Investigation of Ion Mobility coupled with mass spectrometry (IMMS) 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
- Pesticides
- Prospect

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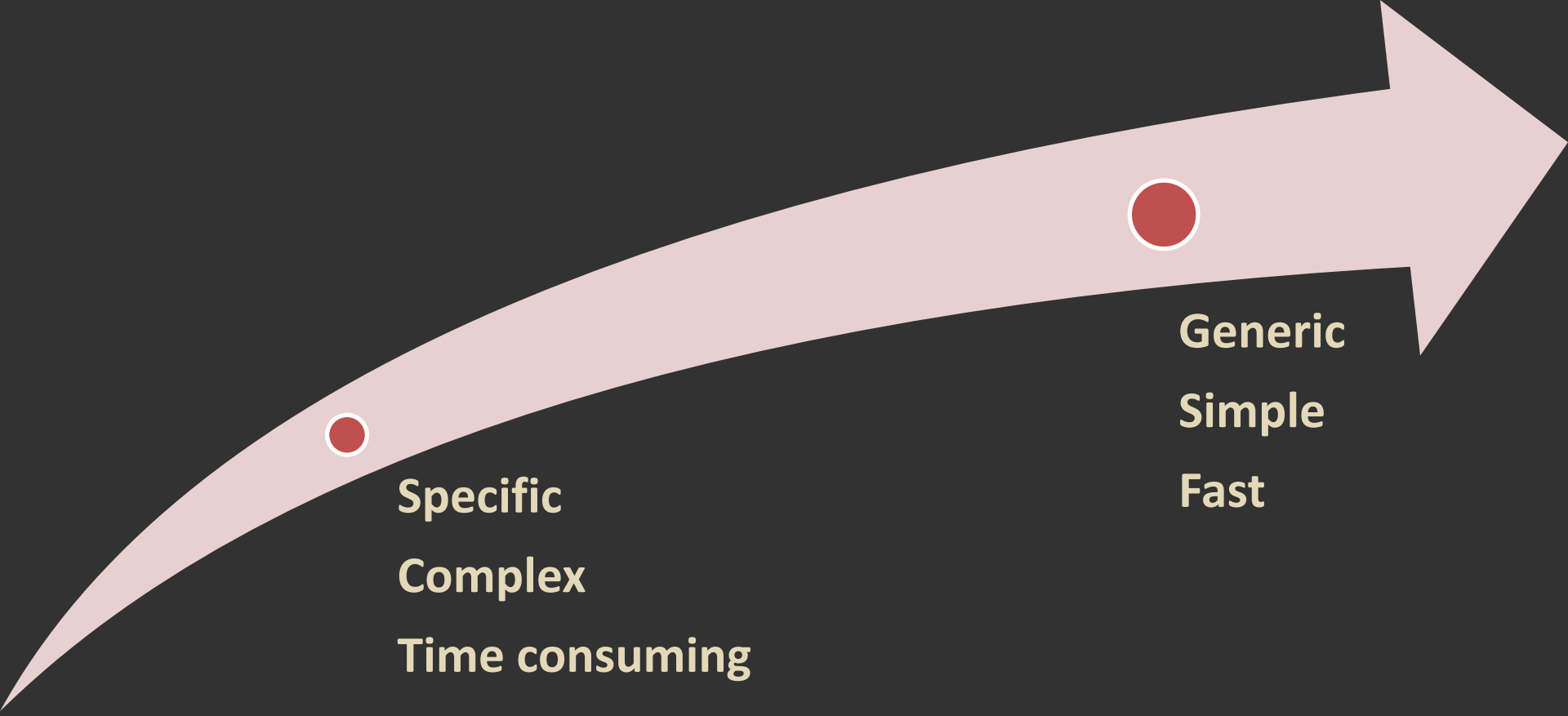
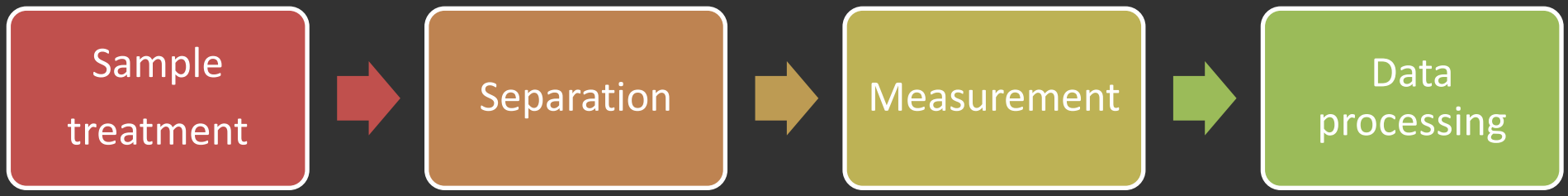
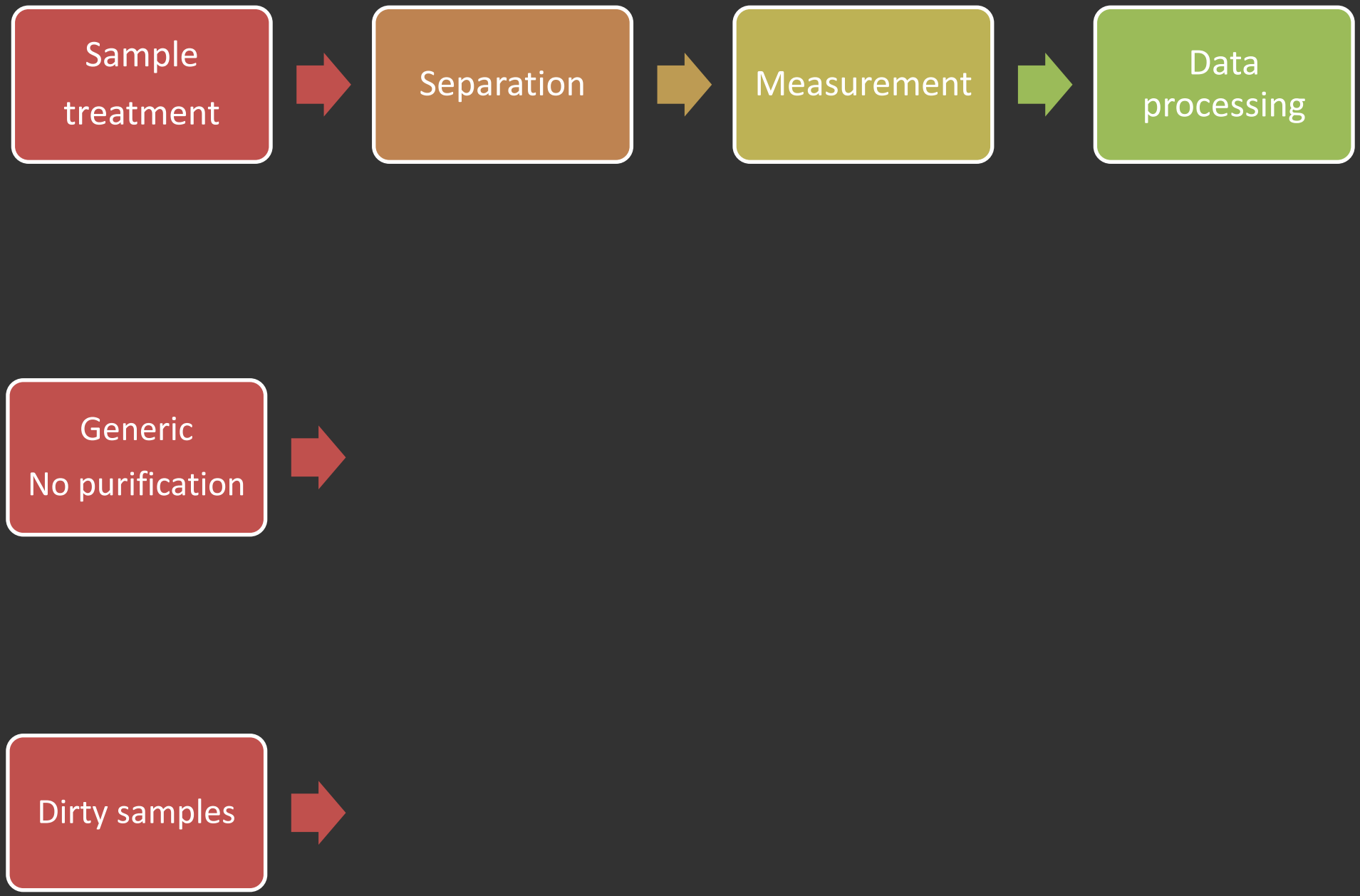
Multiresidue Methods are required tools for the determination of a great number of various compounds in one analysis

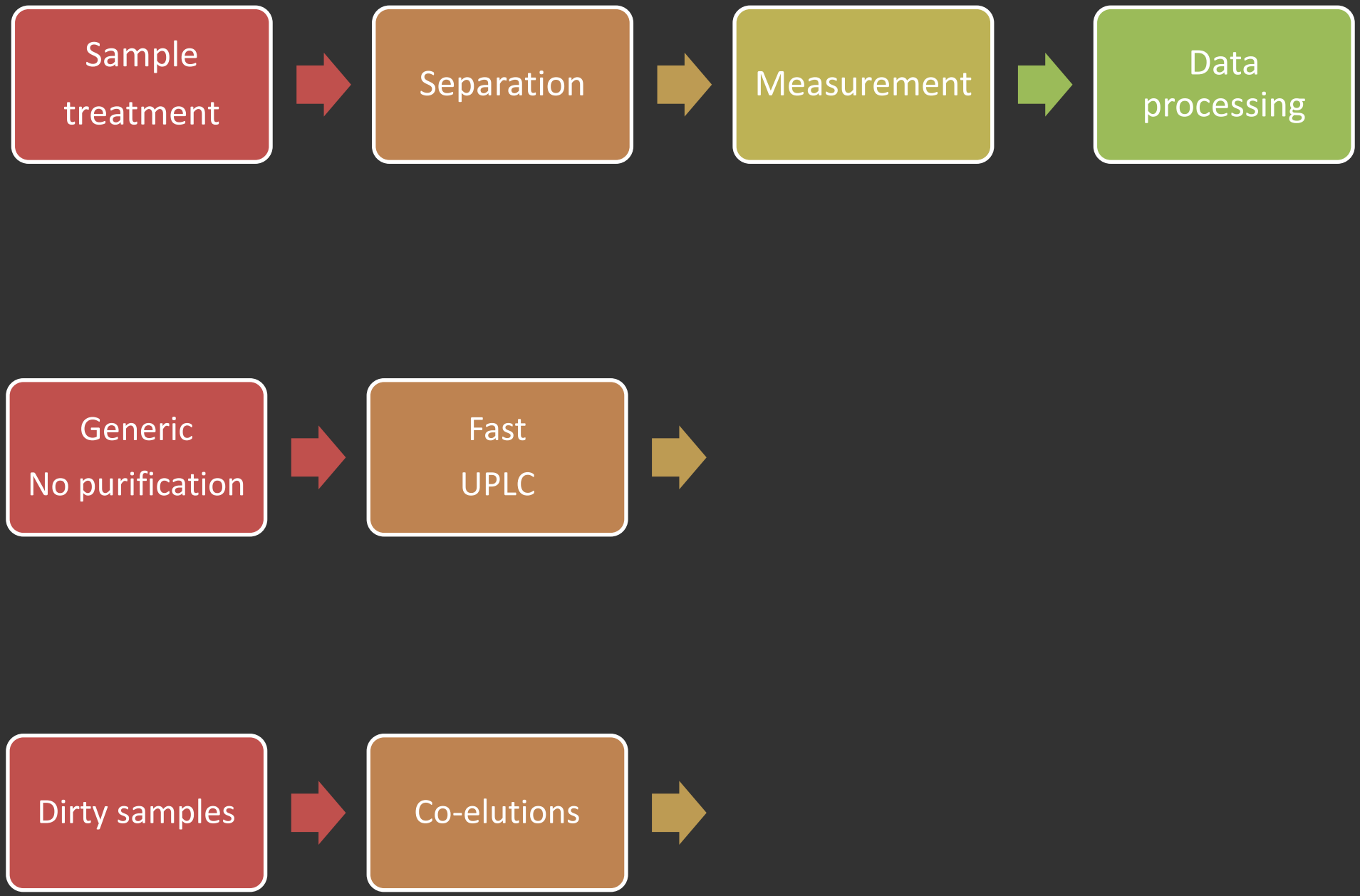
→ Has to be viable for the lab

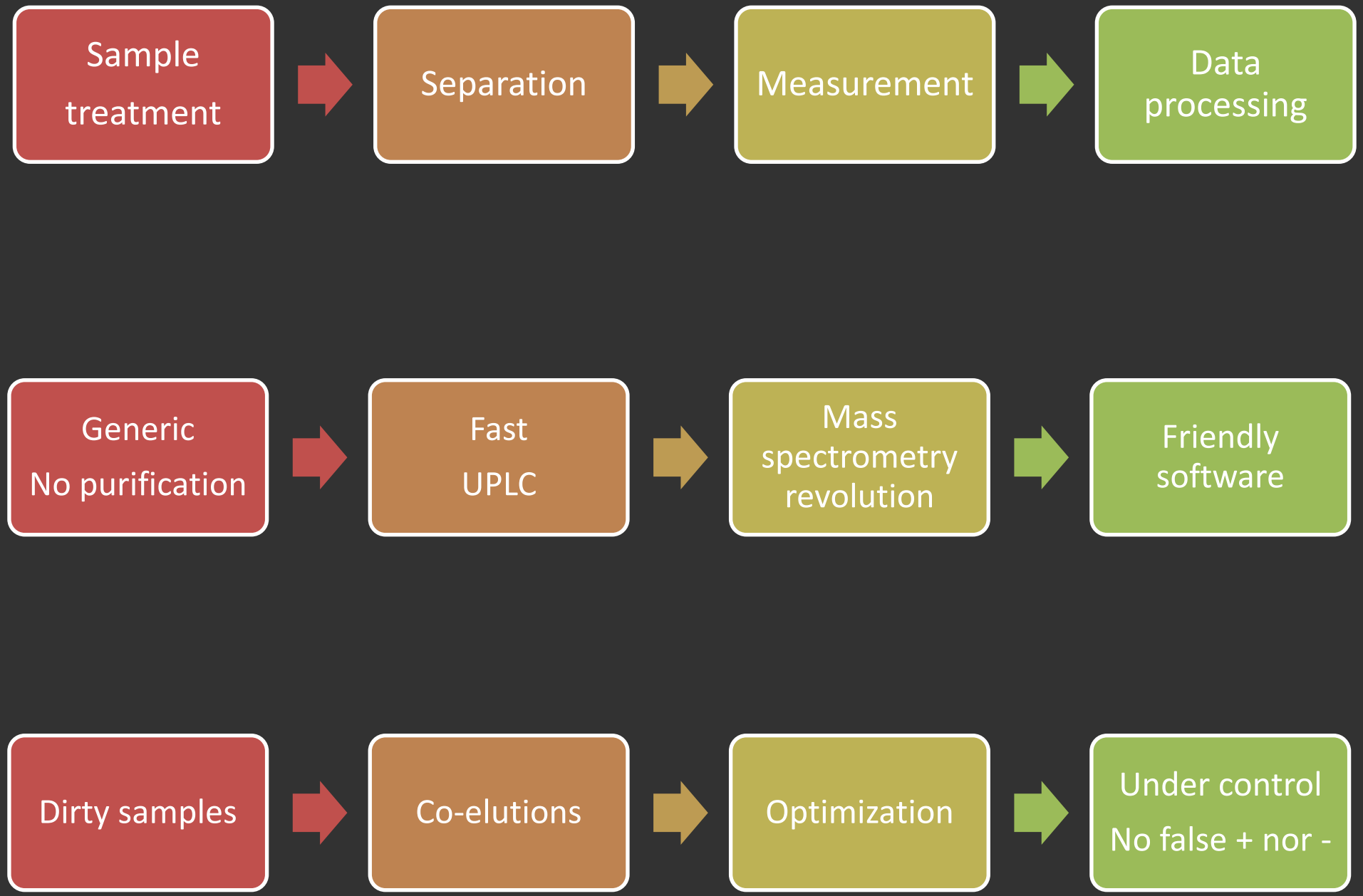


Analytical trend for MRM


Sample treatment
Separation
Measurement
Data processing

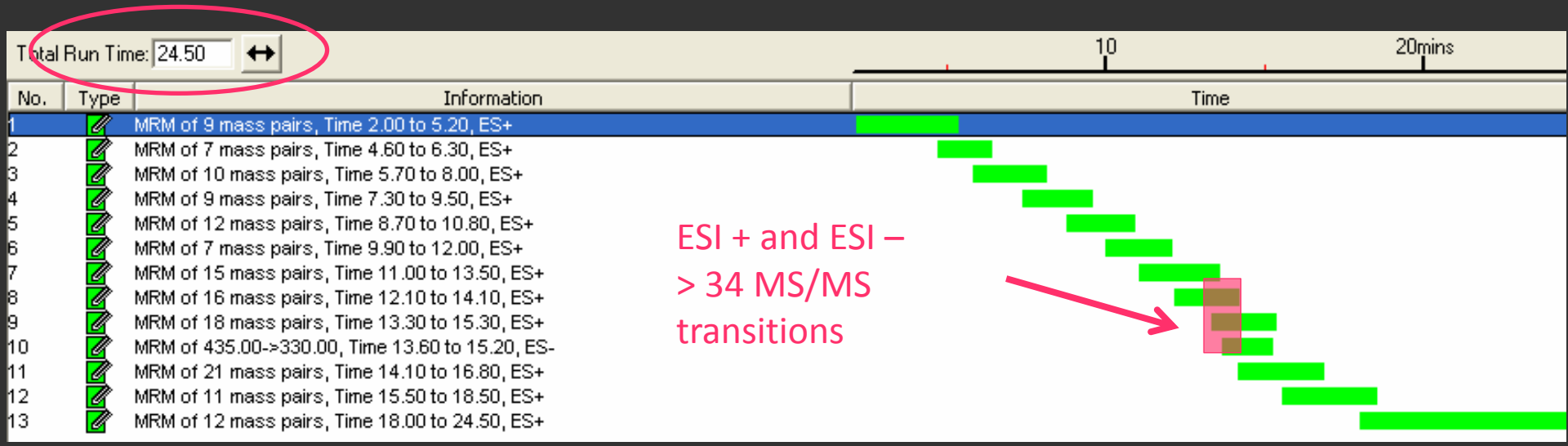

Sample treatment
Separation
Measurement
Data processing
Generic No purification
Dirty samples


