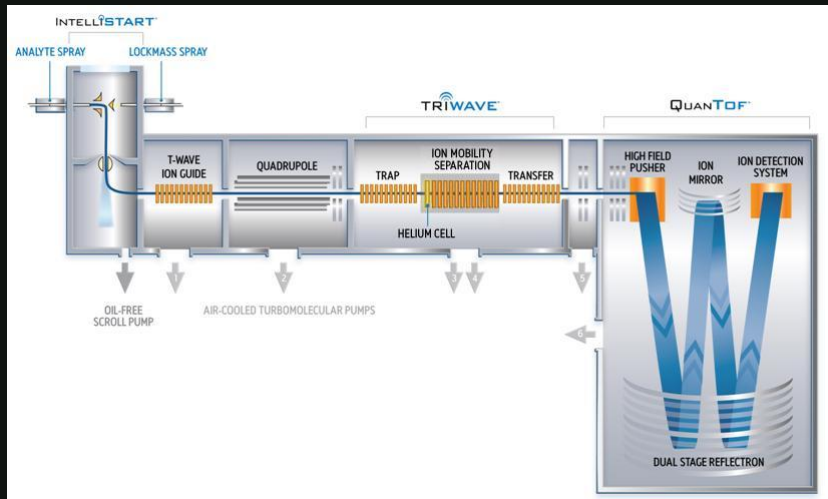
DUAL STAGE REFLECTRON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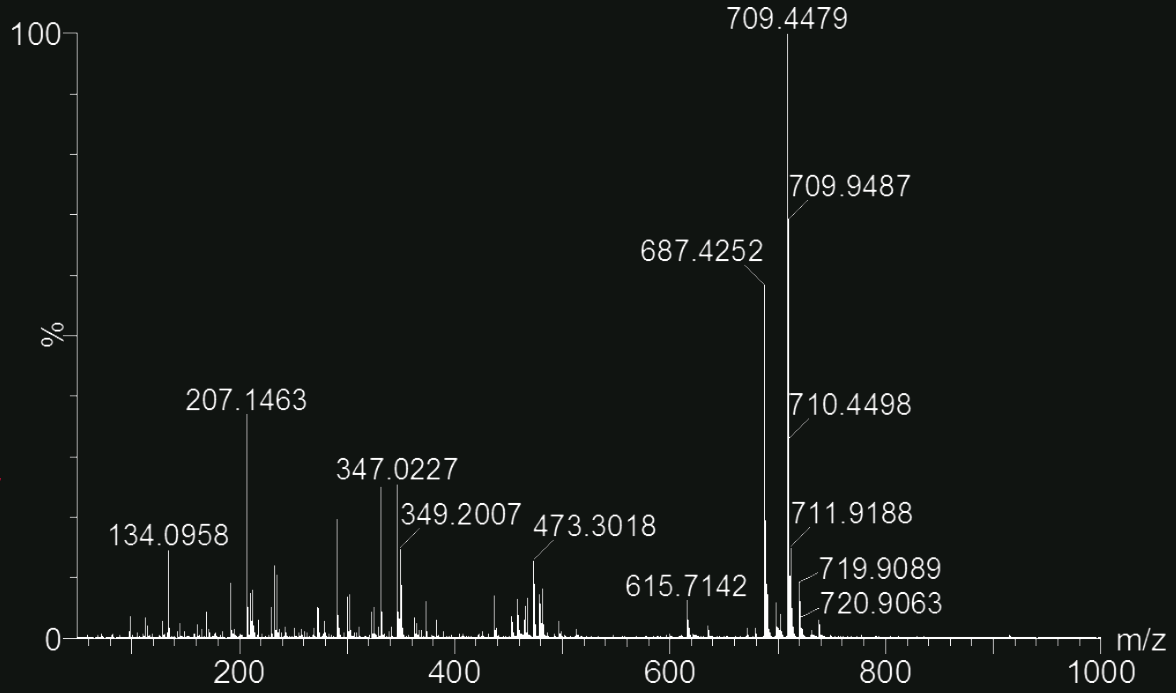
Diuron

