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

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S. Goscinny, L. Joly, E. De Pauw, V. Hanot and G. Eppe
Our Path today:

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

Only ESI +
In a perfect stairs shape

Fragile zones
Pesticides residue analysis

Continuous challenge;

Increasing number of compounds, at low levels, in complex matrices
Houston,
We have a problem
Strategy
Screening
Screening method

Method to detect analyte(s) in samples in an easy/rapid way
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Synapt G2
Synapt G2
Synapt G2
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 through the IM cell

Ions are moved through the IM cell in PULSES as WAVES

- faster IMS duty cycles
- MS sensitivity is not compromised
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

- Too low: bad transmission
- Too high: Ion fragmentation

Biais (V)
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 performed with the 2 most influencing parameters:

- **Gas Pressure**
- **Biais (V)**

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

- **3 responses**
  - Intensity
  - Resolution
  - Relative drift time
Ion Mobility of 5 classes of pesticide

Drift Time vs Measured Mass

- Carbamate
- Composés azotés
- Organophosphate
- Pyrethroid
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How can we help the Detection?
Diuron
m/z (+1) 233.0248
Rt 6.38 min
Diuron
m/z (+1) 233.0248
Rt 6.38 min
Diuron
m/z (+1) 233.0248
Rt 6.38 min
Propamocarb
m/Z (+1) 189.1603
Rt 1.84 min
Indoxacarb
m/Z (+1) 528.0785
Rt 9.1 min
Leek

0.01 mg/kg Imaxalil

Retention time (min)

IM-MS

566

MS

3.03 e3
How can we help the Identification process?
New IP ?
Matrix effect on mobility time?

- Mobility time (ms) on the y-axis.
- M/Z on the x-axis.
- Data points showing the effect of matrix on mobility time.
Matrix effect on mobility time?

![Graph showing the relationship between M/Z and Mobility time (ms).](image-url)
Matrix effect on mobility time?

- STD
- Orange
- Leek
- Pepper
False positive: case study (SM 3)
<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar Mass (MR)</th>
<th>MS/MS Confirmation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenamidone</td>
<td>312.1172 (+1)</td>
<td>YES</td>
</tr>
<tr>
<td>Mevinphos</td>
<td>225.0528 (+1)</td>
<td>YES</td>
</tr>
<tr>
<td>Phentoate</td>
<td>321.0384 (+1)</td>
<td>NO</td>
</tr>
<tr>
<td>Quinalphos</td>
<td>299.0619 (+1)</td>
<td>YES</td>
</tr>
<tr>
<td>Terbuthylazine</td>
<td>230.1172 (+1)</td>
<td>YES</td>
</tr>
</tbody>
</table>
Unusual Suspect

Quinalphos  299.0619 (+1)  8.22 (min)

Phenthoate  321.0384 (+1)  8.27 (min)

Co-elution
<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Mass Number</th>
<th>Electron Configuration</th>
<th>Atomic Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>11</td>
<td>22.989770</td>
<td>[Ne]3s1</td>
<td>22.989770</td>
</tr>
<tr>
<td>Mg</td>
<td>12</td>
<td>24.3050</td>
<td>[Ne]3s2</td>
<td>24.3050</td>
</tr>
<tr>
<td>Ca</td>
<td>20</td>
<td>40.078</td>
<td>[Ar]4s2</td>
<td>40.078</td>
</tr>
</tbody>
</table>

**Caution:** The atomic weight of Sodium (Na) is highlighted with a pink circle.
<table>
<thead>
<tr>
<th>Substance</th>
<th>Molecular Weight</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinalphos</td>
<td>299.0619</td>
<td>(+1)</td>
</tr>
<tr>
<td>Phenthoate</td>
<td>321.0384</td>
<td>(+1)</td>
</tr>
<tr>
<td>Quinalphos + Na</td>
<td>321.0439</td>
<td>(+1)</td>
</tr>
</tbody>
</table>
Unusual Suspect

Quinalphos 299.0619 (+1)

Phenthoate 321.0384 (+1)

Quinalphos + Na 321.0439 (+1)

Can IMS help?
Unusual Suspect

Normalized intensity

Drift time (ms)

Phenthoate
Unusual Suspect

Normalized intensity

Drift time (ms)

Phenthoate
Quinalphos + Na
**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)
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In progress

Establishing the drift times of the salt adducts

Testing the impact of post-IM fragmentation for identification

Processing data faster with new software (ex. MS^

E)
Supp. data
Nature of the Gas

**He**

- Spectre complet
- Methamidophos
- Dichlorvos
- Mepanipyrim
- Spinosad

**N₂**

- Spectre complet
- Methamidophos
- Dichlorvos
- Mepanipyrim
- Spinosad

**CO₂**

- Spectre complet
- Methamidophos
- Dichlorvos
- Mepanipyrim
- Spinosad
<table>
<thead>
<tr>
<th>Compound</th>
<th>m/z</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methamidophos</td>
<td>141.0013</td>
<td><img src="image1" alt="Methamidophos" /></td>
</tr>
<tr>
<td>Dichlorvos</td>
<td>219.9459</td>
<td><img src="image2" alt="Dichlorvos" /></td>
</tr>
<tr>
<td>Mepanipyrim</td>
<td>223.1109</td>
<td><img src="image3" alt="Mepanipyrim" /></td>
</tr>
<tr>
<td>Spinosad</td>
<td>731.4608</td>
<td><img src="image4" alt="Spinosad" /></td>
</tr>
</tbody>
</table>
Methamidophos 141.9976
Dichlorvos 220.9004
Mepamipyrim 224.0638
Spinosad 732.4915
How does it work?