Sample treatment
Separation
Measurement
Data processing
Generic No purification
Fast UPLC
Dirty samples
Co-elutions


Sample treatment
Separation
Measurement
Data processing
Generic
No purification
Fast
UPLC
Mass spectrometry revolution
Friendly software
Dirty samples
Co-elutions
Optimization
Under control
No false + nor -

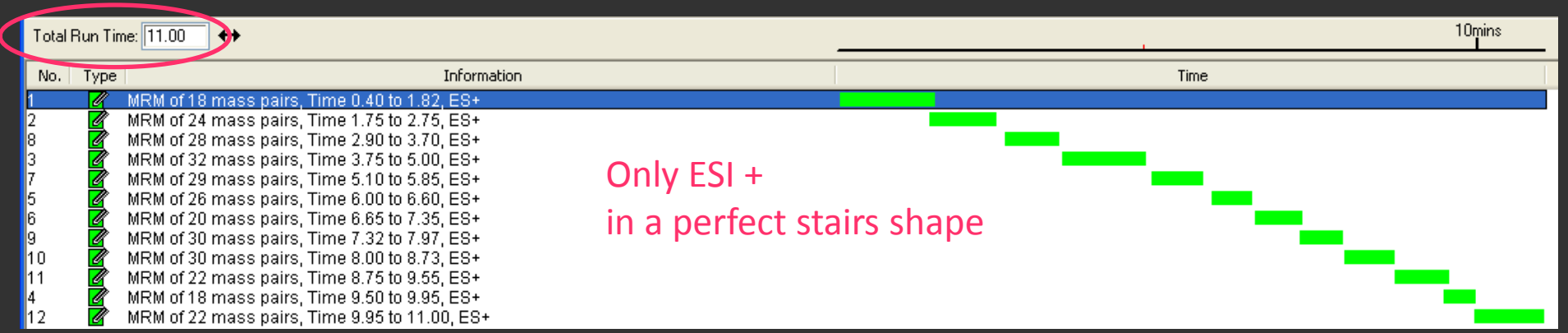
But…

Optimize the acquisition



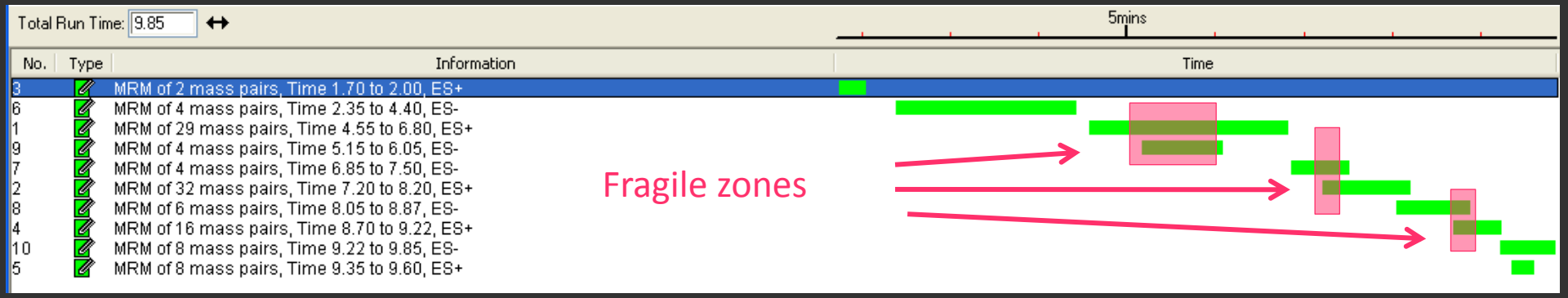
But…

Optimize the acquisition

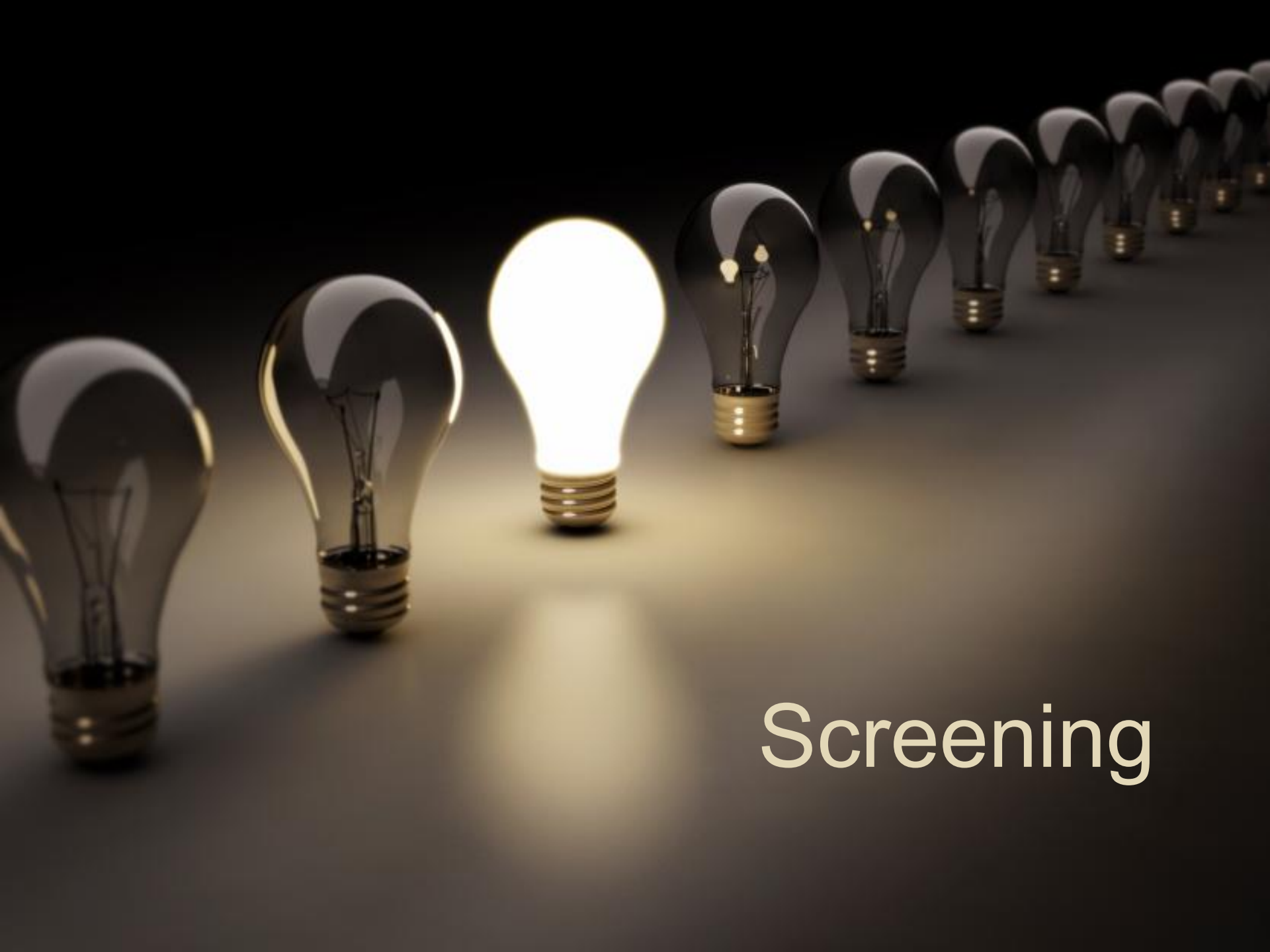


But…

Optimize the acquisition




Labor intensive
What's next?


Screening

Screening method

Method to **detect** analyte (s)
in samples
in an easy/rapid way

- Qualitative
- No full identification
- No value with uncertainty but result with a level of confidence

How can we help the Detection ?

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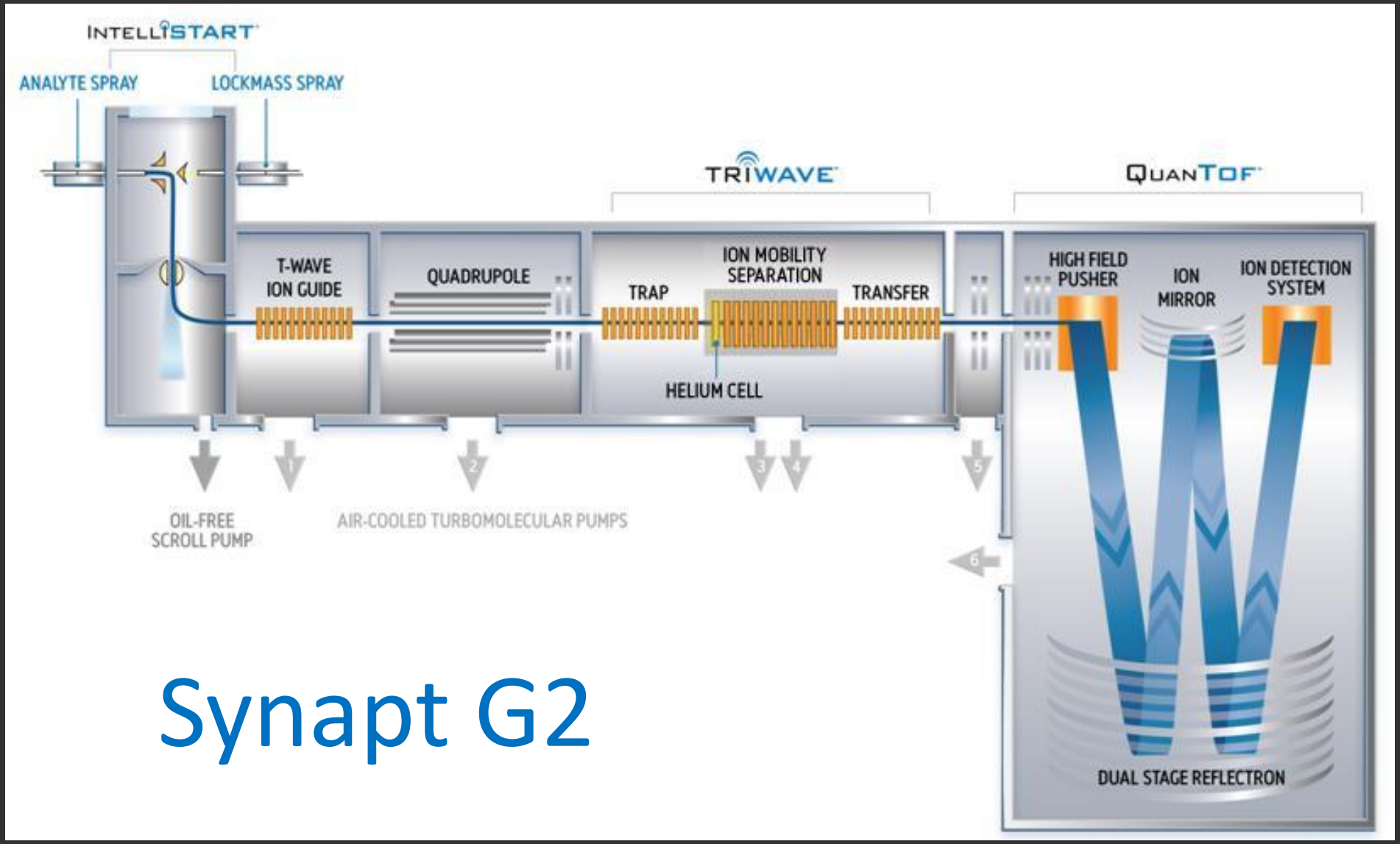
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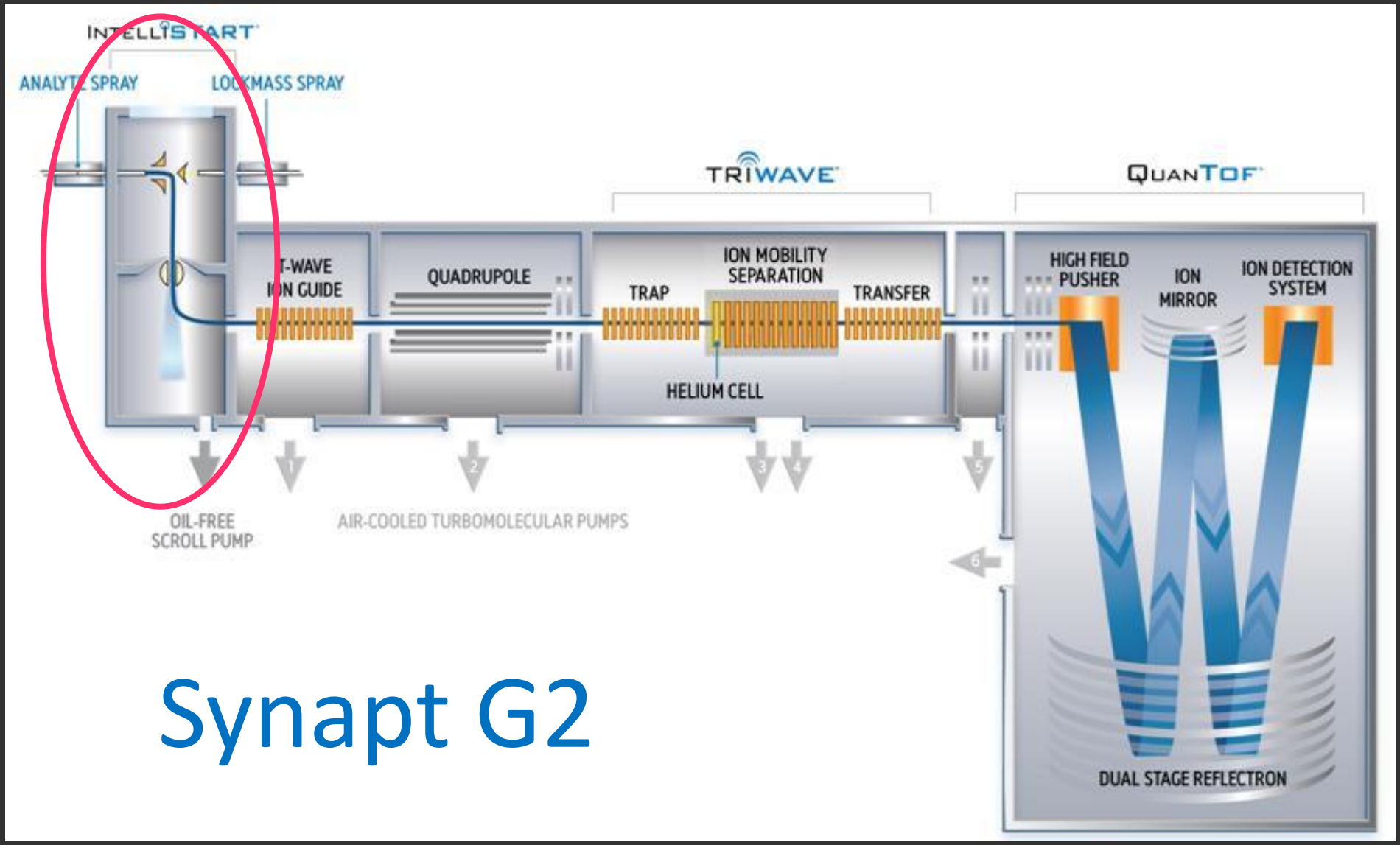
ANALYTE SPRAY
LOCKMASS SPRAY
TRIWAVE
QUANTOF
T-WAVE
ION GUIDE
QUADRUPOLE
TRAP
ION MOBILITY
SEPARATION
TRANSFER
HELIUM CELL
HIGH FIELD
PUSHER
ION
MIRROR
ION DETECTION
SYSTEM
OIL-FREE
SCROLL PUMP
AIR-COOLED TURBOMOLECULAR PUMPS
DUAL STAGE REFLECTRON