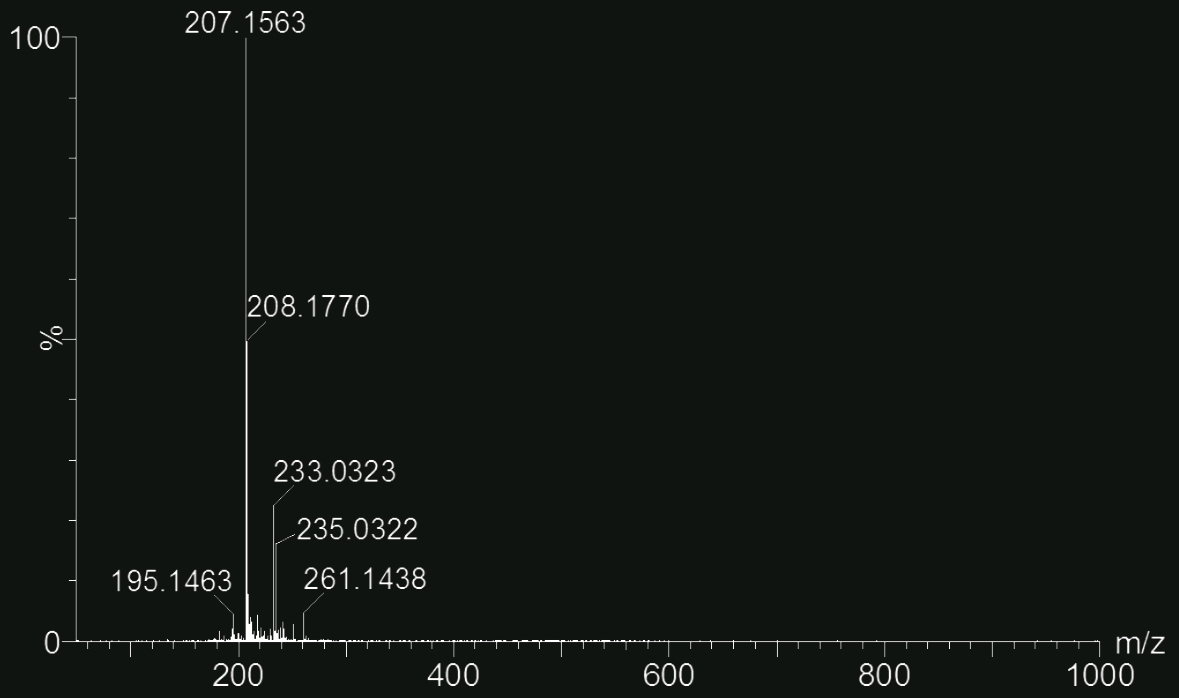
m/z (+1) 233.0248

Rt 6.38 min

MS

IM-MS





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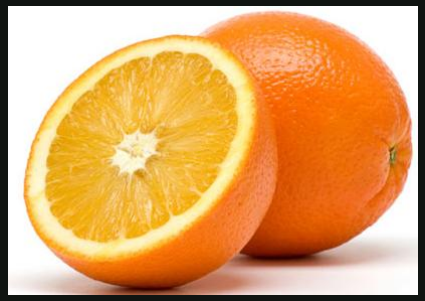
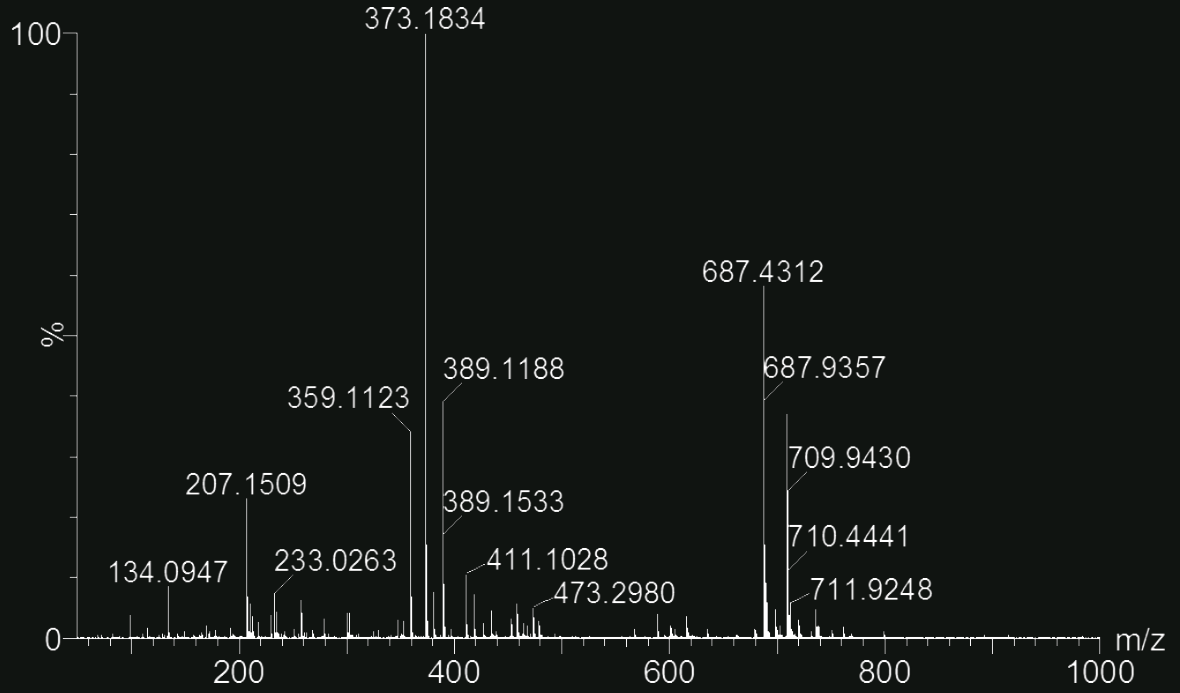
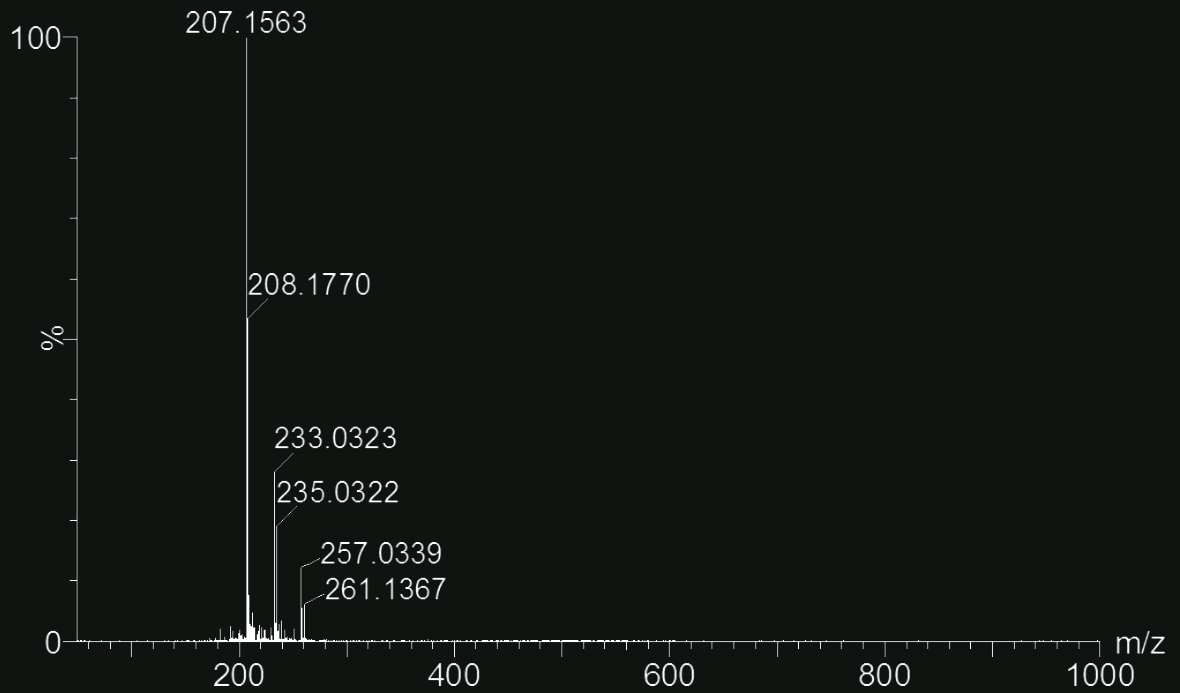


MS

IM-MS





Diuron

m/z (+1) 233.0248

Rt 6.38 min

MS

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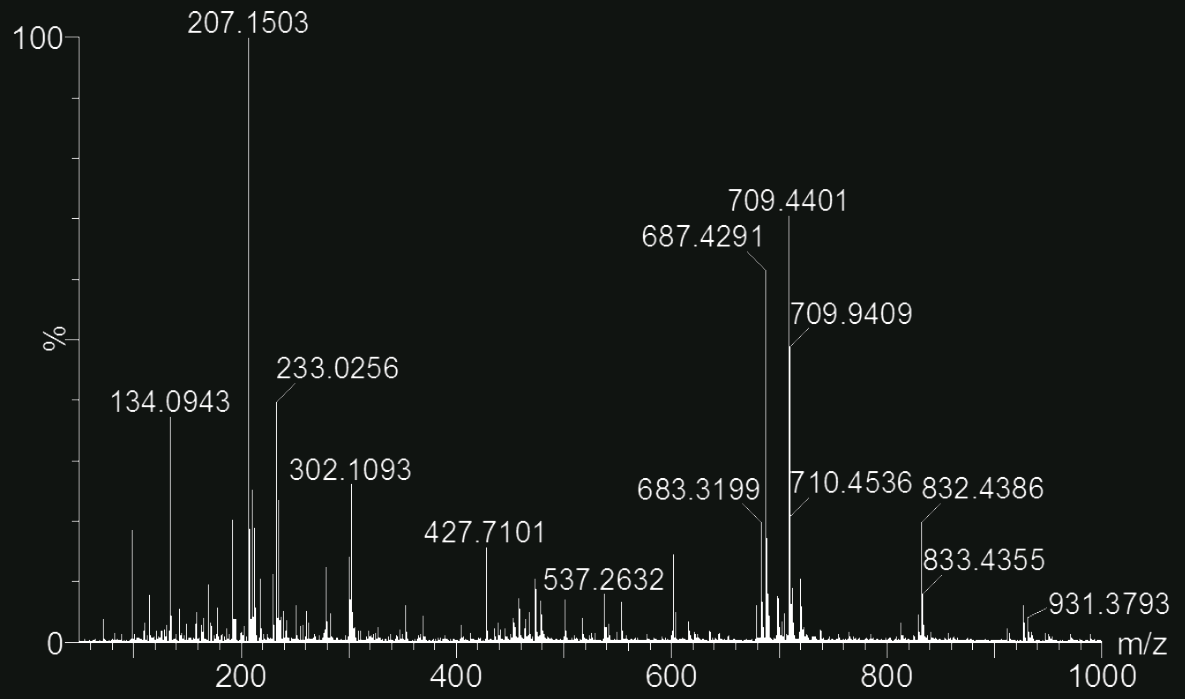
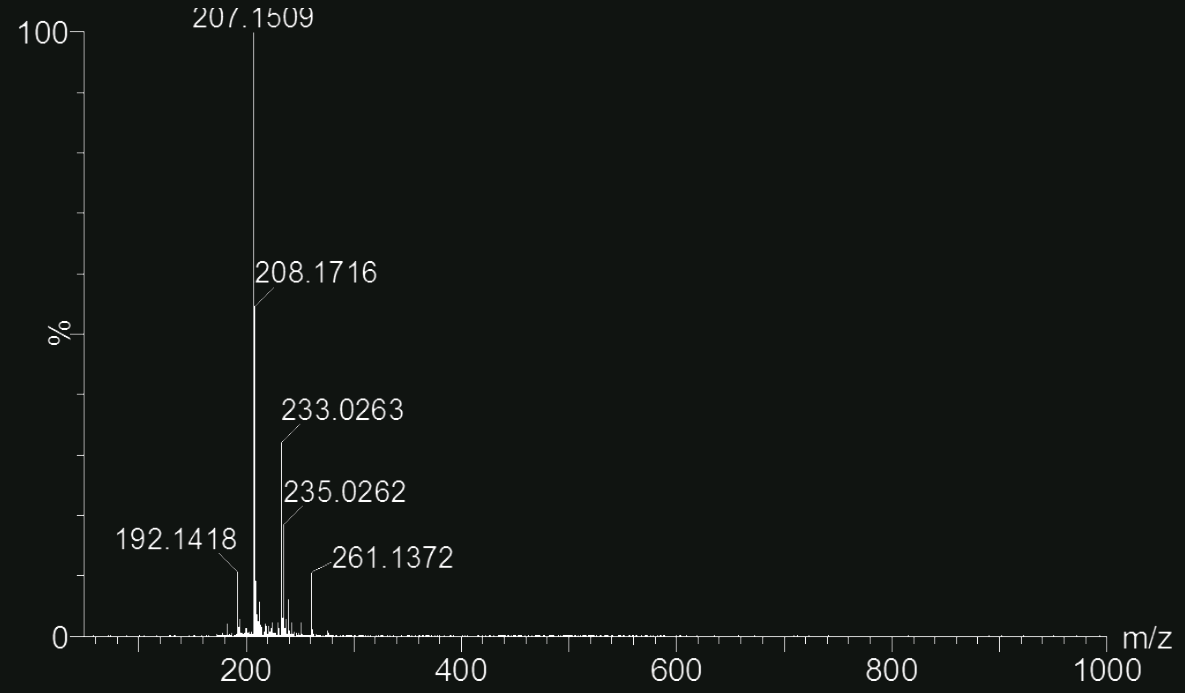




