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\(^1\)
- Rich in diversity
  Chemical structure, solubility, volatility…
- Hidden in complex food matrices

\(^1\) 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\textsuperscript{rd} 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

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

\[ P \approx 10^{-2} \text{ mbar} \]
\[ P \approx 5 \times 10^{-1} \text{ mbar} \]
\[ P \approx 10^{-2} \text{ mbar} \] within IM
Synapt G2 HDMS @ Waters

Ion mobility cell

ESI

Quadrupole + Ion Guide

ToF
Discrimination between isomers

Quinalphos + Phoxim

m/z = 299.0619

C_{12}H_{15}N_{2}O_{3}PS

\Omega = 122 \text{ Å}^2

Quinalphos

\Omega = 125 \text{ Å}^2

Phoxim

In this case parameters will optimized to separated these 2 molecules
Optimization of mobility cell parameters

- Bias
- Determination of used gas
- Travelling voltage wave
- Wave height
- Wave velocity
- Helium cell Pressure
- IMS cell pressure

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

- 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
Choice of separation gas

methamidophos
\[ \text{m/z = 141.0013} \]

\[
\begin{array}{c}
\text{H}_3\text{C} \equiv \text{S} \equiv \text{P} \equiv \text{O} \equiv \text{O} \equiv \text{CH}_3 \\
\text{NH}_2
\end{array}
\]

dichlorvos
\[ \text{m/z = 219.9459} \]

\[
\begin{array}{c}
\text{Cl} \equiv \text{O} \equiv \text{PO} \equiv \text{O}
\end{array}
\]

mepanipyrim
\[ \text{m/z = 223.1109} \]

\[
\begin{array}{c}
\text{H}_3\text{C} \equiv \text{C} \equiv \text{N} \equiv \text{NH} \equiv \text{N} \equiv \text{CH}_3
\end{array}
\]

spinosad
\[ \text{m/z = 731.4608} \]

The best performance is obtained with Nitrogen
Precursor ion fragmented

Product ions separated by IMS

Precursor and products share same drift time
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>
<thead>
<tr>
<th>MS mode: Typical systems (examples)</th>
<th>Single MS (standard mass resolution)</th>
<th>Single MS (high resolution/high mass accuracy)</th>
<th>MS/MS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acquisition:</strong></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Full scan, Limited m/z range, Selected Ion monitoring (SIM)</td>
<td>Full scan, Limited m/z range, Selected Ion monitoring (SIM)</td>
<td>Selected/multiple reaction monitoring (SRM/MRM), full scan product-ion spectra</td>
</tr>
<tr>
<td><strong>Requirements for identification:</strong></td>
<td>≥ 3 diagnostic ions, preferably including quasi molecular ion</td>
<td>≥ 2 diagnostic ions (preferably including the quasi molecular ion). Mass accuracy &lt; 5 ppm. At least one fragment ion.</td>
<td>≥ 2 product ions</td>
</tr>
<tr>
<td>Ion ratio(s):</td>
<td>according to Table 4</td>
<td></td>
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