Synapt G2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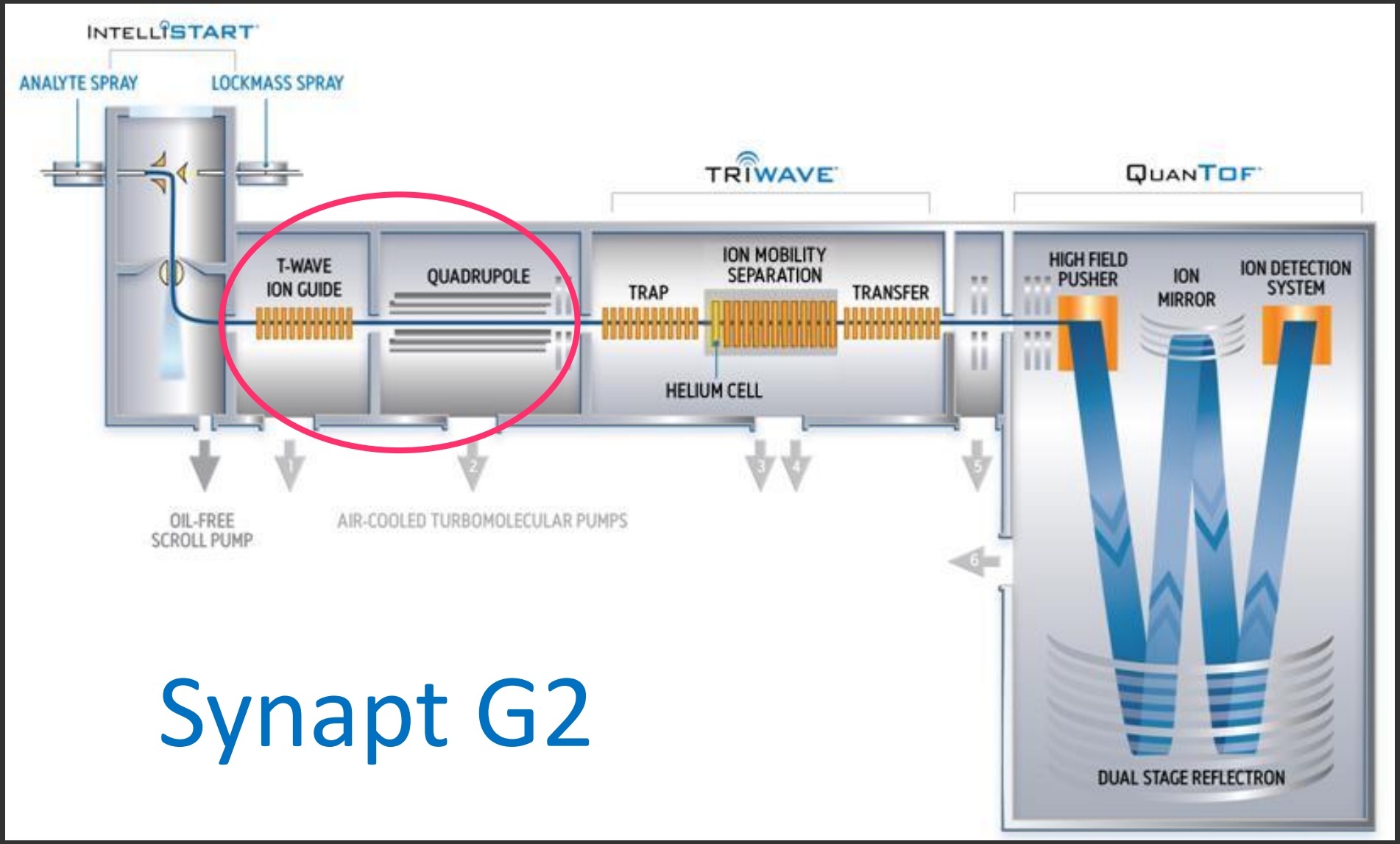
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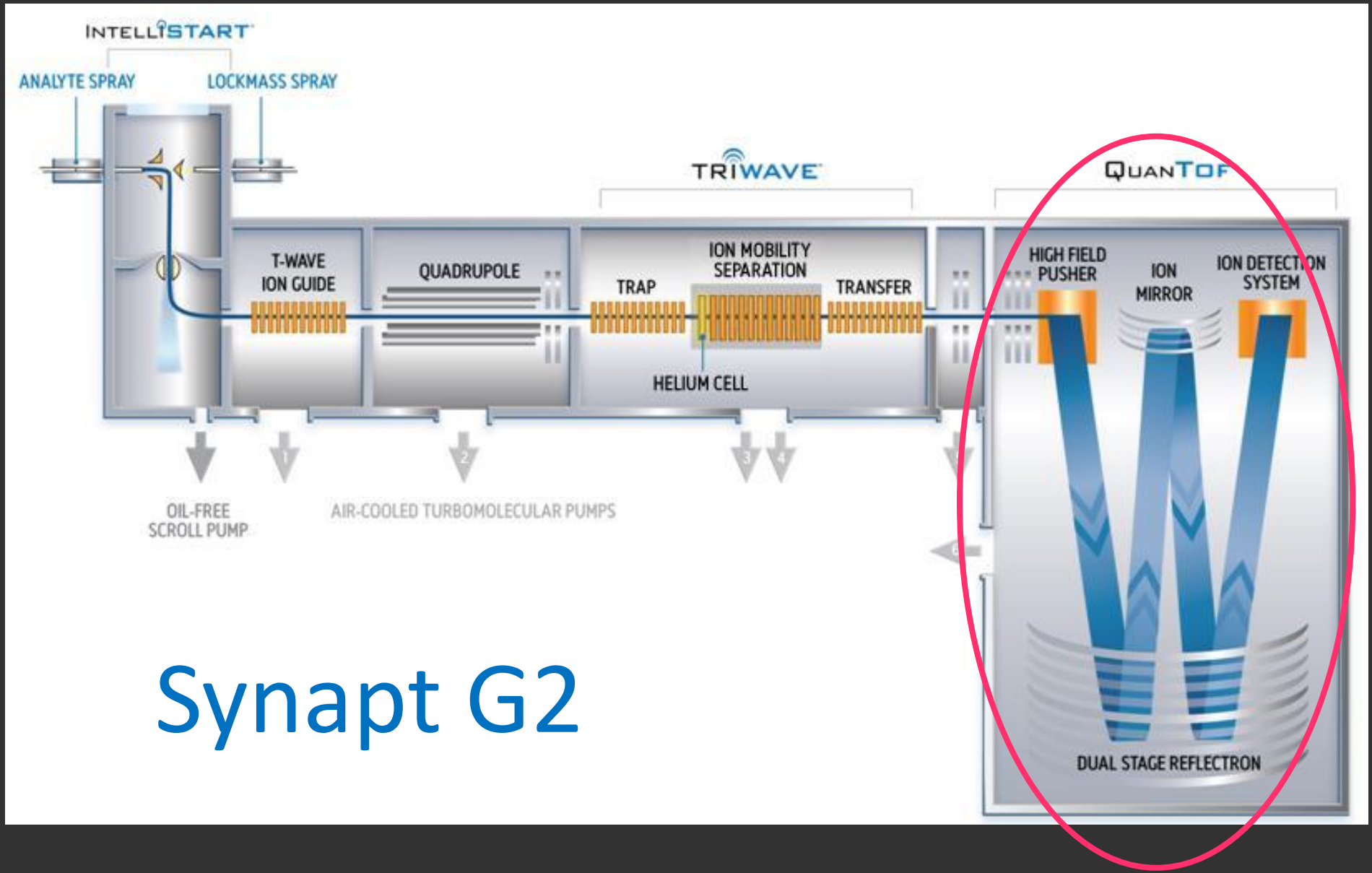
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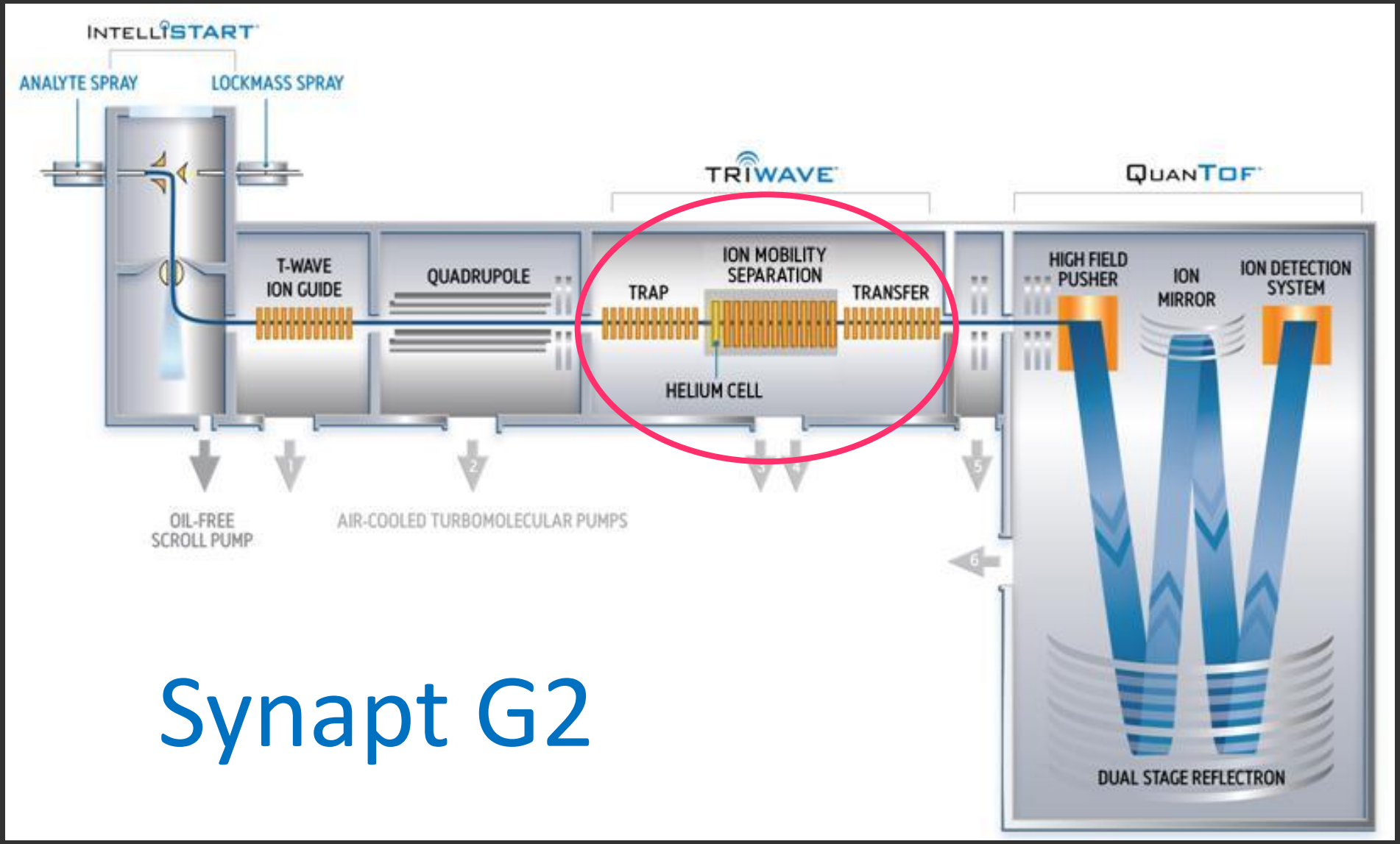
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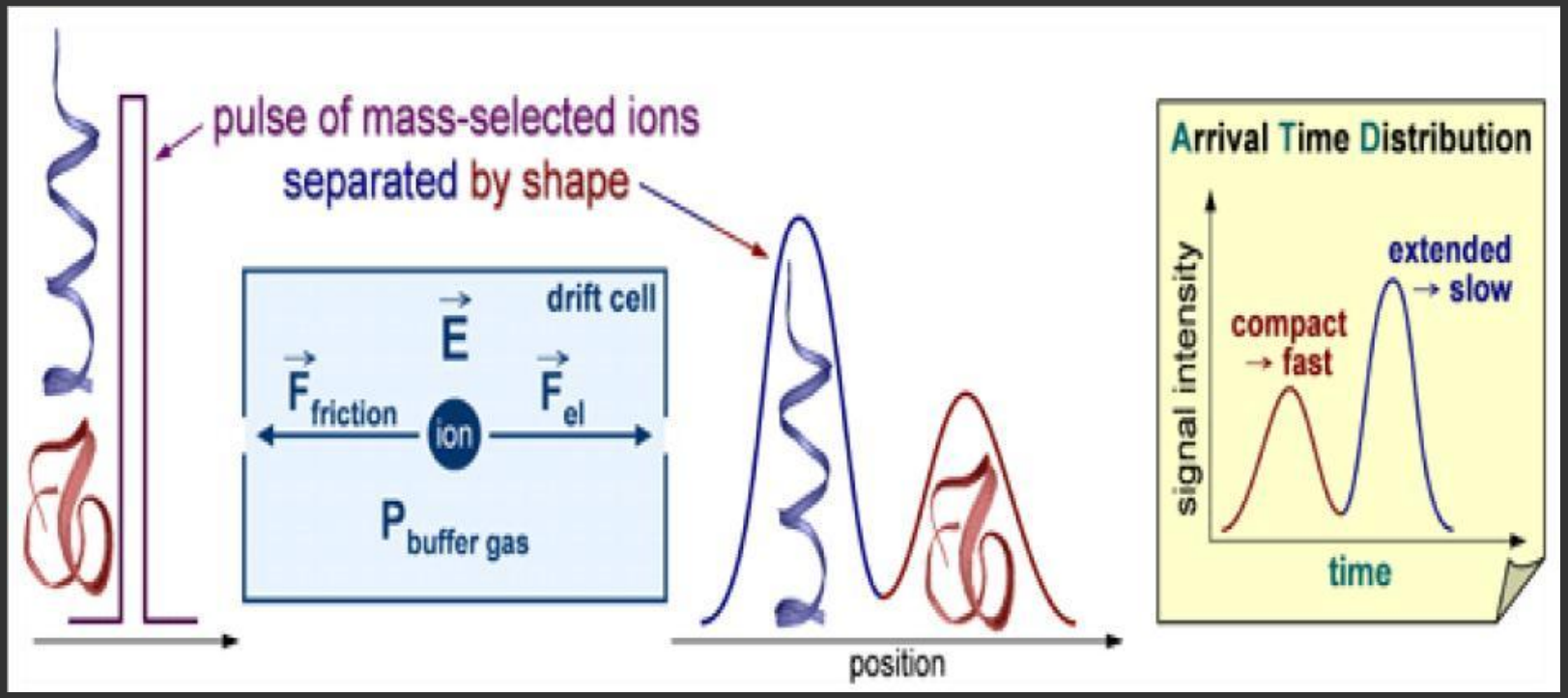
DUAL STAGE REFLECTRON