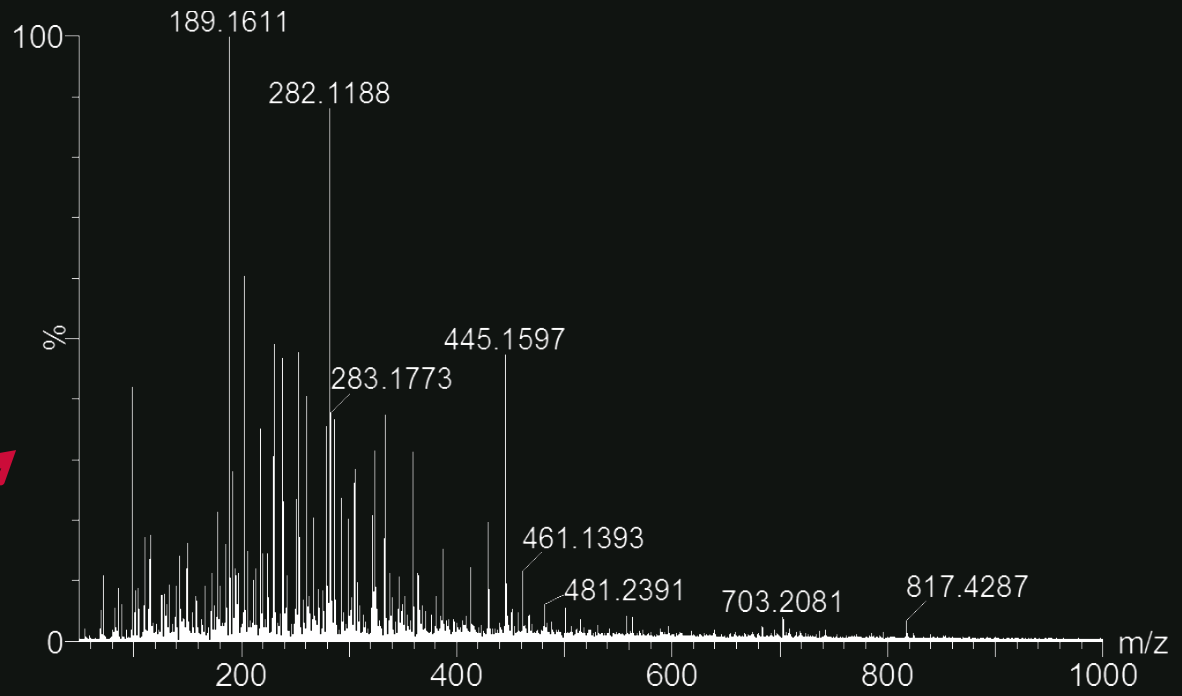
Propamocarb

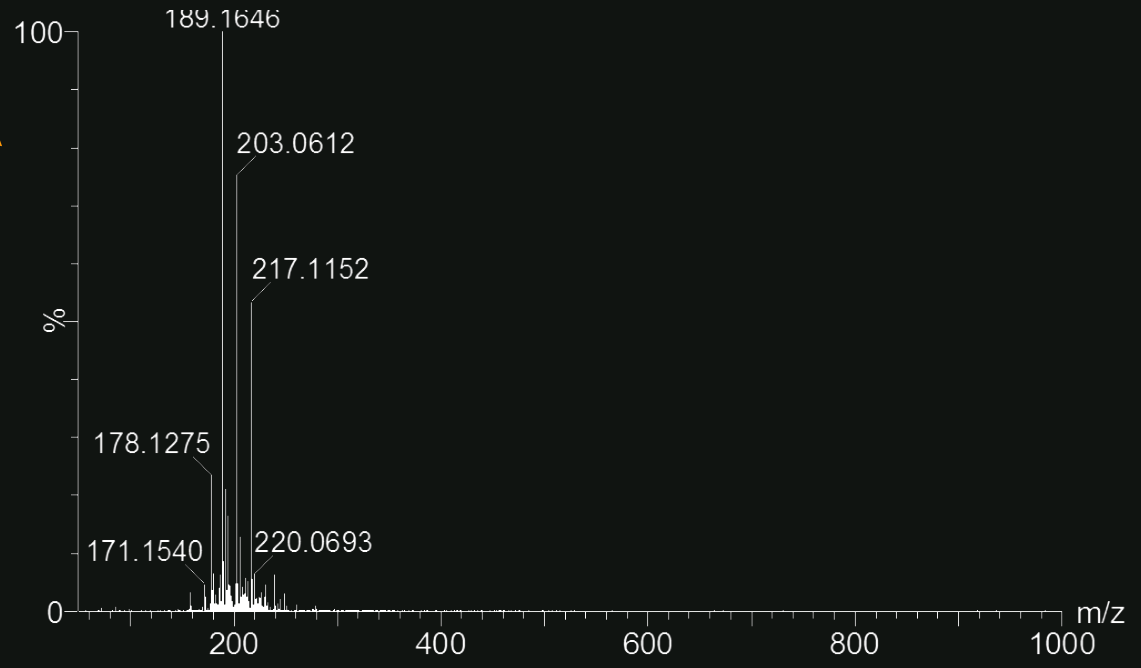
m/Z (+1) 189.1603

Rt 1.84 min

MS

IM-MS





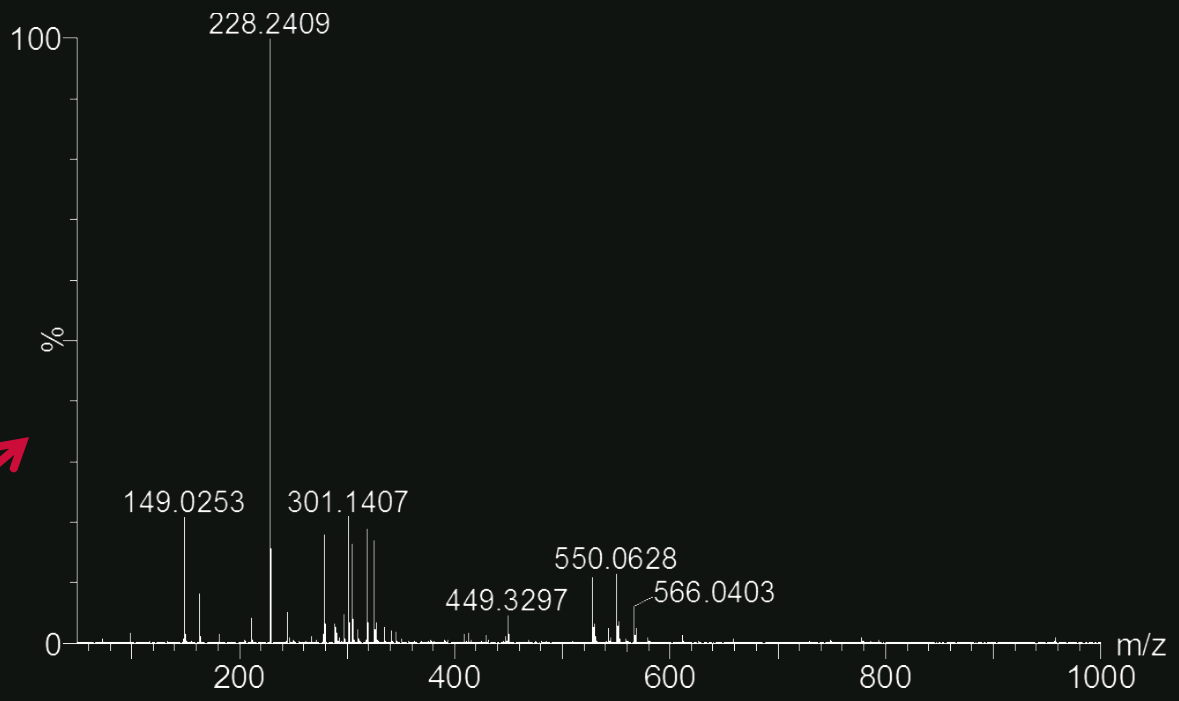
Indoxacarb

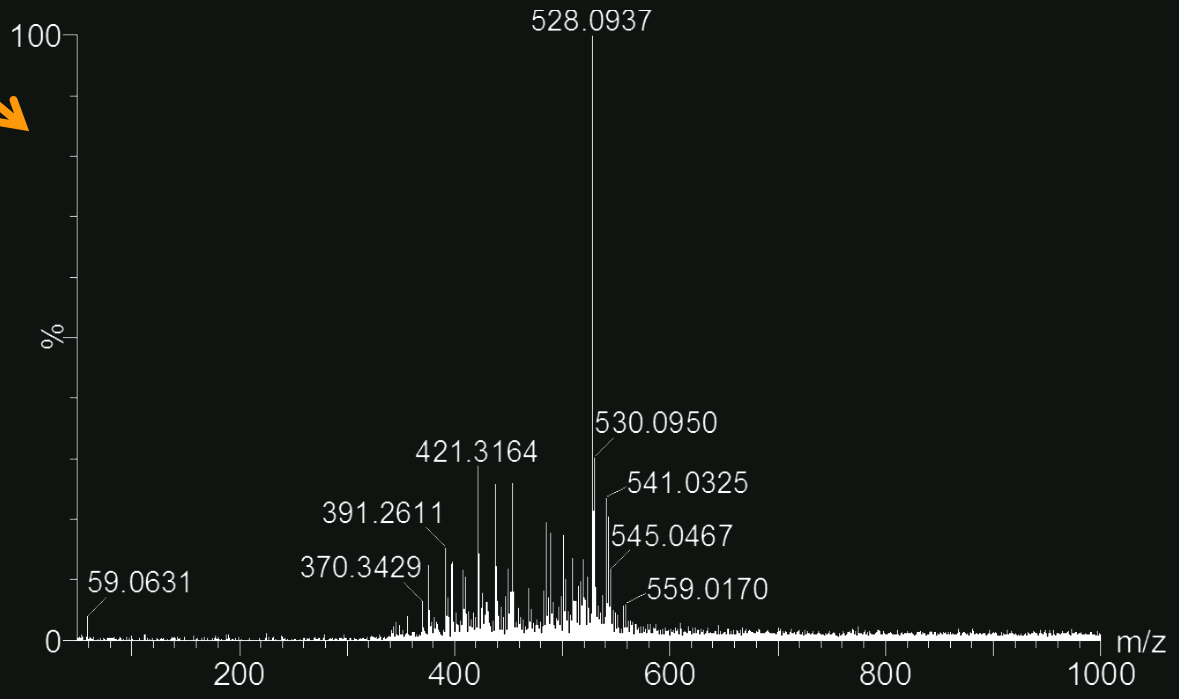
m/Z (+1) 528.0785

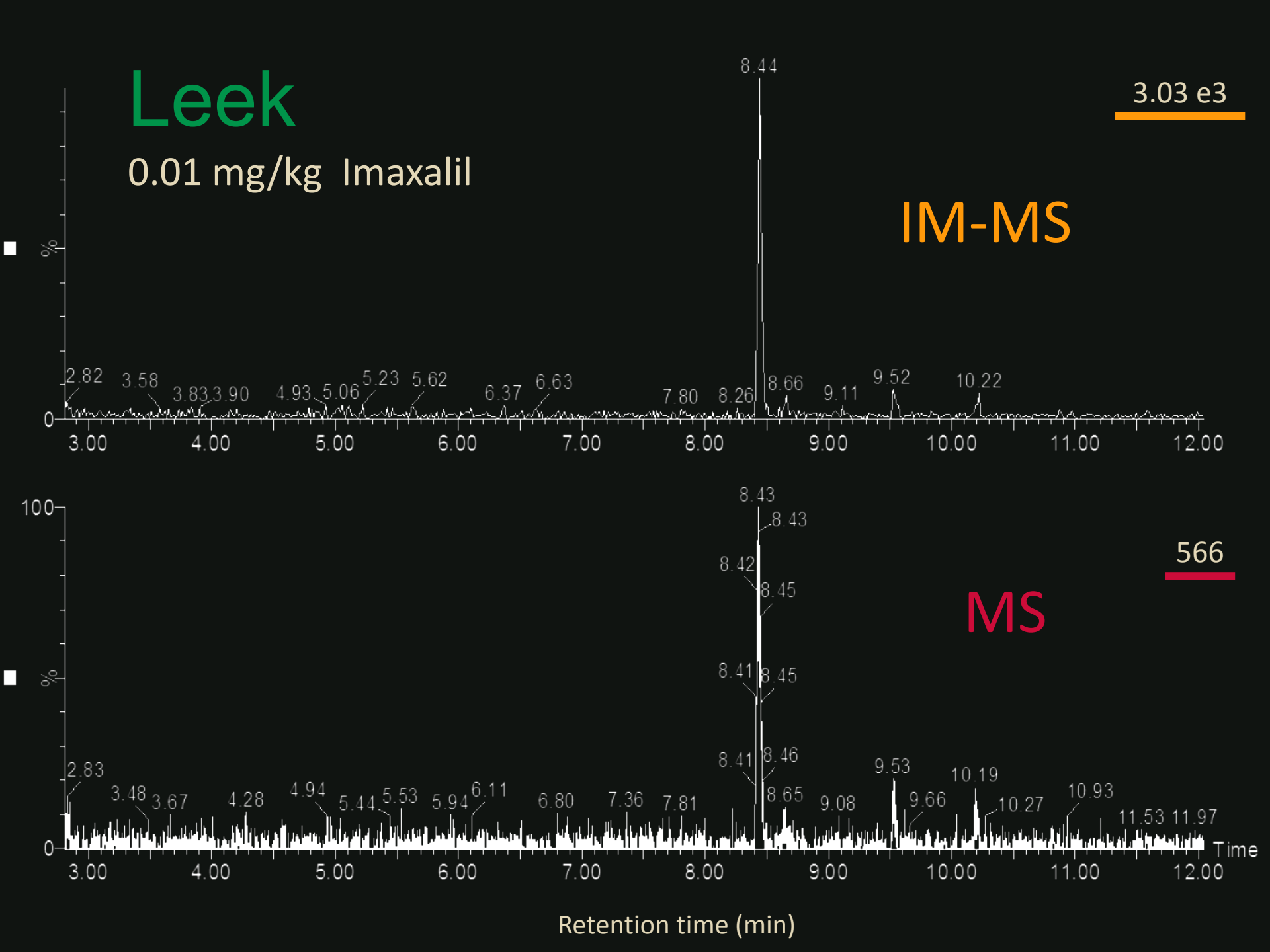
Rt 9.1 min

MS

IM-MS



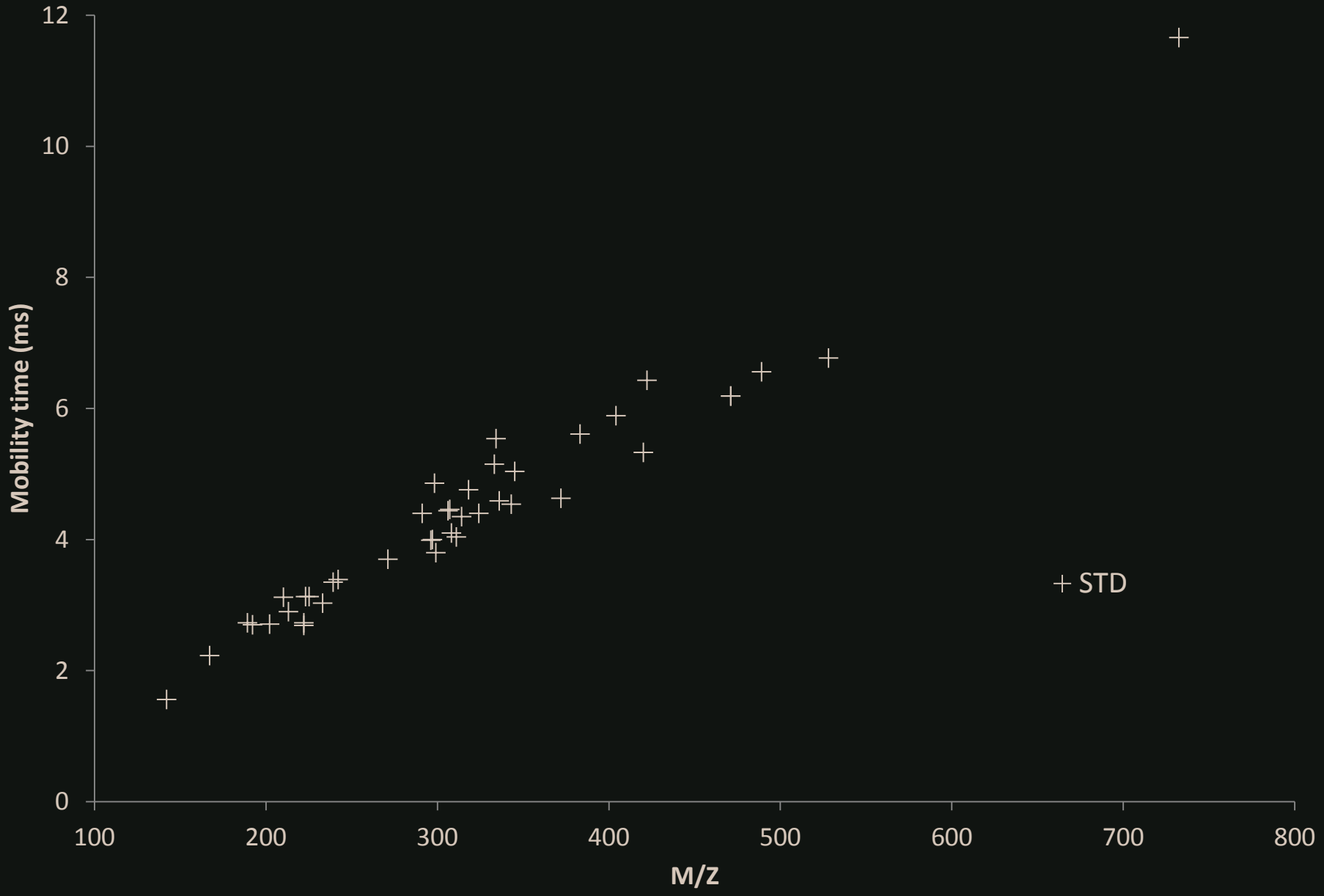



Leek
0.01 mg/kg Imaxalil
IM-MS
3.03 e3
MS
566
Retention time (min)
Time

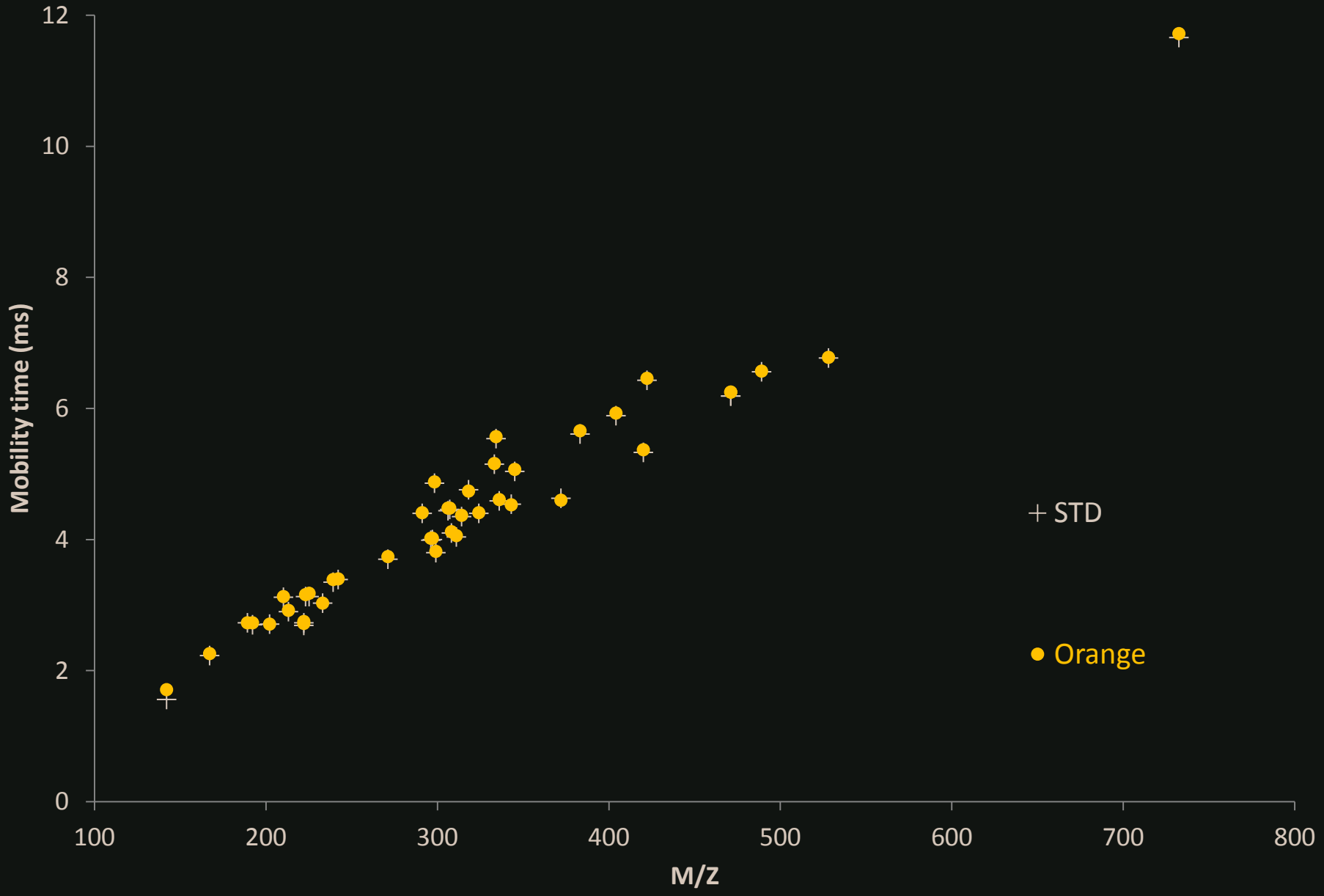