Synapt G2

Ion Mobility

Small, compact

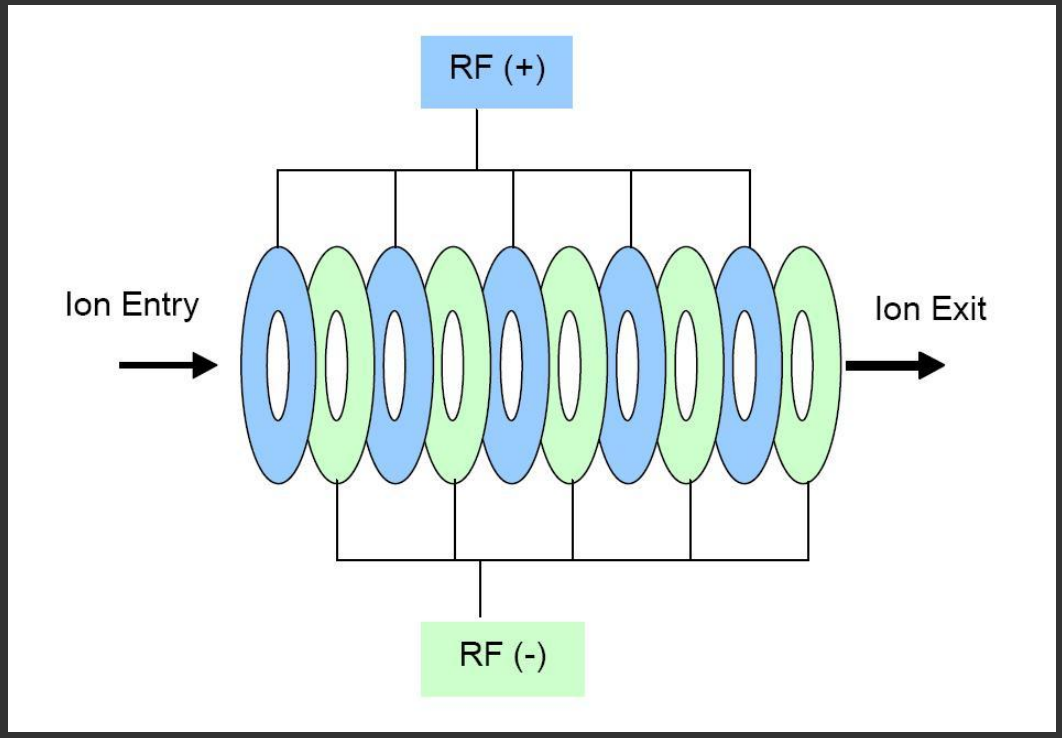
Large extended



- 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

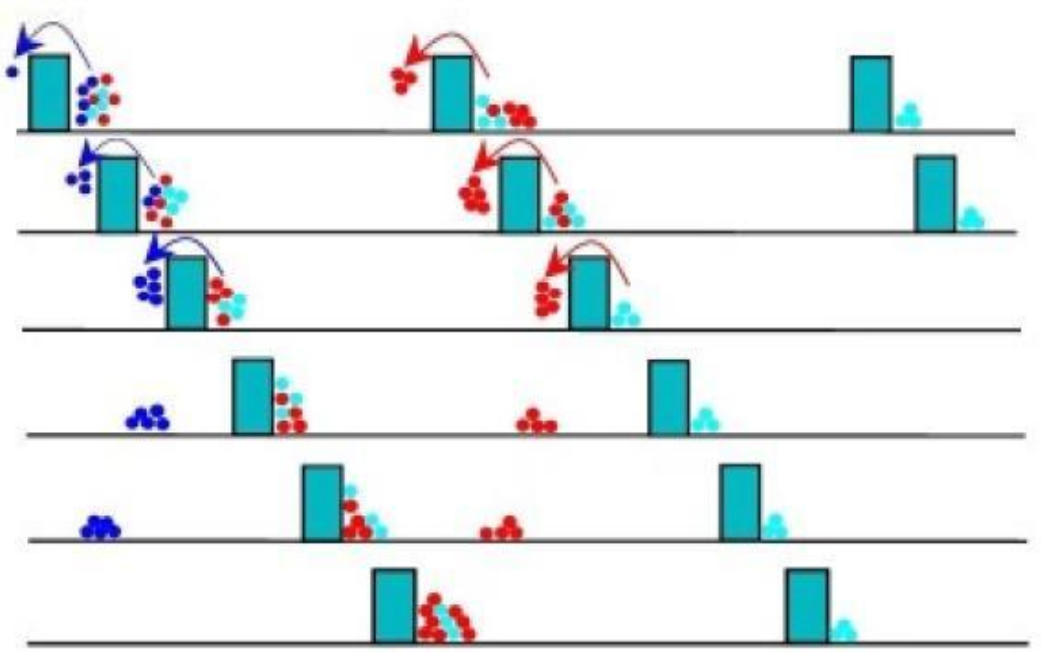
Ions are moved through the IM cell in PULSES as WAVES

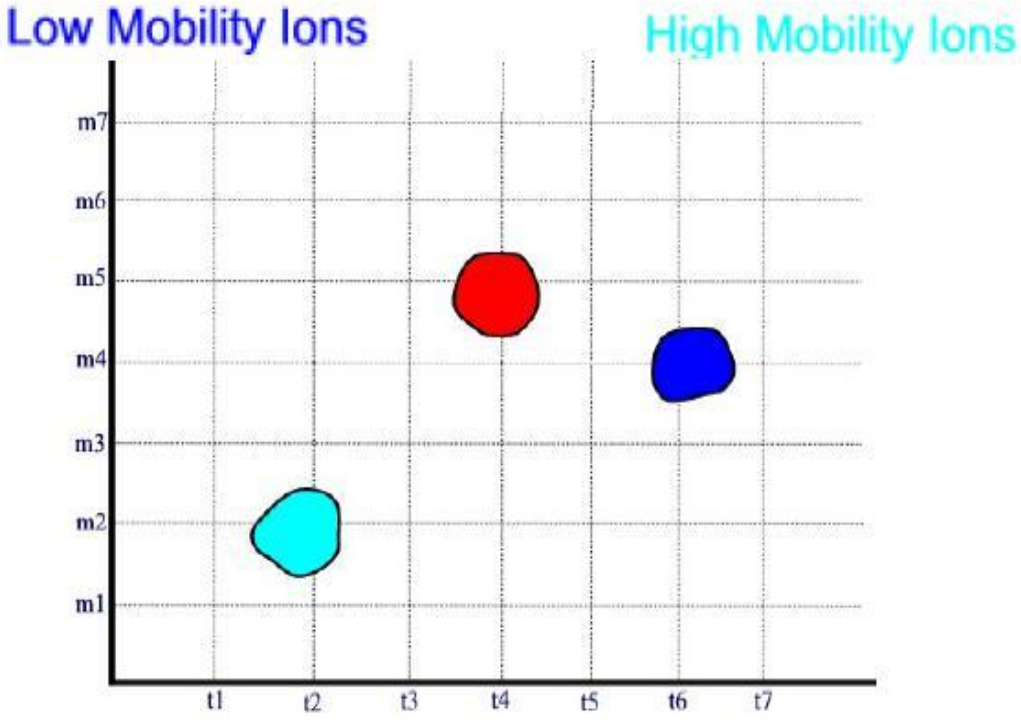
↓

faster IMS duty cycles

↓

MS sensitivity is not compromized





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Pesticides

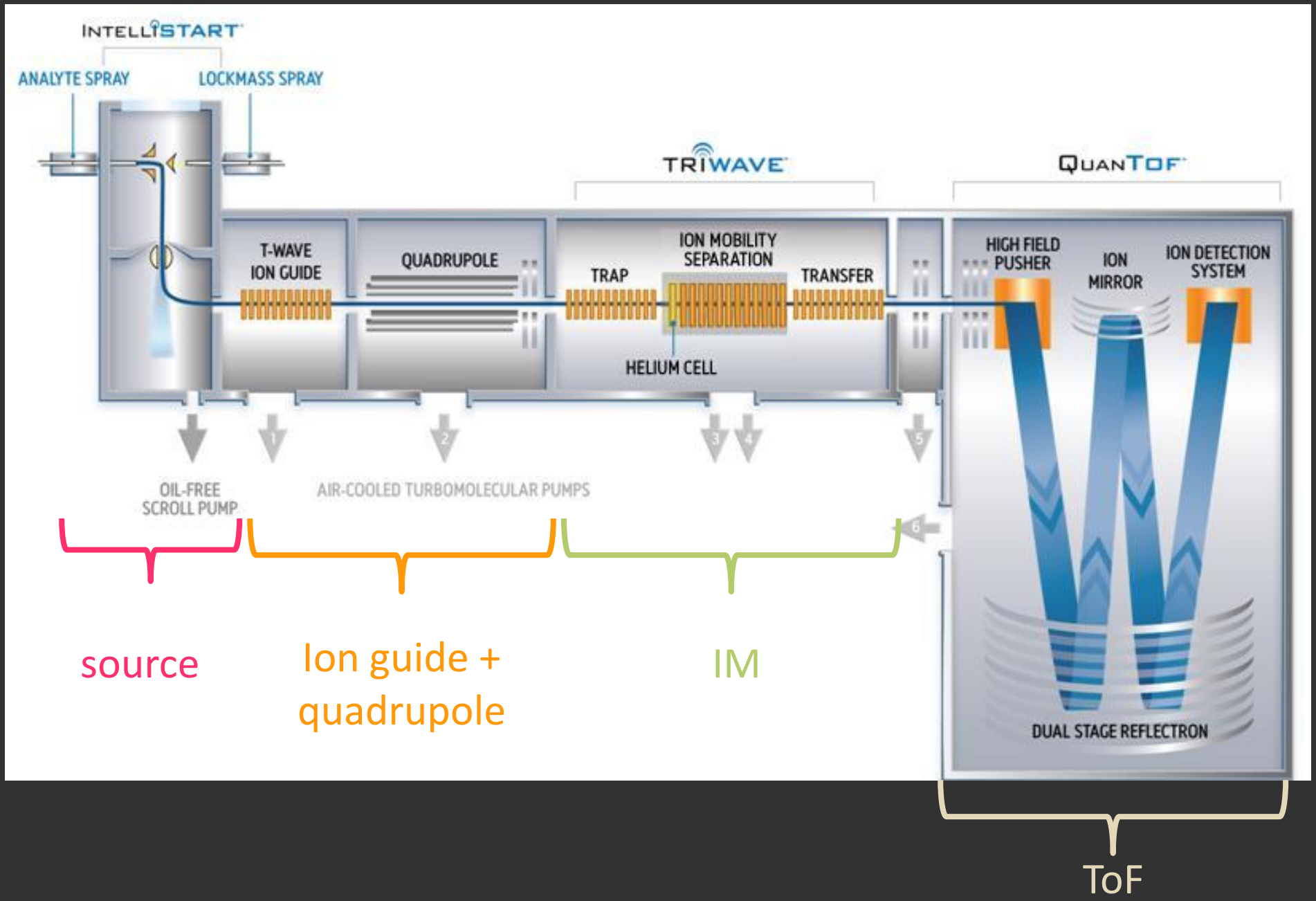
Broad term for products that are used to control pests

Rich in diversity;

Chemical structure, solubility, volatility, potential for degradation…

Perfect

Challenge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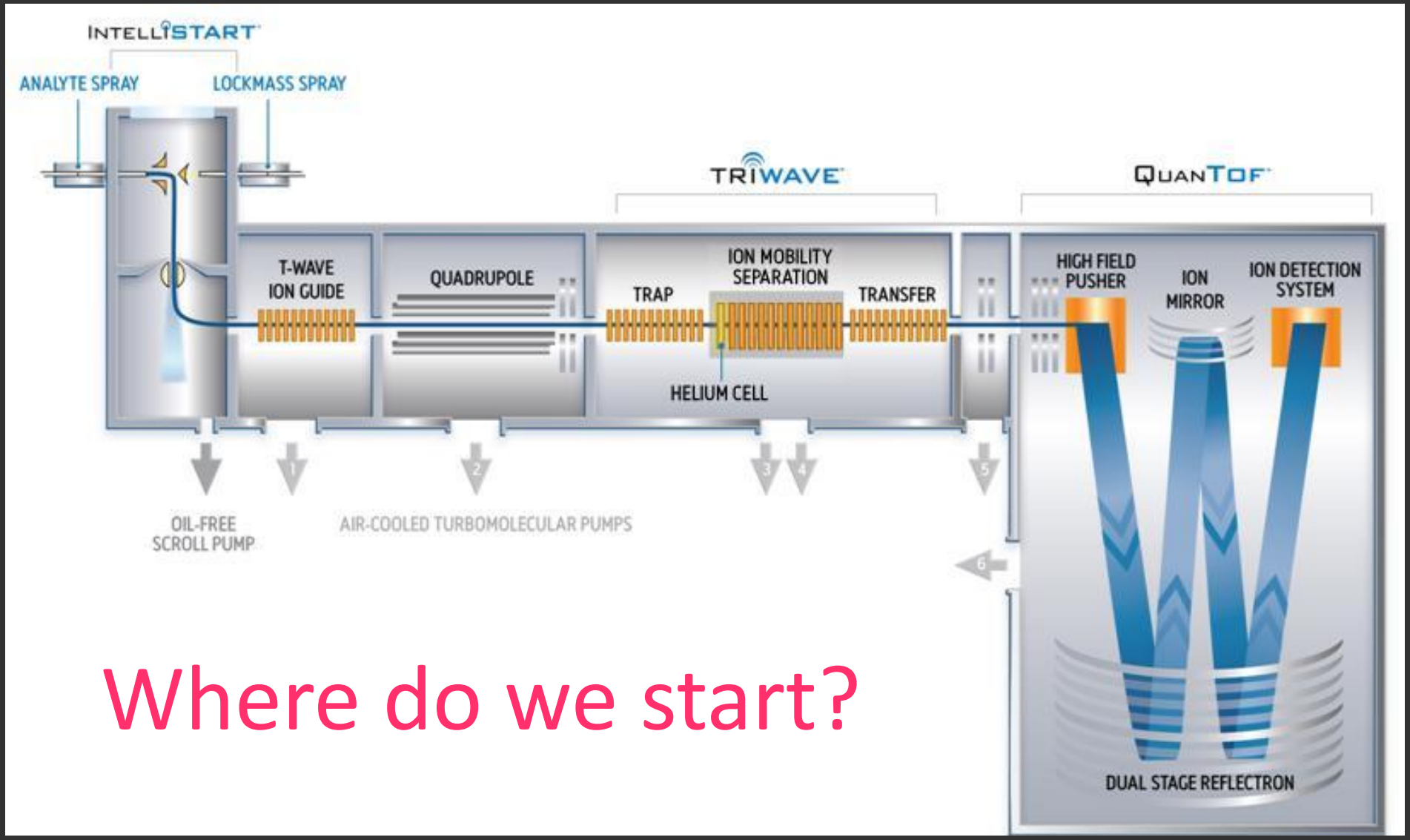
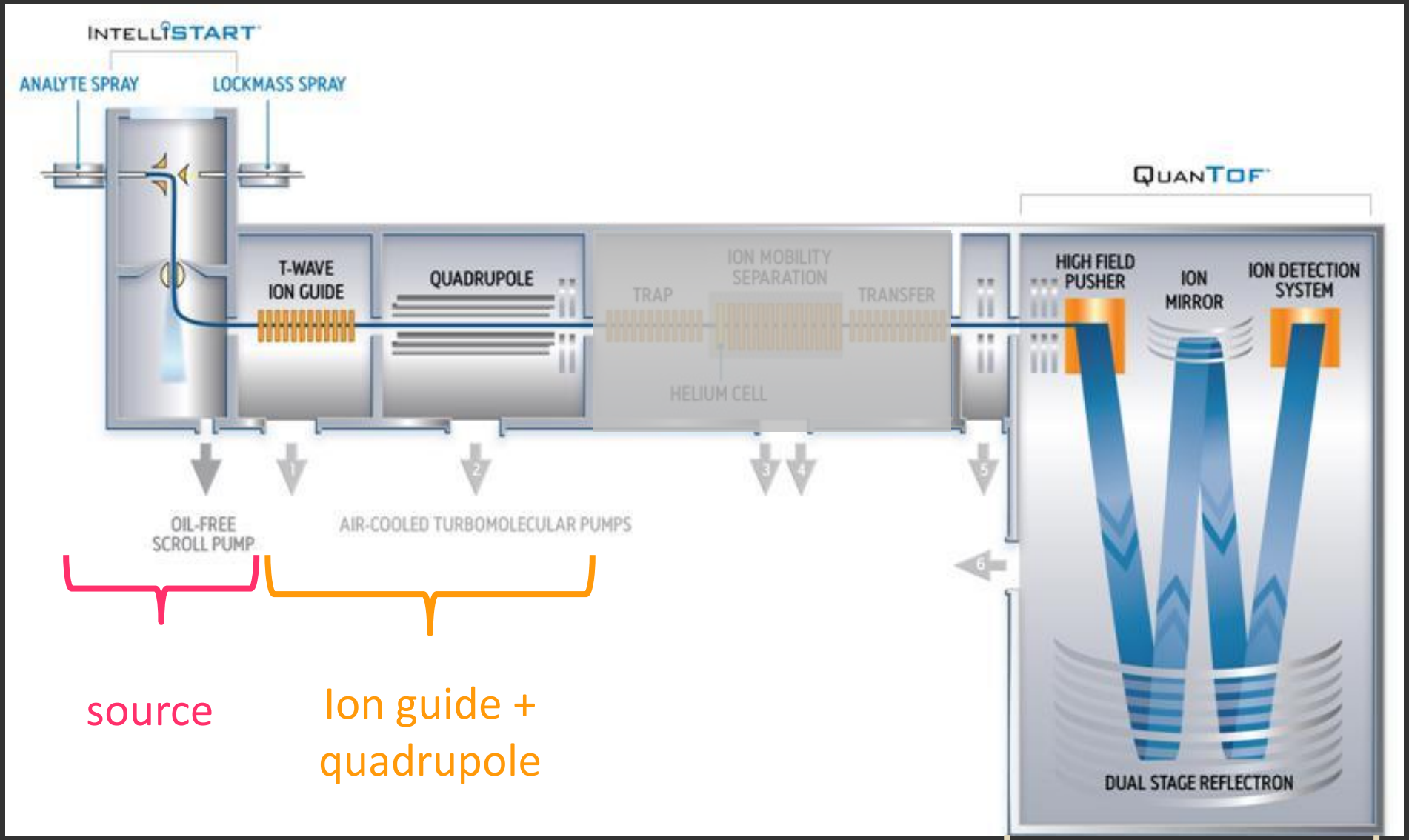
OIL-FREE SCROLL PUMP
AIR-COOLED TURBOMOLECULAR PUMPS
source
Ion guide + quadrupole
IM
ToF



Where do we start?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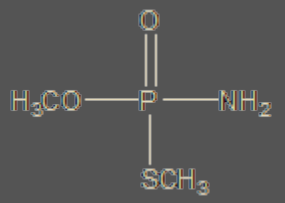
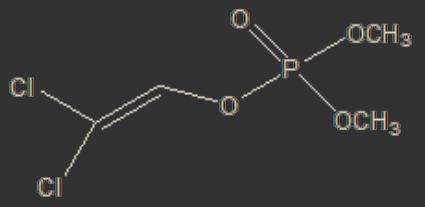
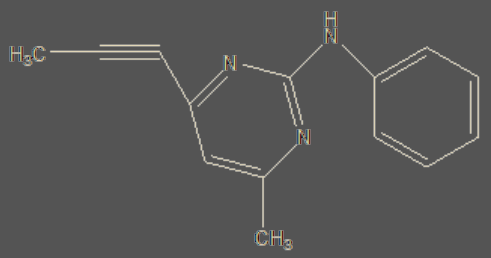
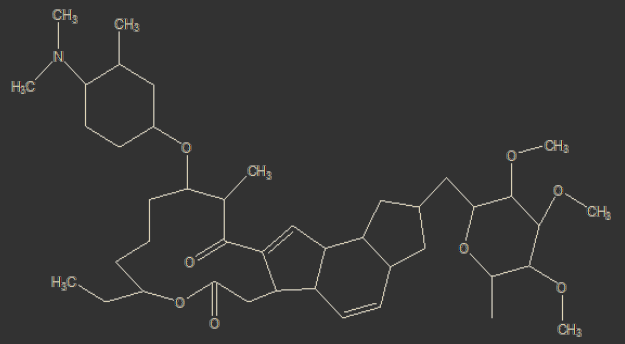
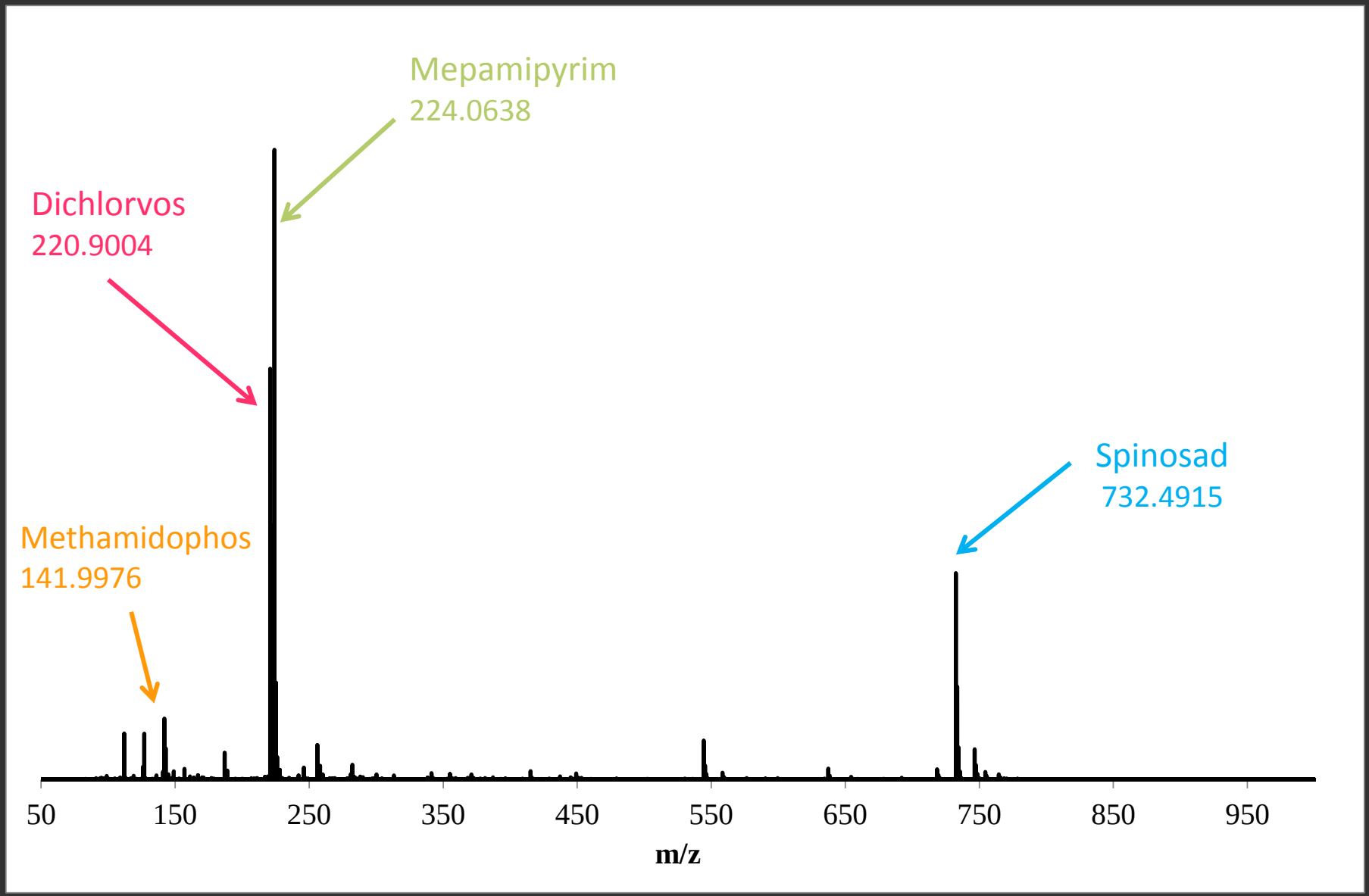
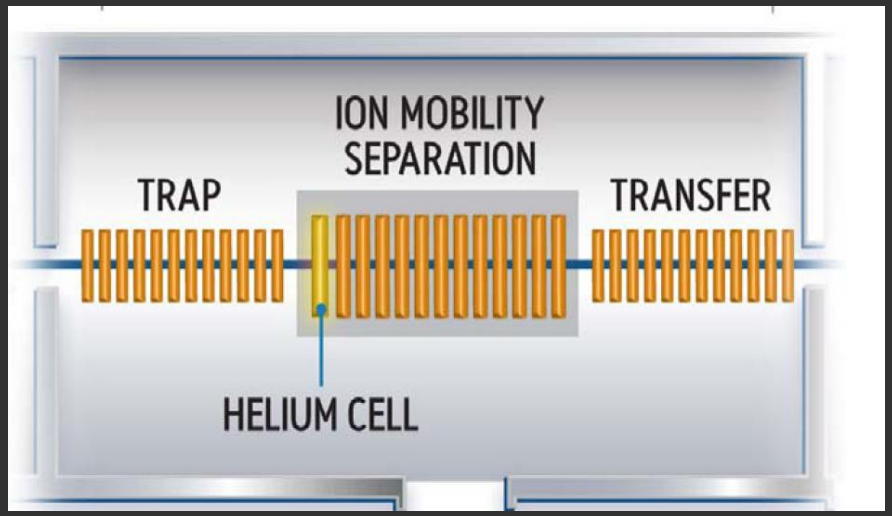
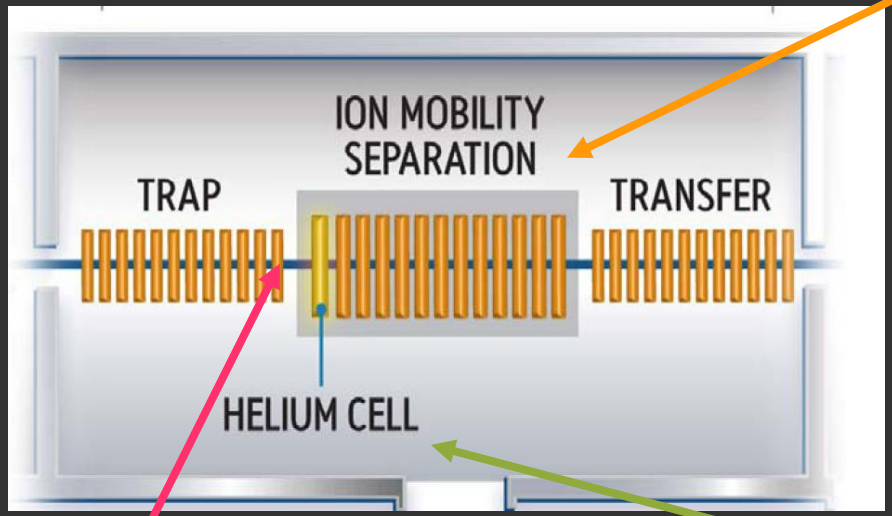
ToF

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



IM cell



Nature of the gas

IMS T-Wave velocity (m/sec)

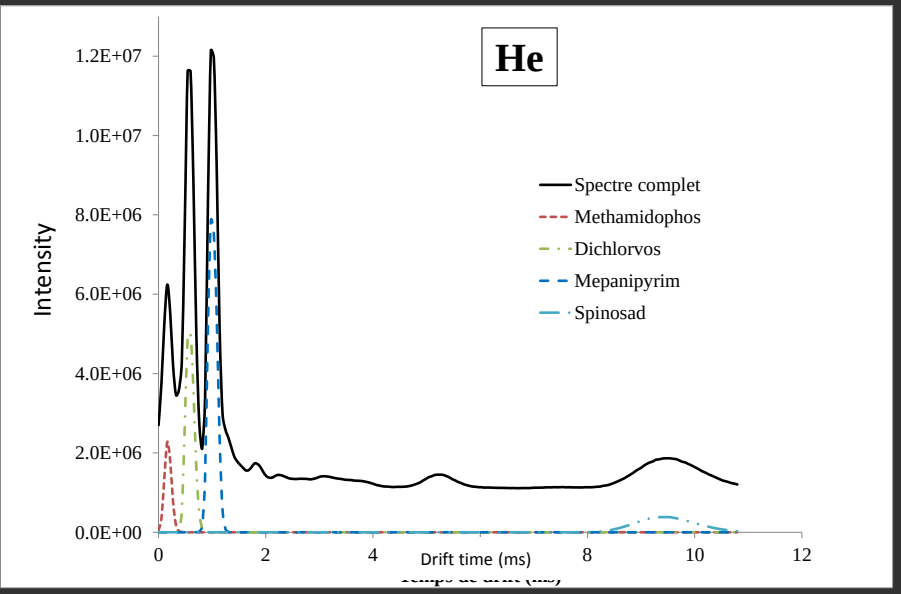
IMS T-Wave Height (V)

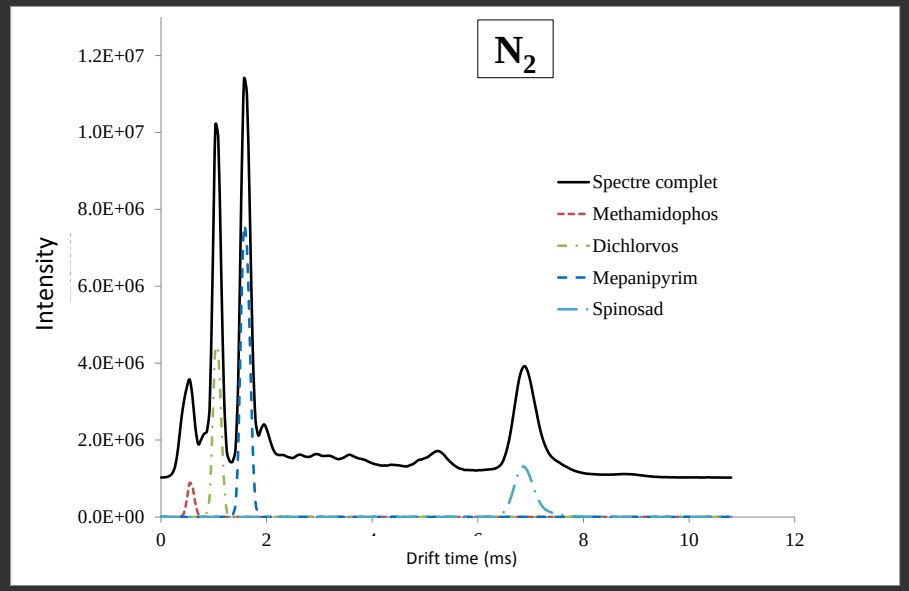
Gas Pressure (mbar)

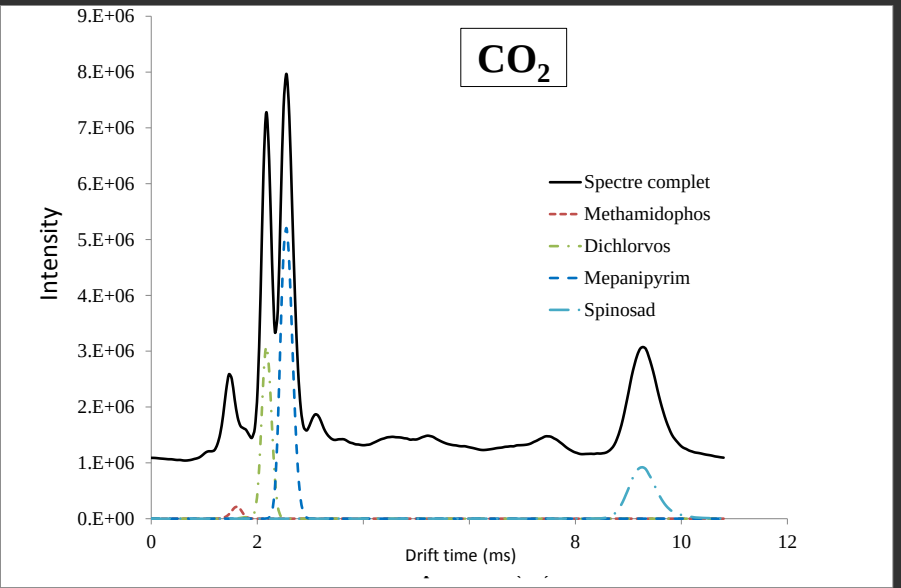
Biais (V)

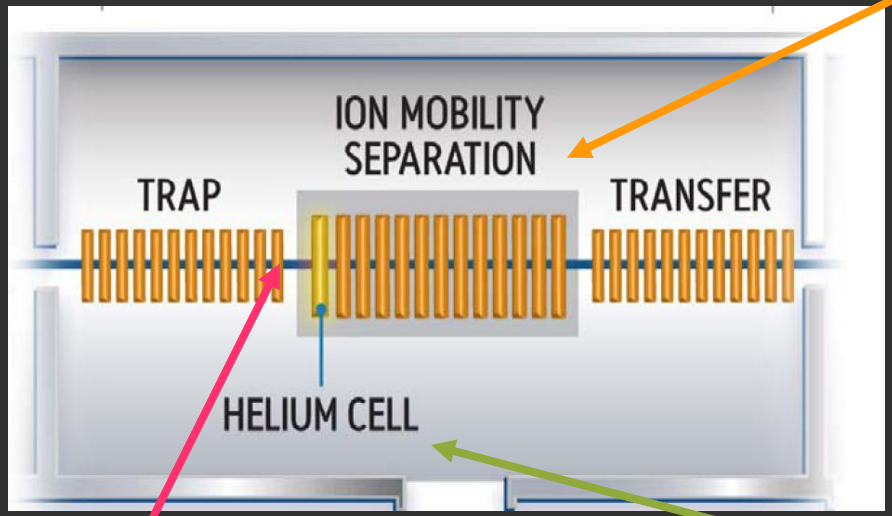
Helium Cell Pressure (mbar)

Nature of the Gas









Nature of the gas : N_2

IMS T-Wave velocity (m/sec)

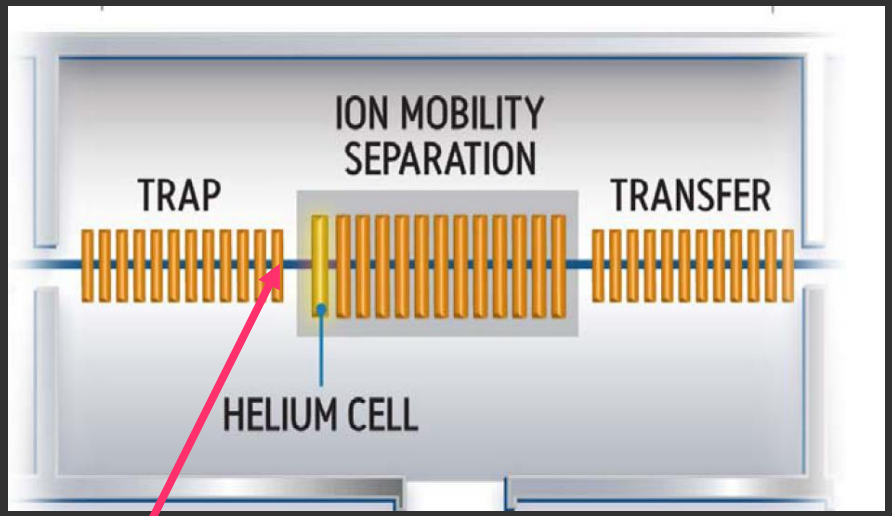
IMS T-Wave Height (V)

Gas Pressure (mbar)

Biais (V)

Helium Cell Pressure

Last voltage before the IM cell



Biais (V)