How can we help the Identification process ?

New IP ?

Matrix effect on mobility time?



Matrix effect on mobility time?



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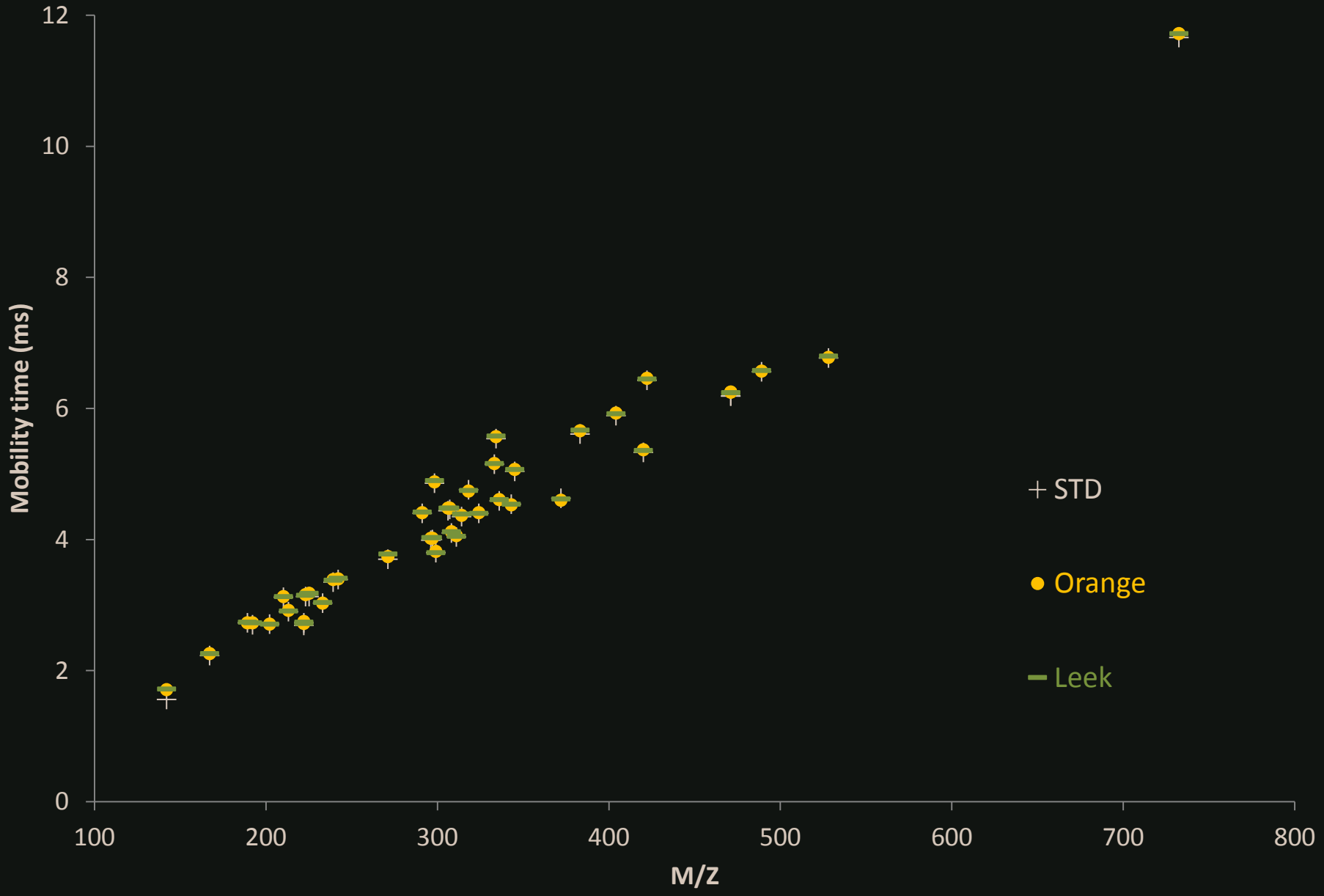
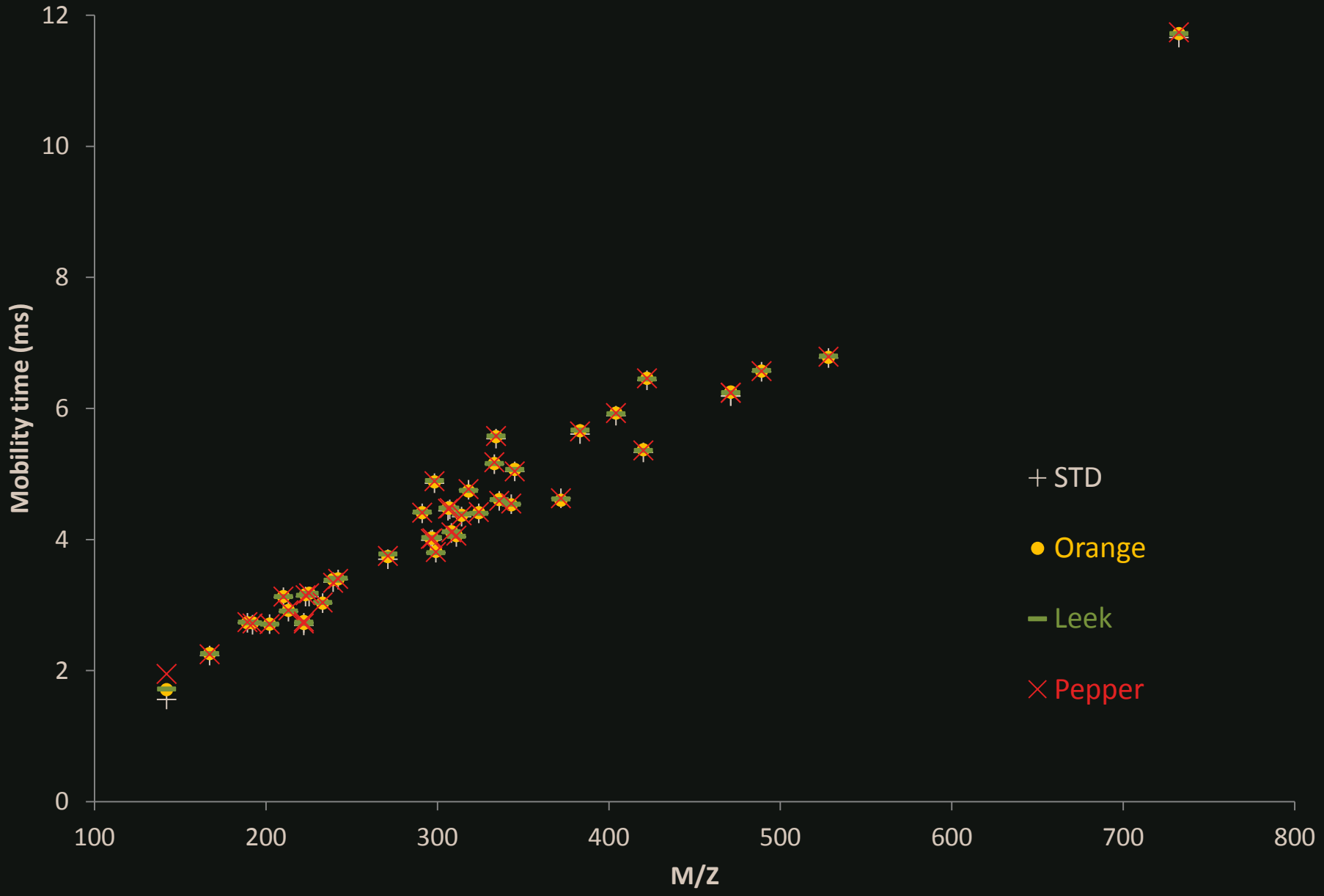