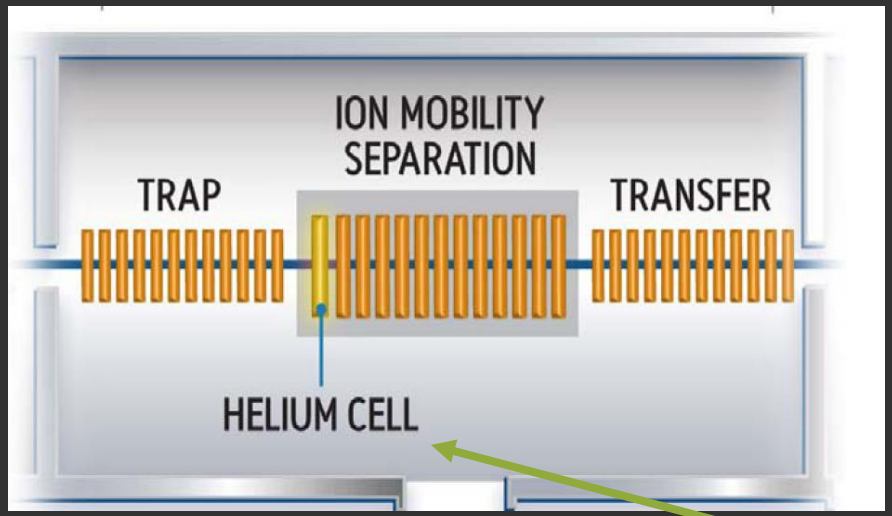
Too low

bad transmission

Too high

Ion fragmentation

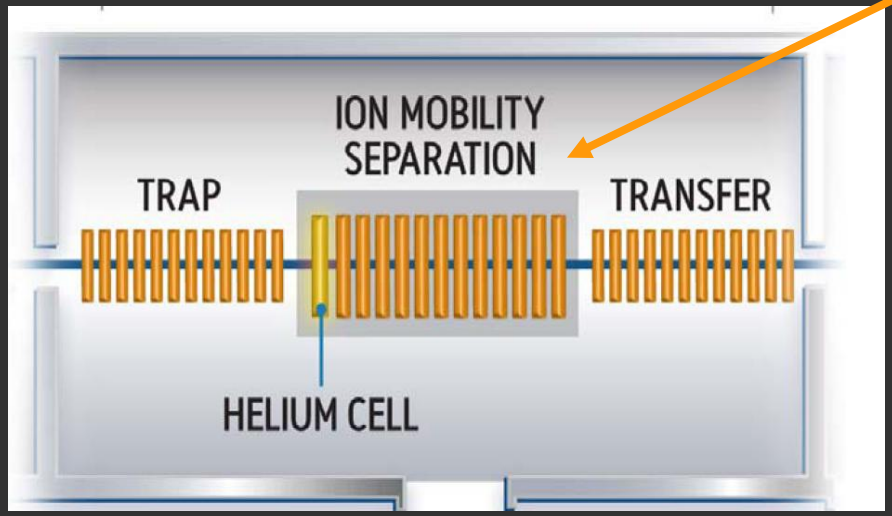
Buffer gas: softly reduces ion velocity



Maximises transmission of ions on entry into the IM cell

Helium Cell Pressure

IMS T-Wave velocity

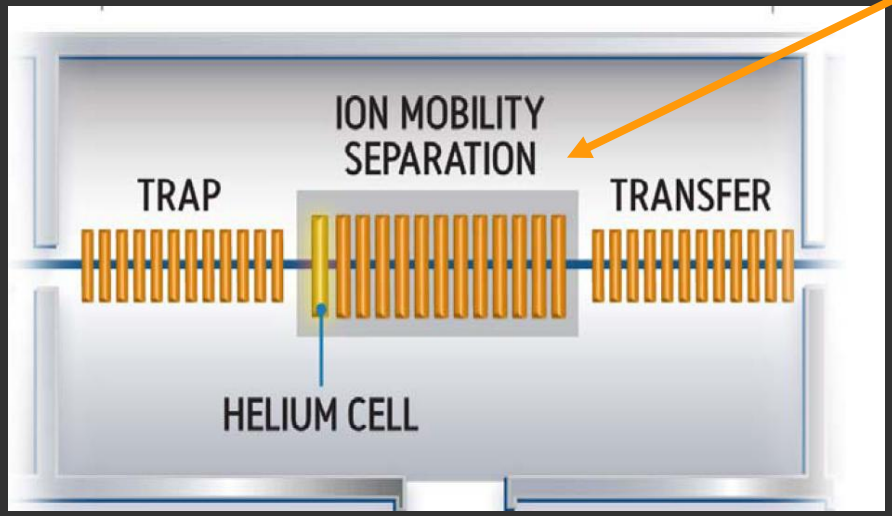


Fast

Ions roll over the wave

Better the separation

IMS T-Wave Height



High field

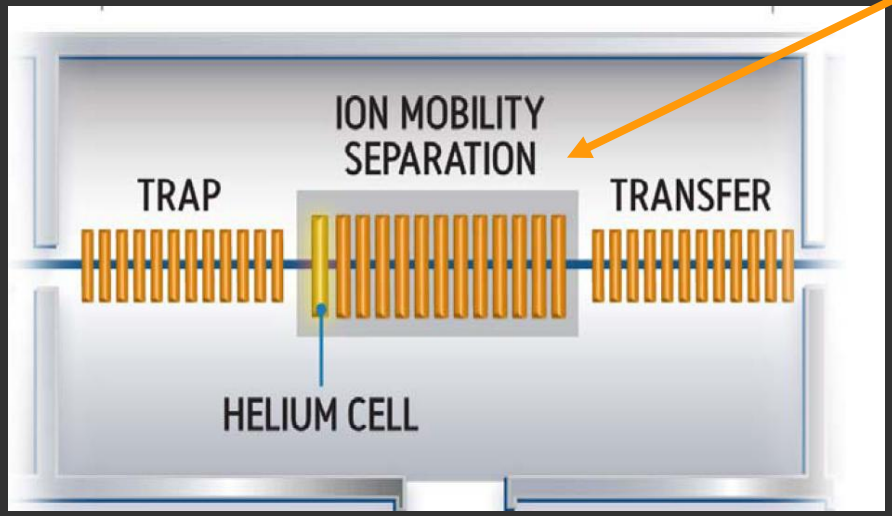
↓

High pulses

↓

Better separation selectivity

Gas Pressure



Higher

Better the resolving power

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

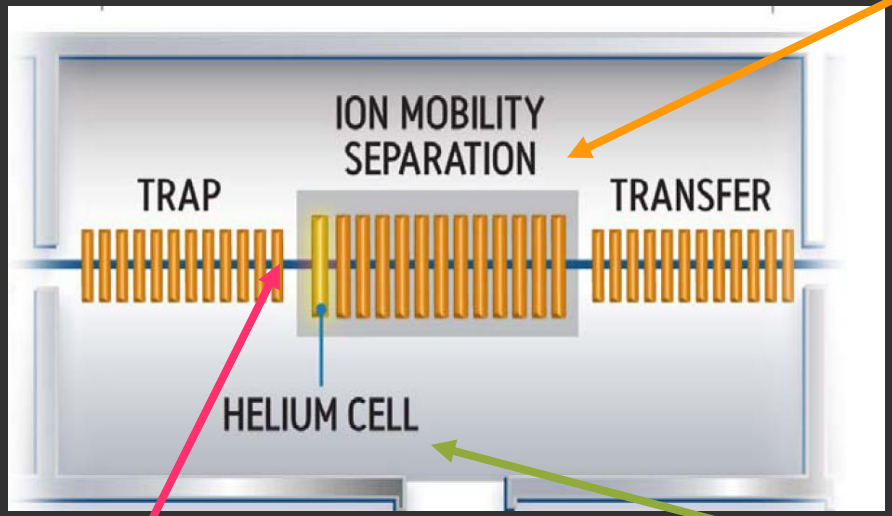
Intensity

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)

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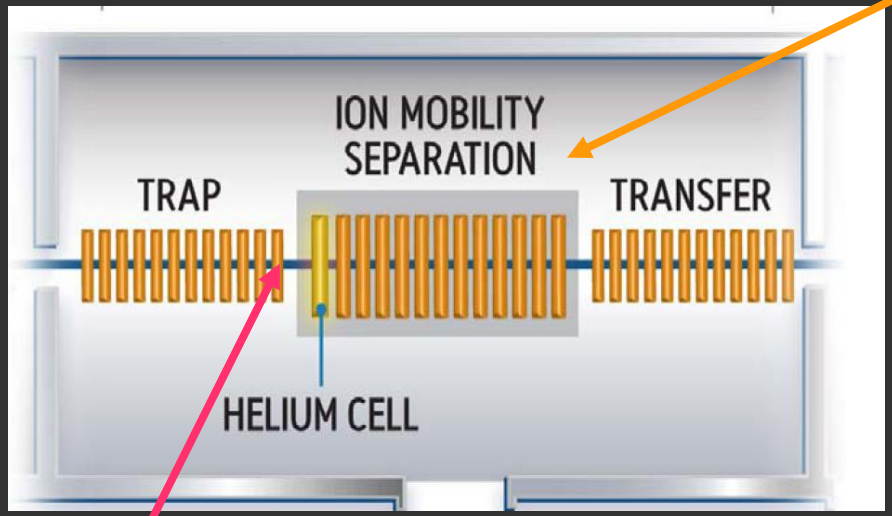
Most influencing factors



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)