Matrix effect on mobility time?



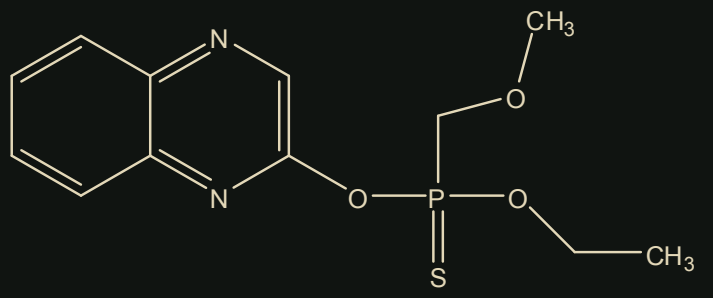
False positive: case study (SM 3)

Unusual Suspect

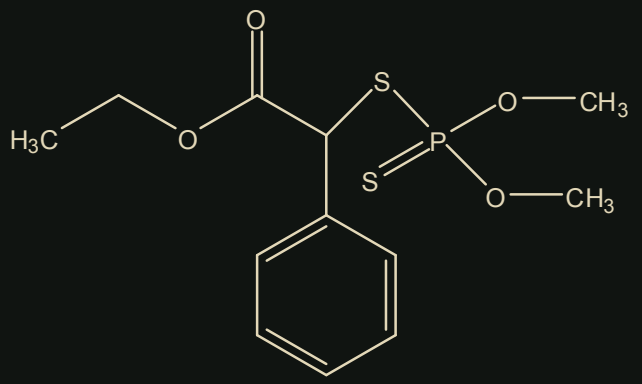
		MS/MS confirmation
Fenamidone	312.1172 (+1)	YES
Mevinphos	225.0528 (+1)	YES
Phentoate	321.0384 (+1)	NO
Quinalphos	299.0619 (+1)	YES
Terbuthylazine	230.1172 (+1)	YES

Unusual Suspect

Quinalphos 299.0619 (+1) 8.22 (min)



Phenthoate 321.0384 (+1) 8.27 (min)

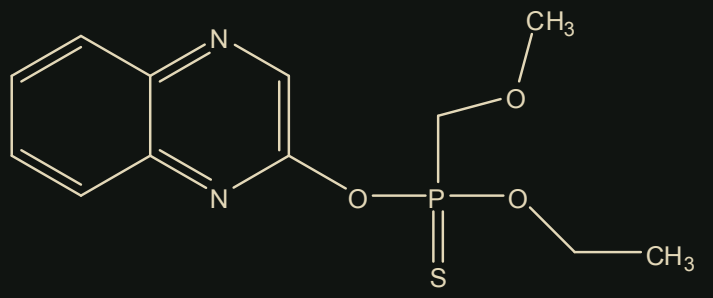


Co-elution

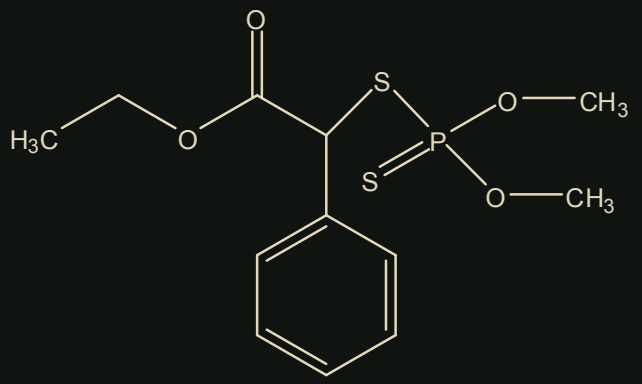

11
Na
Sodium
22.989770
[Ne]3s
5.1391
2S1/2
12
Mg
Magnesium
24.3050
[Ne]3s2
7.6462
1S0
20
Ca
19
K
2S1/2

Unusual Suspect

Quinalphos 299.0619 (+1)



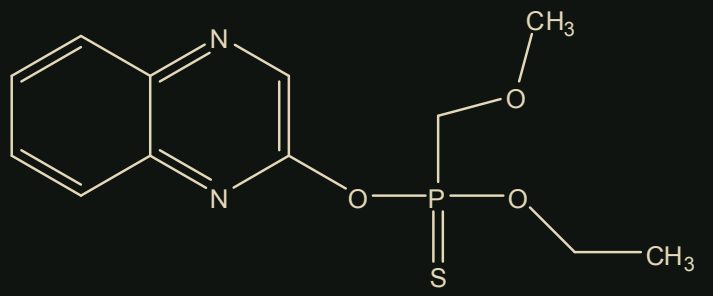
Phenthoate 321.0384 (+1)



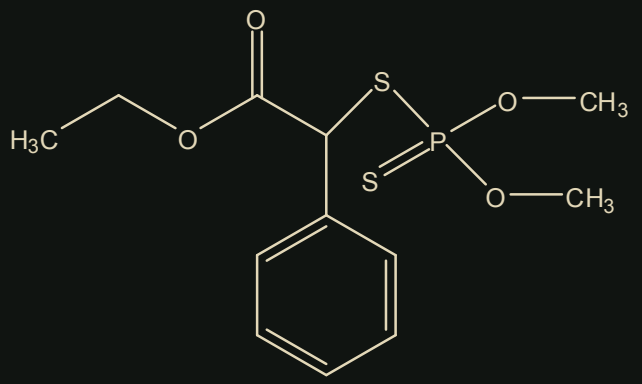
Quinalphos + Na 321.0439 (+1)

Unusual Suspect

Quinalphos 299.0619 (+1)