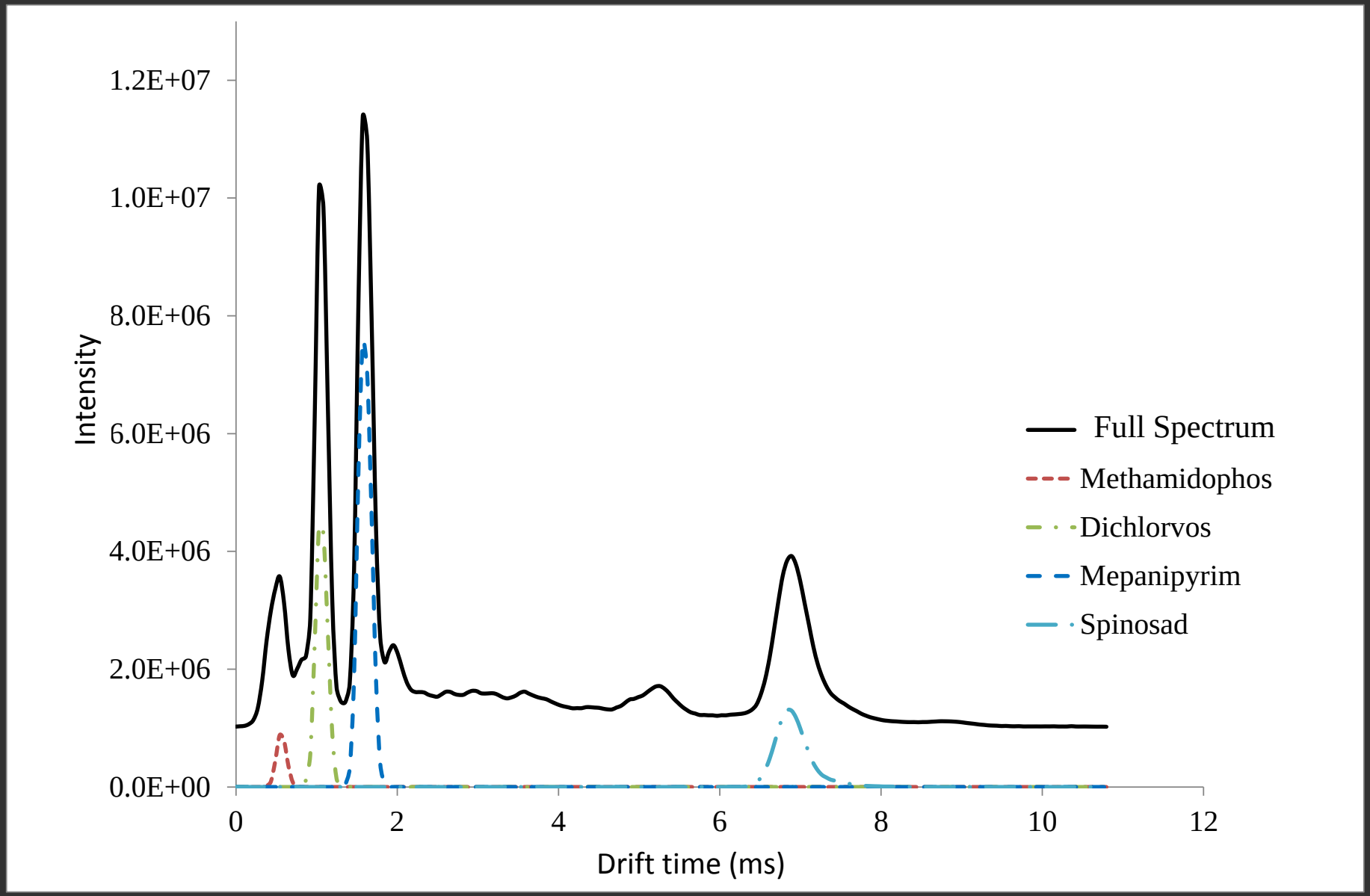
3 responses

Intensity

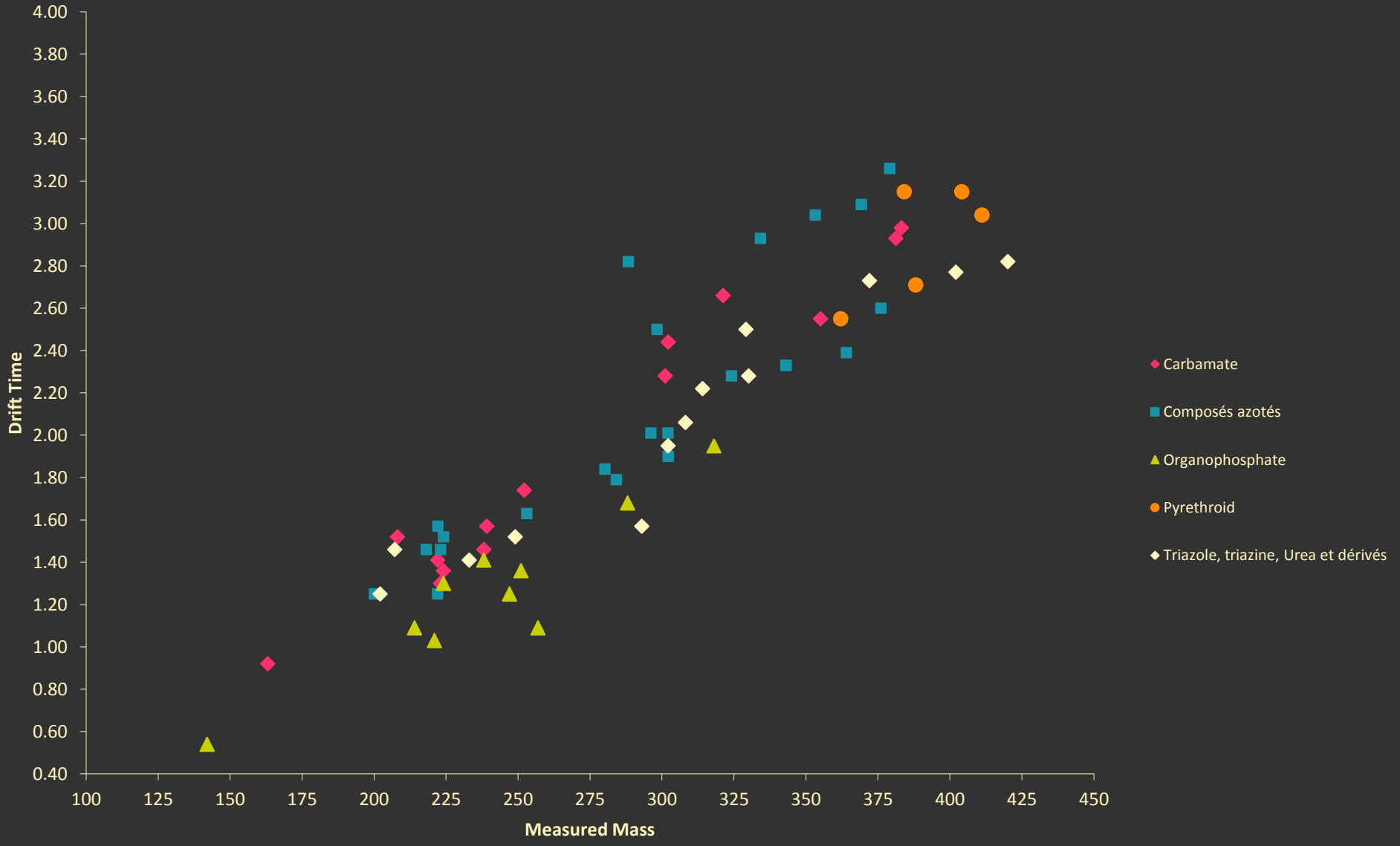
Resolution

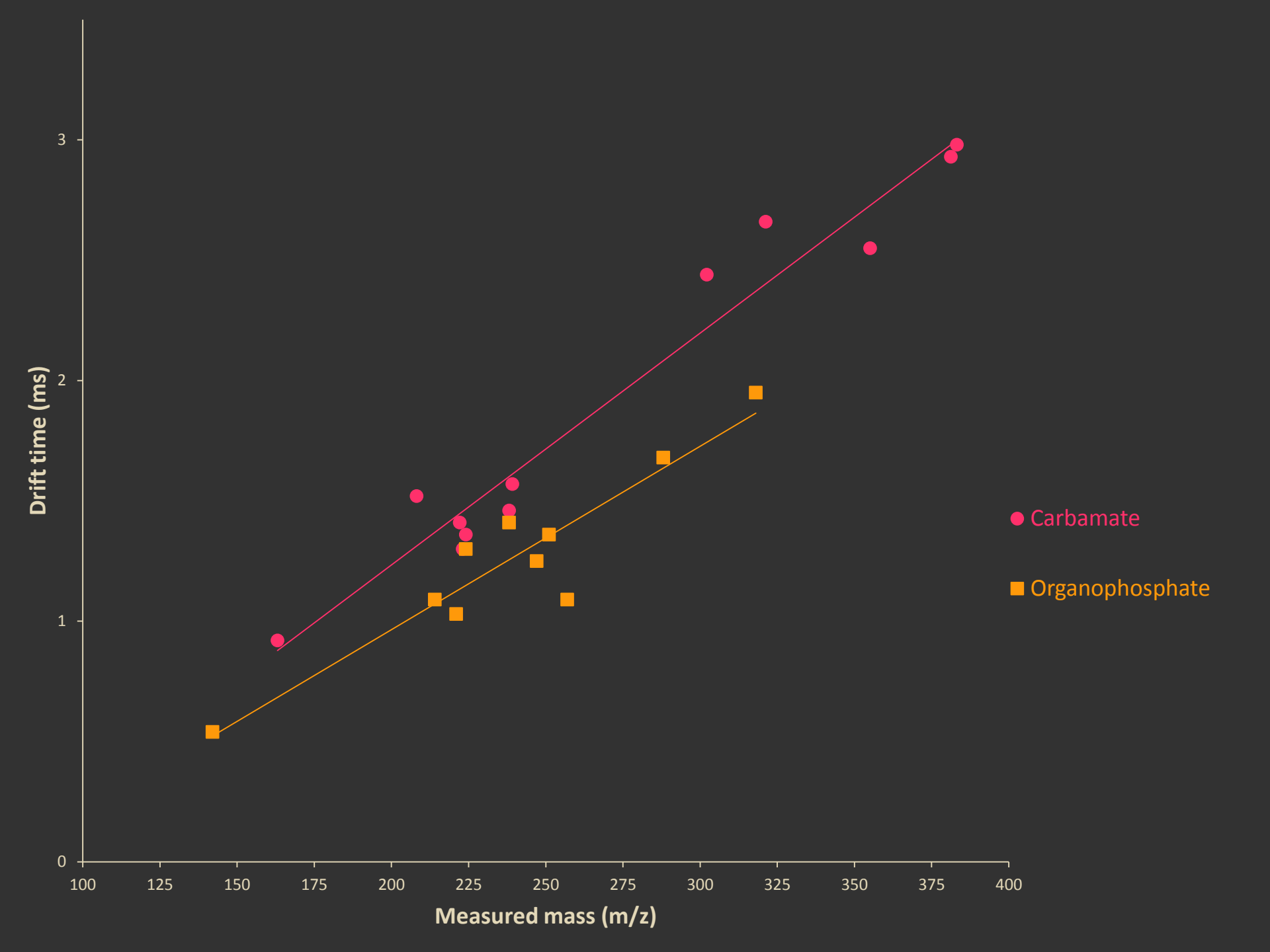
Relative drift time

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


1.2E+07
1.0E+07
8.0E+06
6.0E+06
4.0E+06
2.0E+06
0.0E+00
Intensity
0
2
4
6
8
10
12
Drift time (ms)
Full Spectrum
Methamidophos
Dichlorvos
Mepanipyrim
Spinosad

Ion Mobility of 5 classes of pesticide



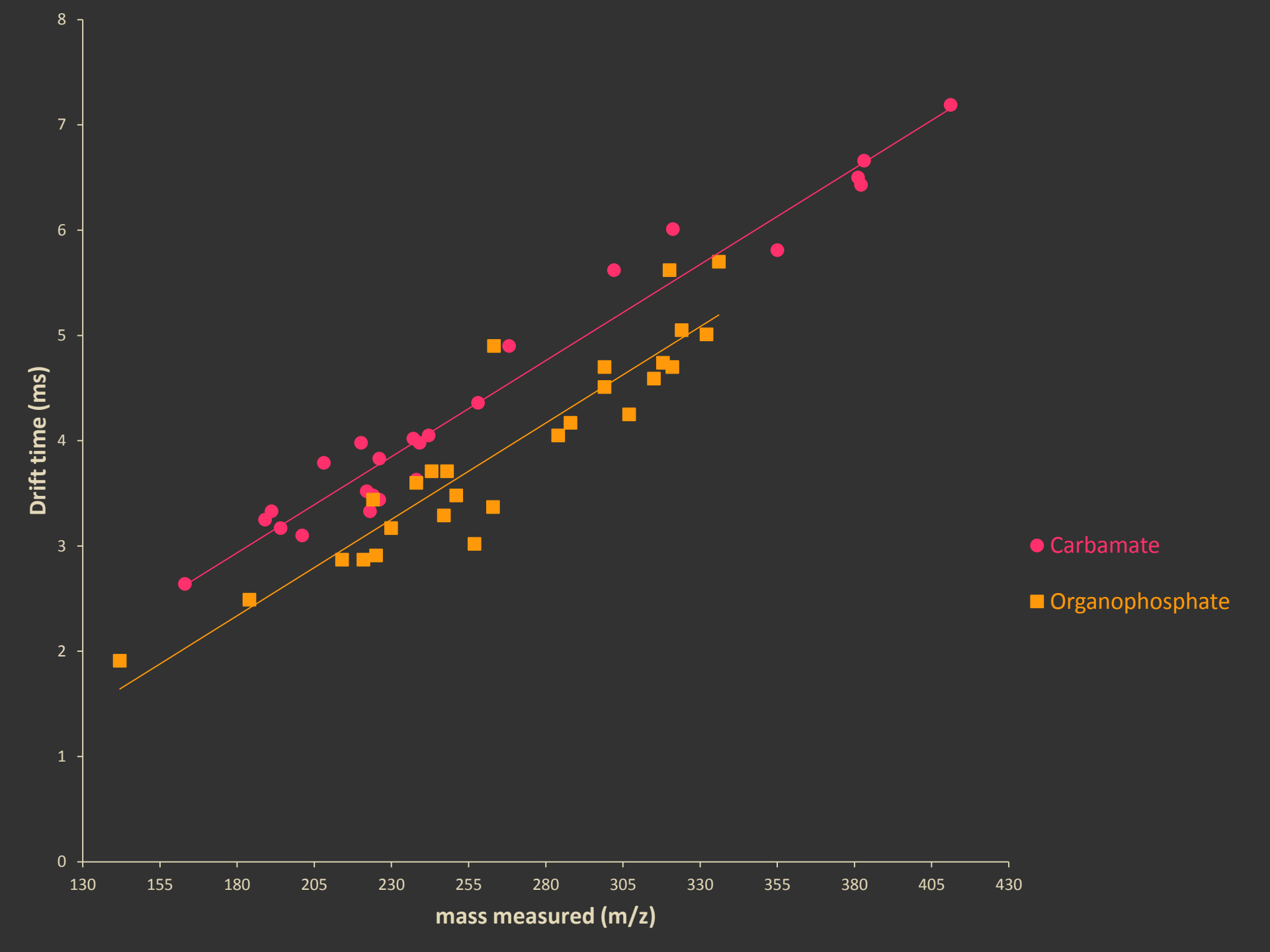

Drift time (ms)
0
1
2
3
100
125
150
175
200
225
250
275
300
325
350
375
400
Measured mass (m/z)
Carbamate
Organophosphate

Nature's best

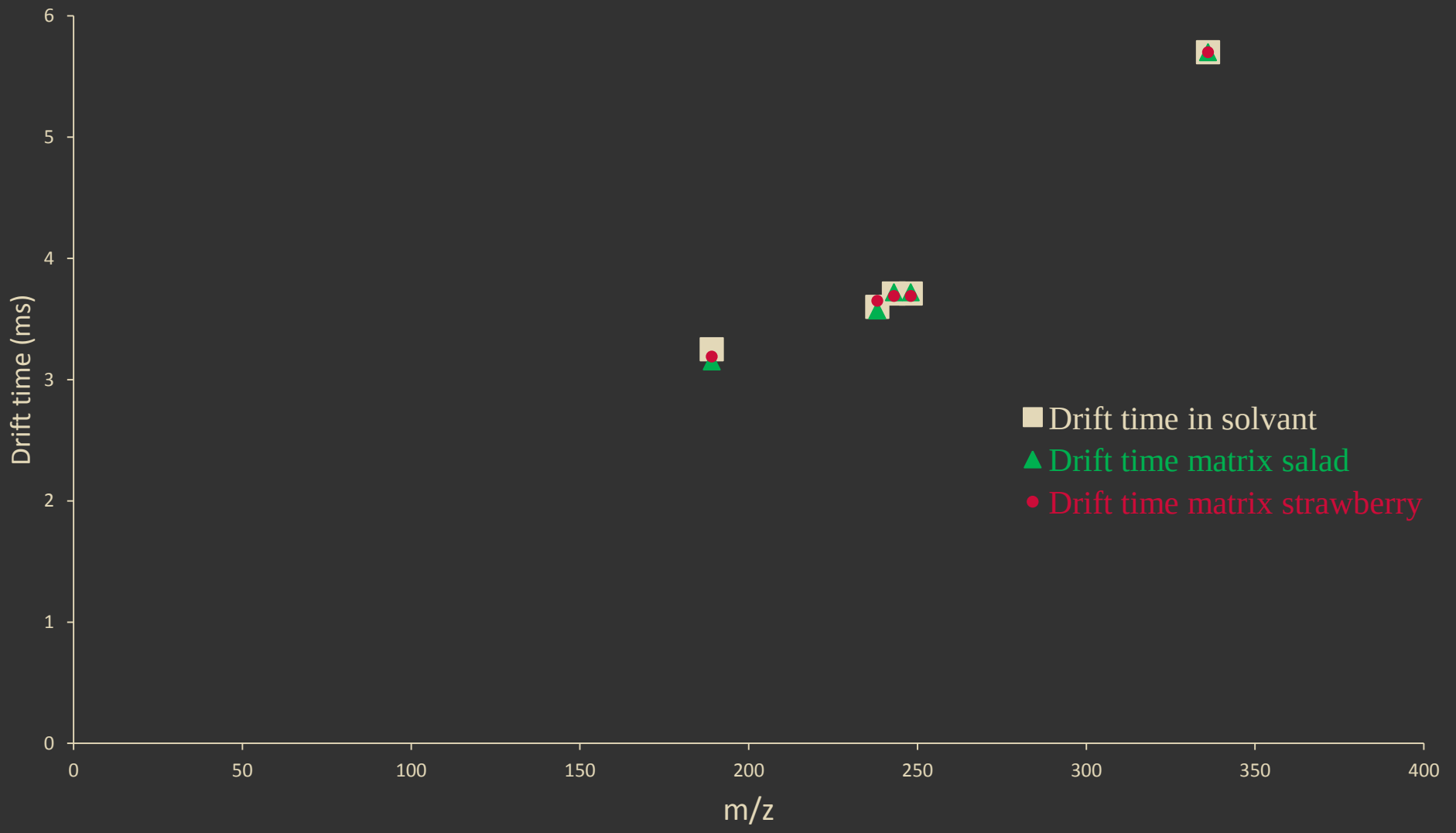
From 510 LC amenable pesticides, we only have 5 with a mass > 600

- 4 belong to the avermectins family (masses > 800 Da)
- Azadirachtin is isolated from Neem tree >700 Da)

Natural products/synthetic analogues


Drift time (ms)
0
1
2
3
4
5
6
7
8
130
155
180
205
230
255
280
305
330
355
380
405
430
mass measured (m/z)
Carbamate
Organophosphate

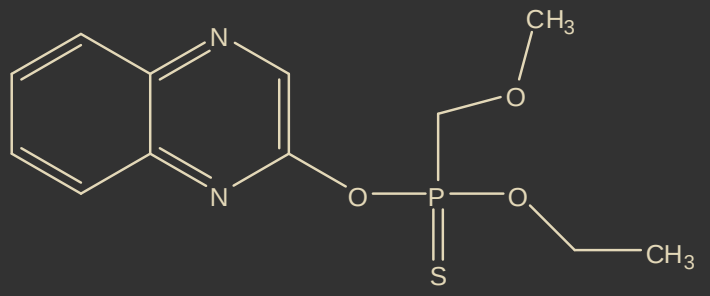
Matrix effect on the drift time



Interesting case study

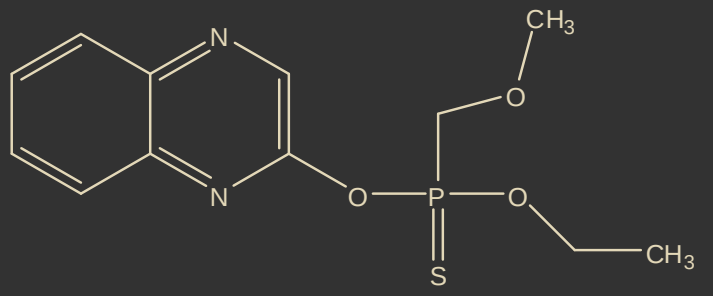
Unusual Suspect

Quinalphos 299.0619 (+1)

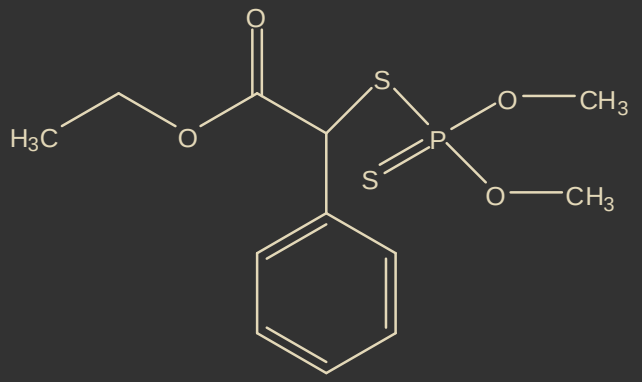


Unusual Suspect

Quinalphos 299.0619 (+1)

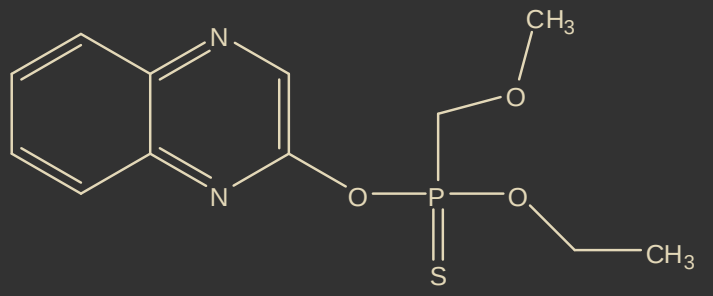


Phenthoate 321.0384 (+1)

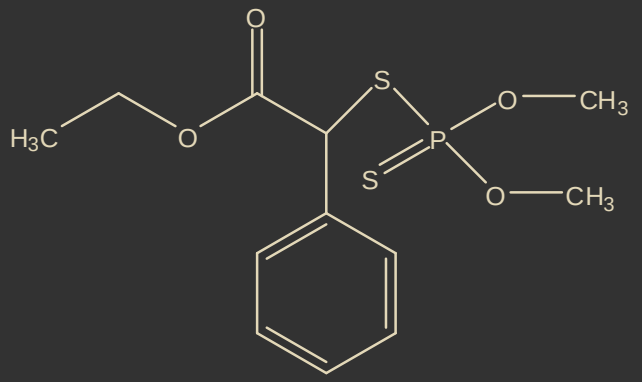


Unusual Suspect

Quinalphos 299.0619 (+1)



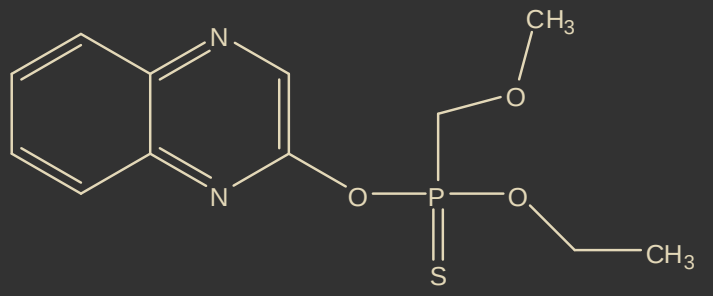
Phenthoate 321.0384 (+1)



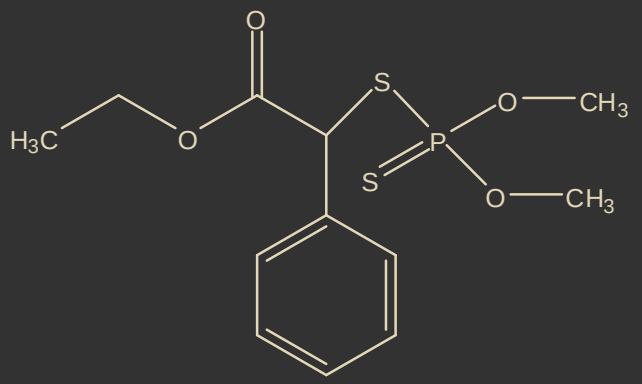
Confirmation by MS/MS

Investigation

Quinalphos 299.0619 (+1)



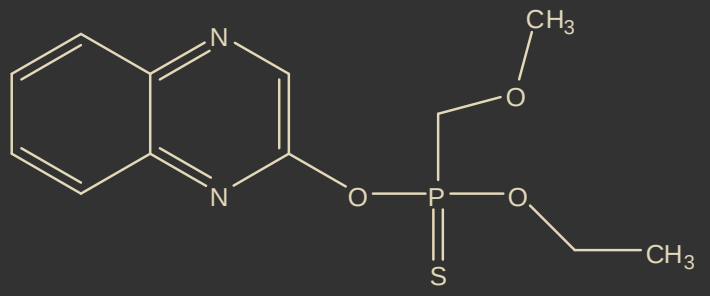
Phenthoate 321.0384 (+1)



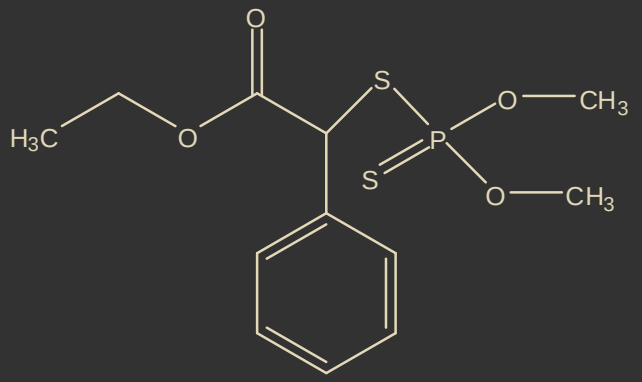
NO Phenthoate !