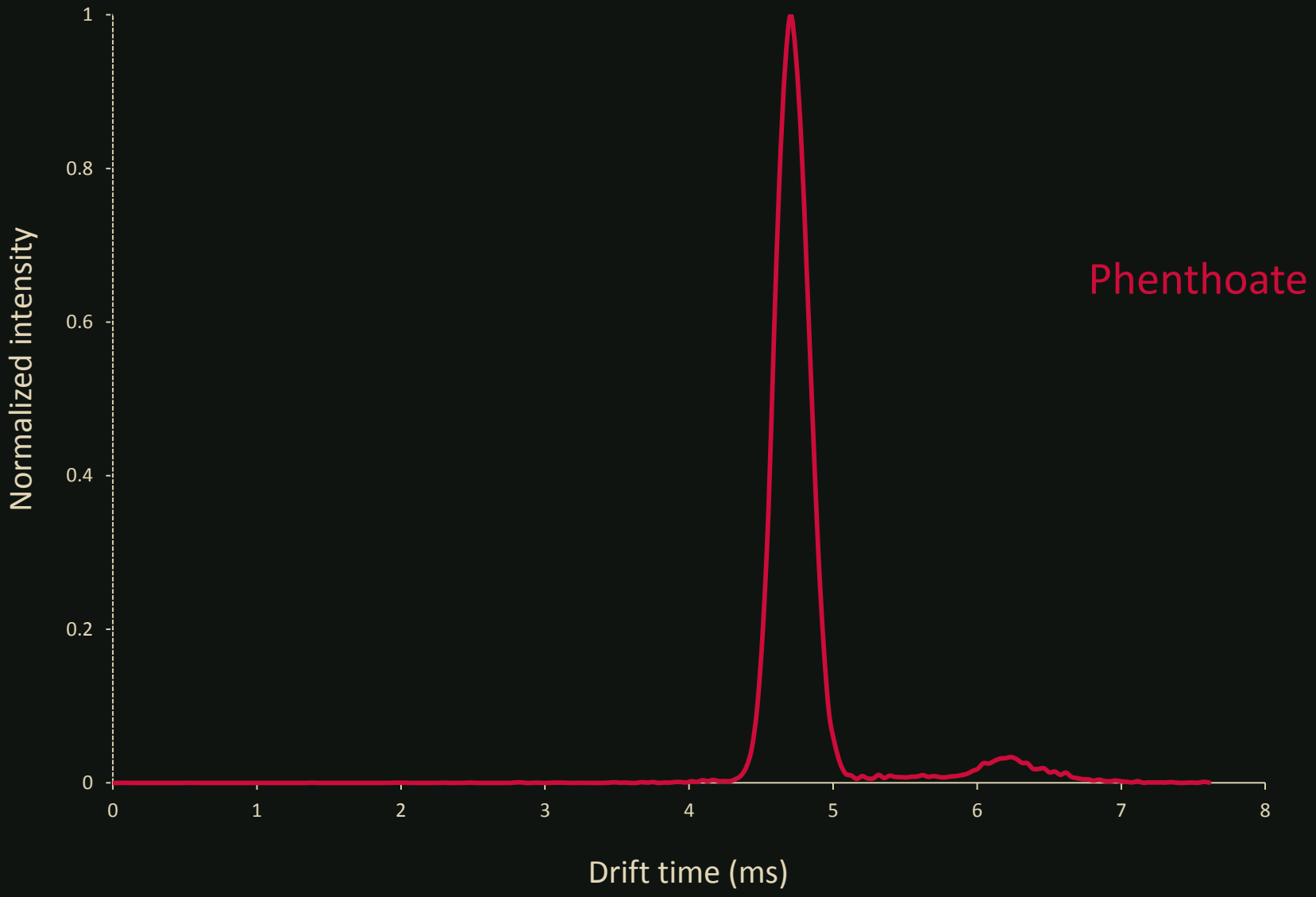
Phenthoate 321.0384 (+1)



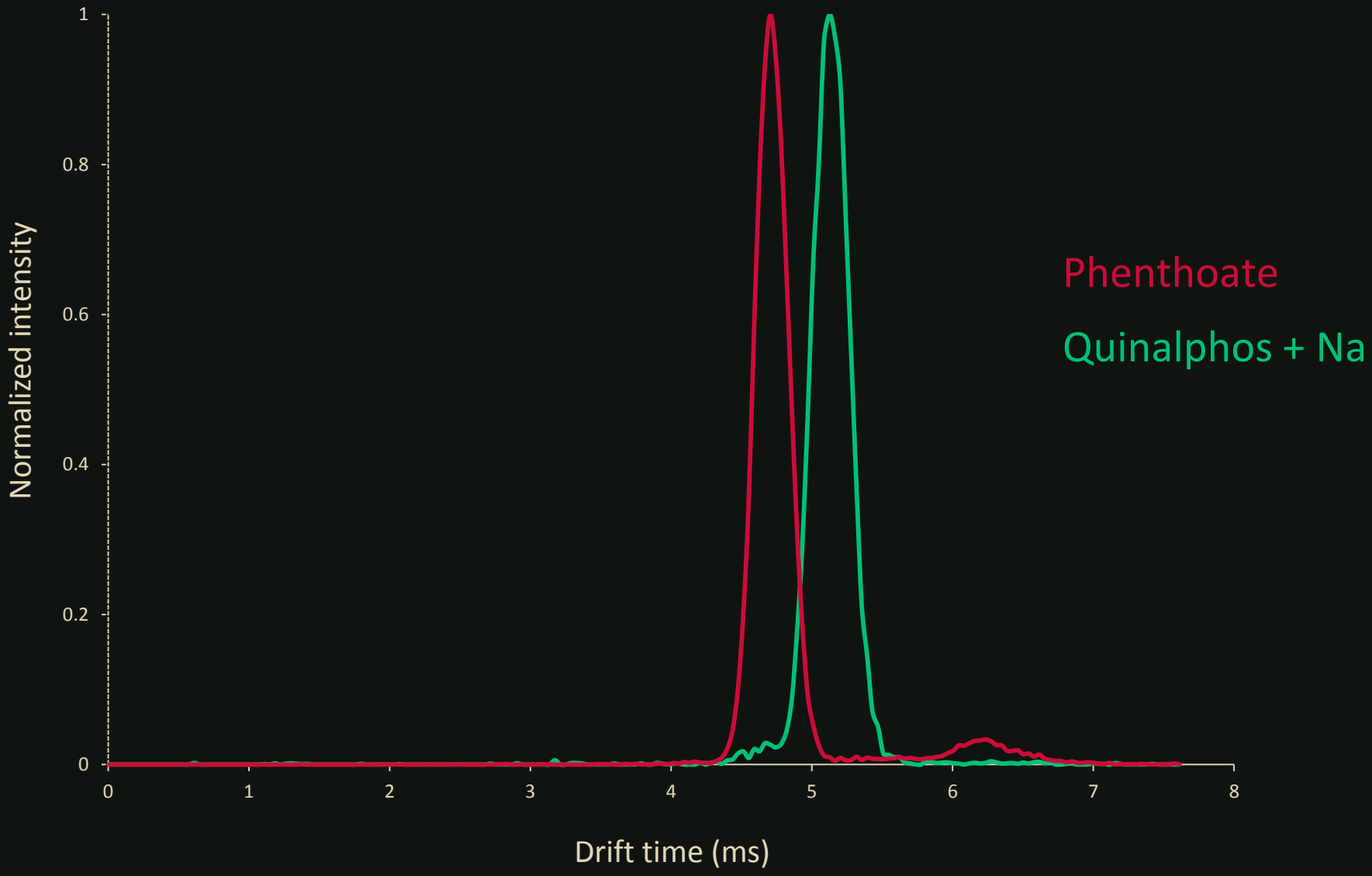
Quinalphos + Na 321.0439 (+1)

Can IMS help?

Unusual Suspect



Unusual Suspect



Quod erat demonstrandum

Q.E.D.

IM adds value to the data obtained;

→ Helps the identification process as a new IP

→ Helps the detection 1) by separating the target compounds from matrix background and 2) by increasing the sensitivity of the method (higher concentration of ions/push)

Our Path today:

- Purpose
- Power
- Plackett-Burman
- Practical
- Prospect

In progress

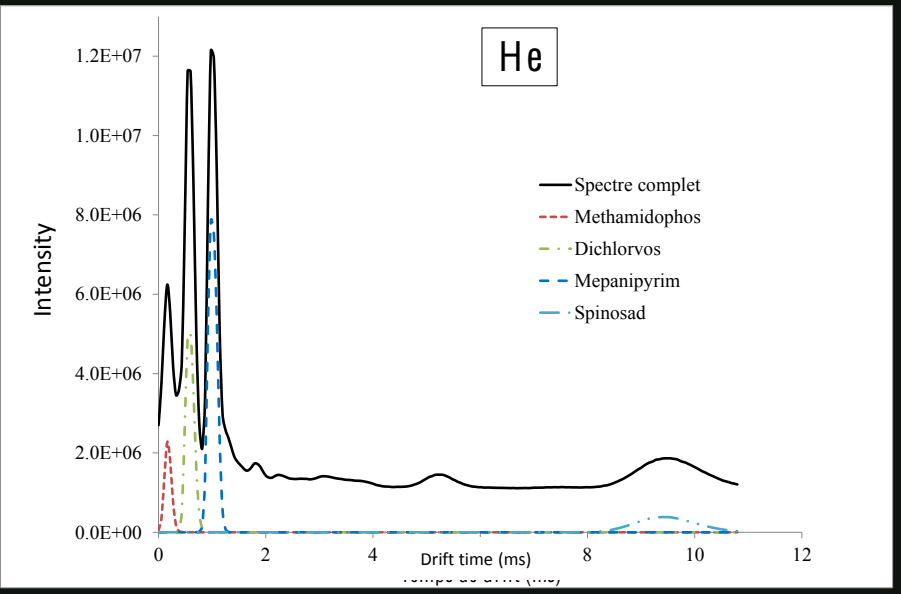
Establishing the drift times of the salt adducs