Investigation

Quinalphos 299.0619 (+1) 8.44 (min)



Phenthoate 321.0384 (+1) 8.48 (min)

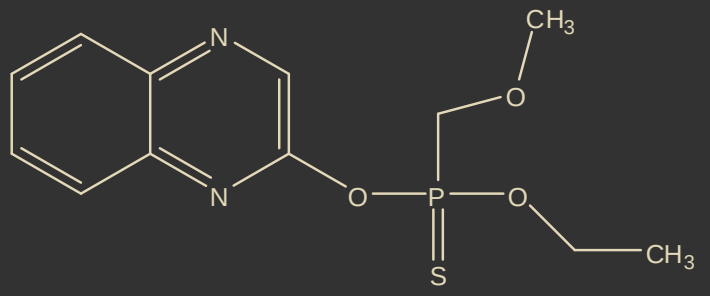


Co-elution

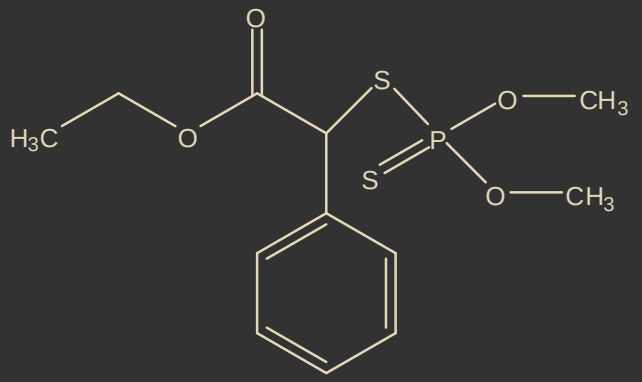
12
Mg
Magnesium
24.3050
[Ne]3s2
7.6462
11
Na
Sodium
22.989770
[Ne]3s
5.1391
2S1/2
1S0
5.3917
20
Ca
Calcium
40.078
19
K
21
3

Unusual Suspect

Quinalphos 299.0619 (+1)



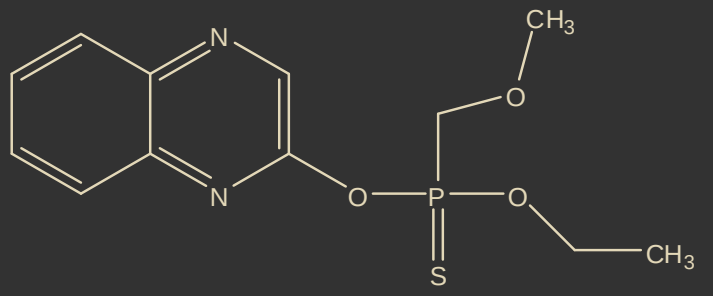
Phenthoate 321.0384 (+1)



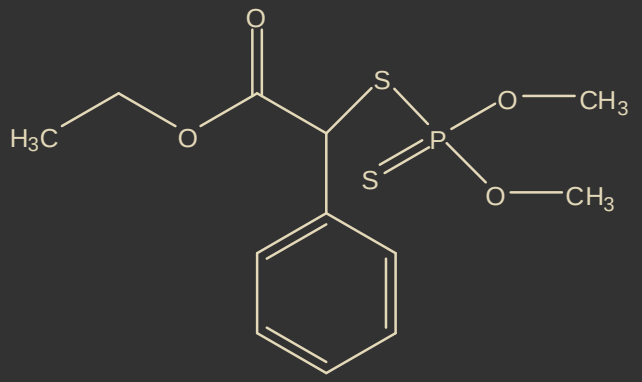
Quinalphos + Na 321.0439 (+1)

Unusual Suspect

Quinalphos 299.0619 (+1)



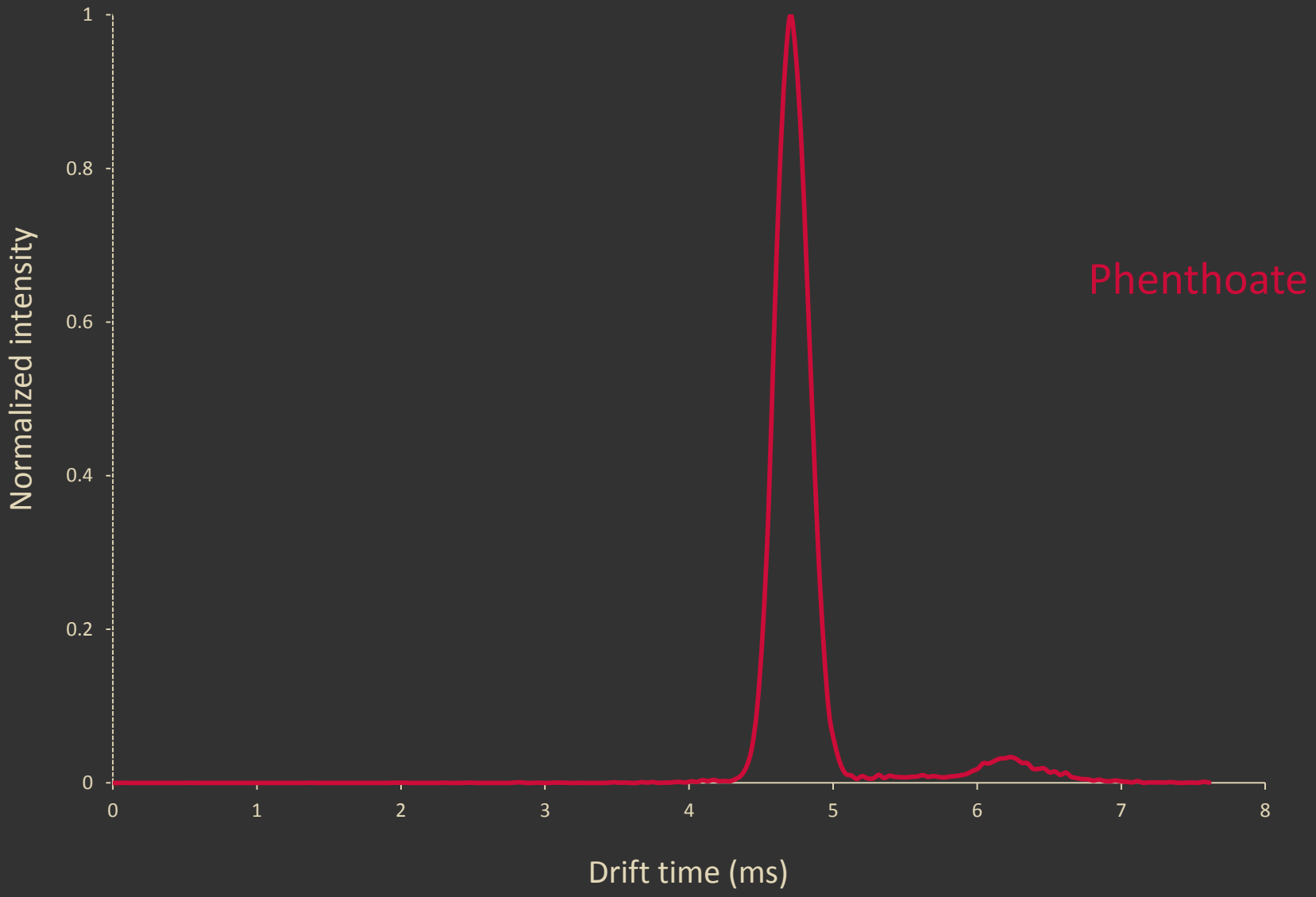
Phenthoate 321.0384 (+1)



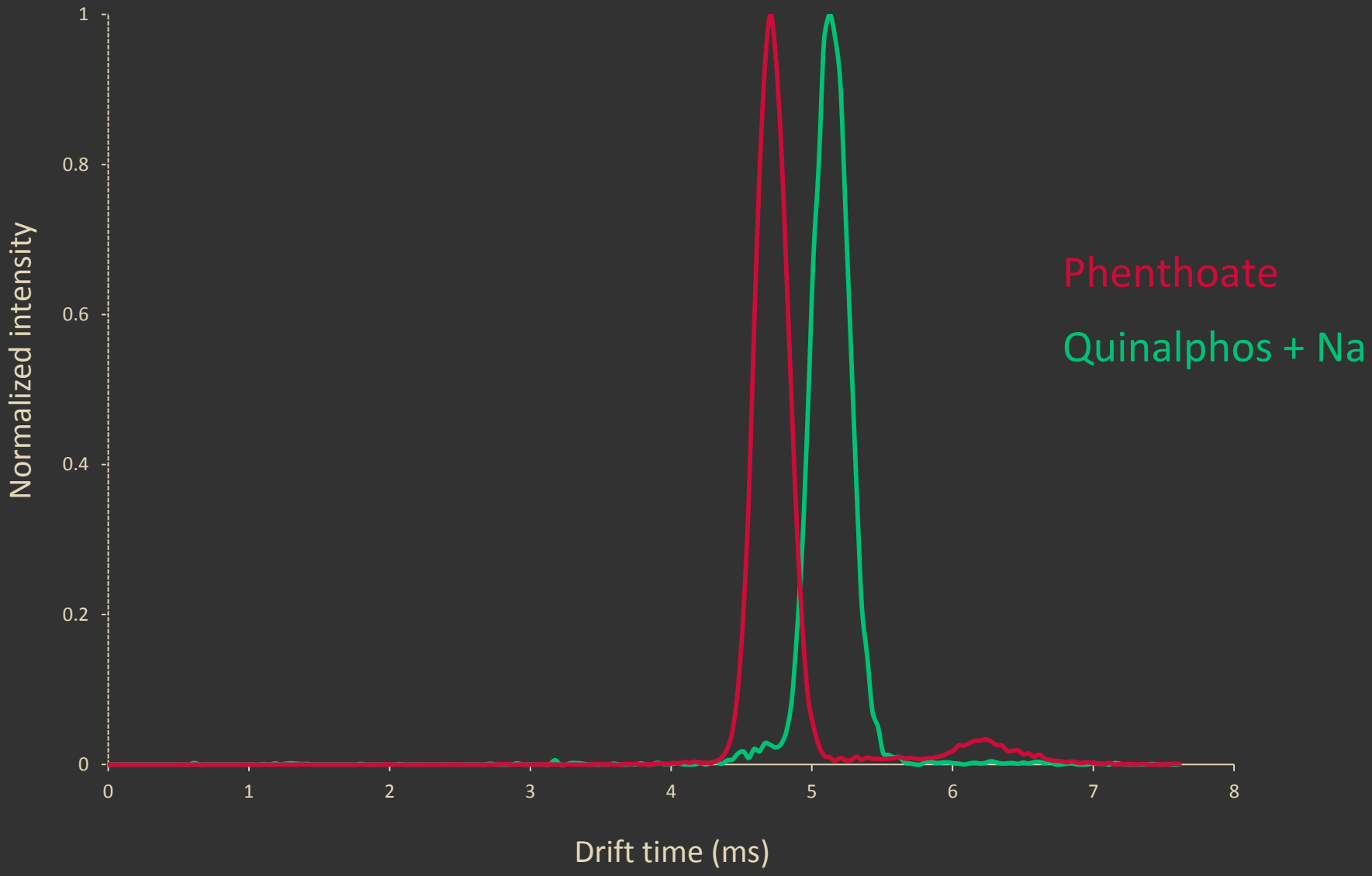
Quinalphos + Na 321.0439 (+1)

Can IMS help?

Unusual Suspect



Unusual Suspect



Our Path today:

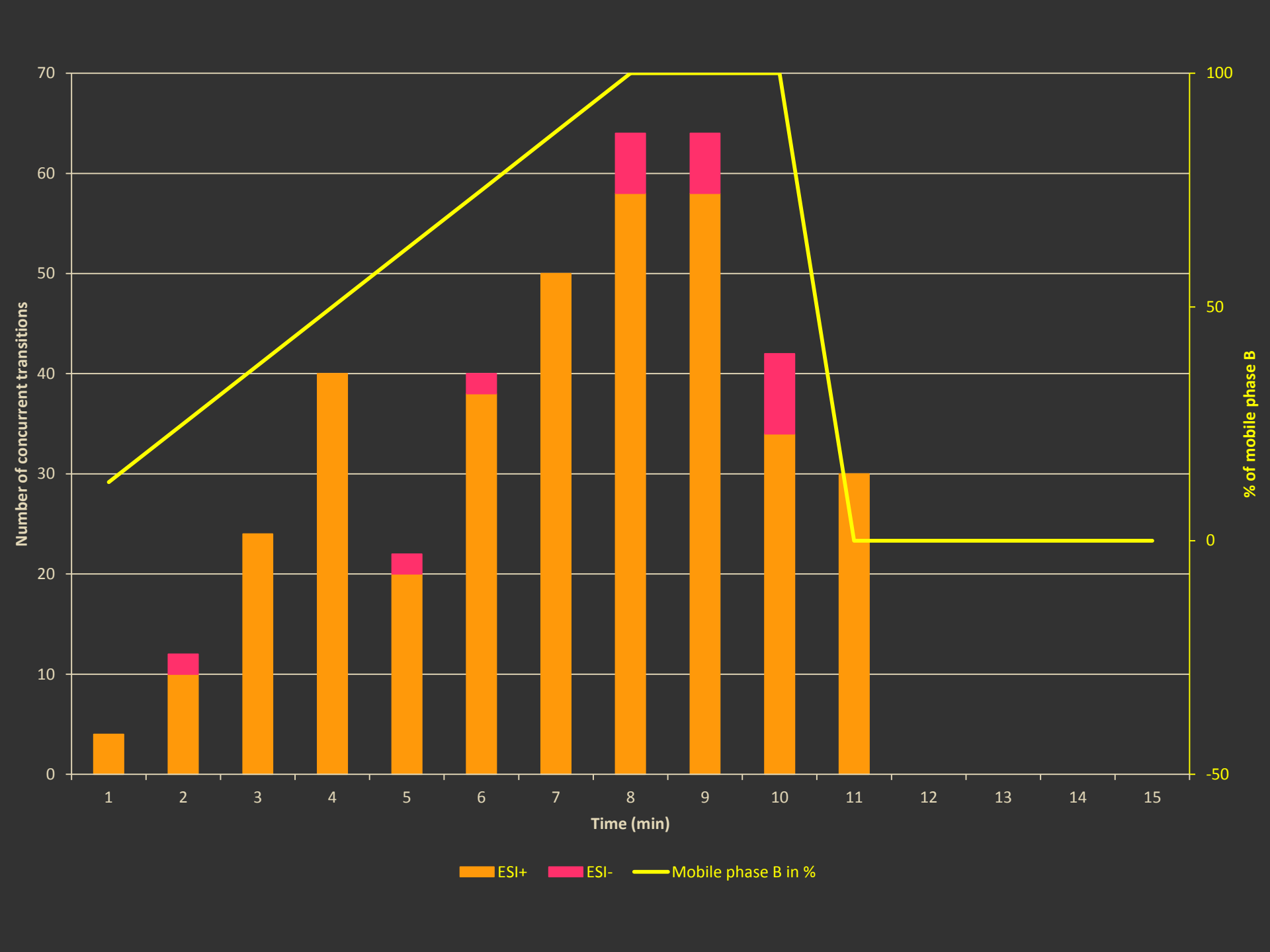
- Purpose
- Power
- Pesticides
- Prospect

Future

- Many optimization options, many possibilities
- IM adds value to the data obtained, …new IP?
- Need to test the UPLC-IMMS application
- Investigate the impact of the chemical functions of the different pesticides on the drift behavior

… and let our curiosity

and imagination run free!!


70
60
50
40
30
20
10
0
Number of concurrent transitions
100
50
0
-50
% of mobile phase B
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Time (min)
ESI+
ESI-
Mobile phase B in %