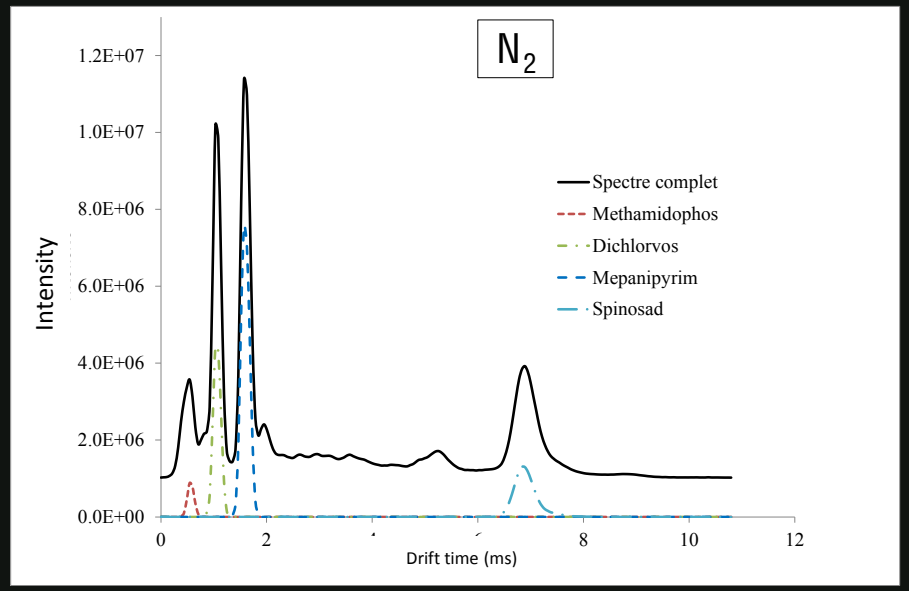
Testing the impact of post-IM fragmentation for identification

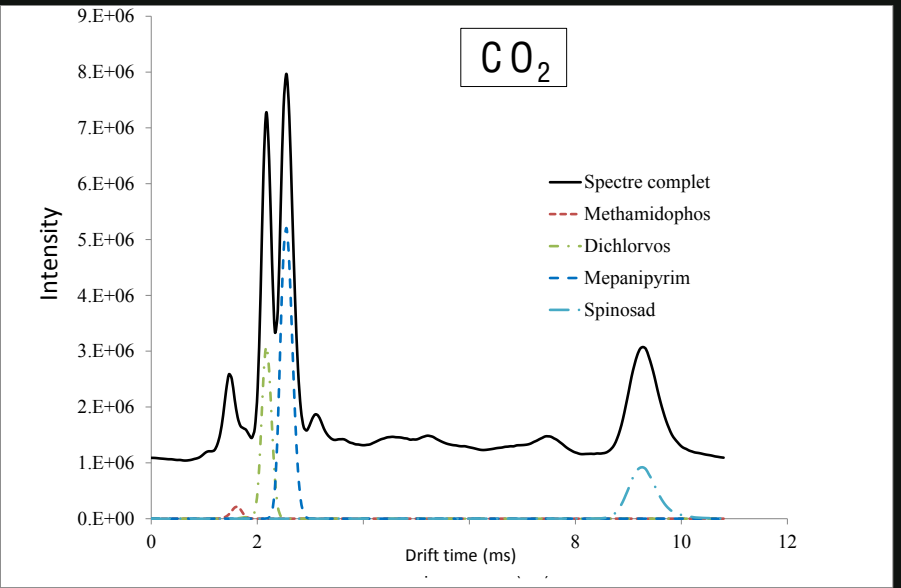
Processing data faster with new software (ex. MS^E)

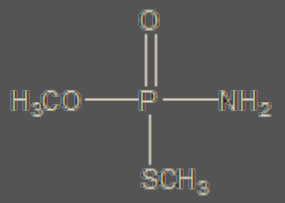
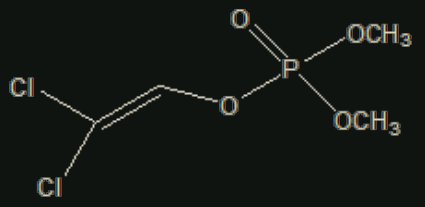
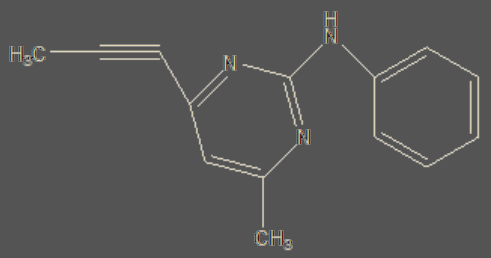
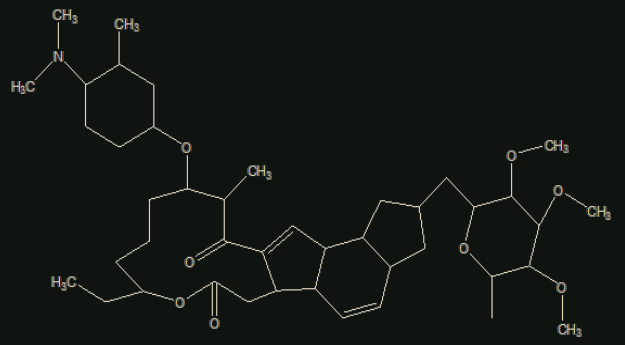
Supp. data

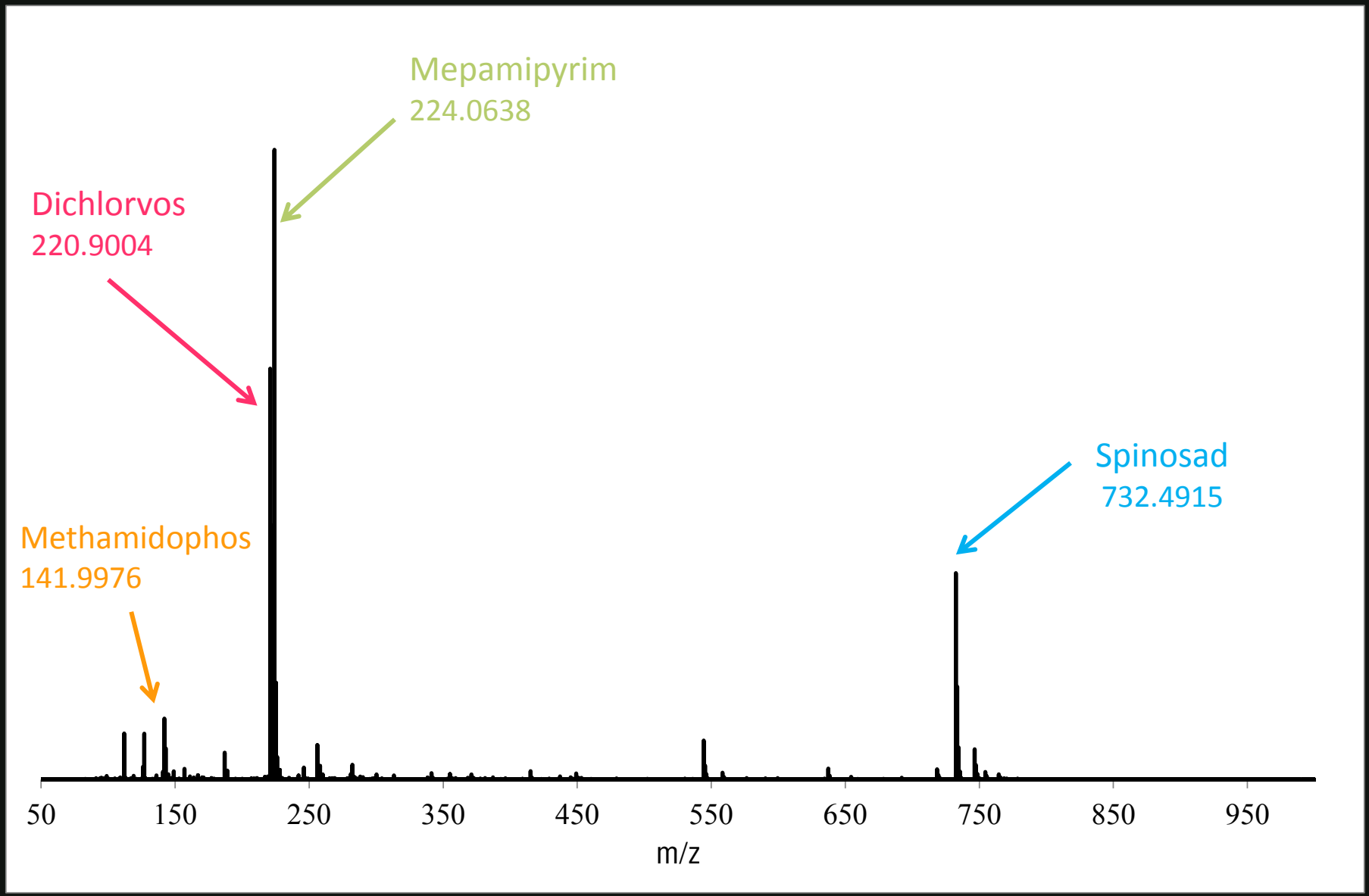
Nature of the Gas







Compound	m/z	Structure
Methamidophos	141.0013	
Dichlorvos	219.9459	
Mepanipyrim	223.1109	
Spinosad	731.4608	


Mepamipyrim
224.0638
Dichlorvos
220.9004
Spinosad
732.4915
Methamidophos
141.9976
50
150
250
350
450
550
650
750
850
950
m/z

How does it work ?