NEW ANALYTICAL TOOLS FOR PESTICIDE RESIDUES IN FOOD CONTROL.

EXPERIENCE GAINED OVER THE LAST 15 YEARS AS THE EURL-FV.

Amadeo Rodríguez Fernández-Alba
OUTLOOK

History

Performance of MRM in OfLs network
Evaluation of MRM through EUPTs

Present

Improved technologies
High sensitive TQ (high benefits)
HRMS (impact and improvements)

Future

Automation
Citius Altius Fortius
2004

183 analytes

1. Extraction
75 g sample
200 ml EtOAc

2. Extraction
75 g sample
200 ml EtOAc + NaOH

GPC clean up
50 min /sample

Evaporation
15 min /sample

Redissolved in EtOAc/ch/MeOH

GC-ECD
GC-FPD
GC-NPD
LC-UV
LC-Fluorsc.

GC-ITD
2004

183 analytes

1. Extraction
   10 g sample
   20 ml EtOAc+NaHCO₃
   3 min Spex shaker
   Na₂SO₄
   Centrifugation
   Filtration
   GC-MS/MS

2. Extraction
   5 g sample
   10 ml water
   10 ml EtOAc (1% HAc)
   3 min Spex shaker
   Na₂SO₄
   Centrifugation
   Filtration
   GC-MS/MS

3. Extraction
   5 g sample
   PSA + C18
   10 ml EtOAc
   3 min Spex shaker
   Na₂SO₄
   Centrifugation
   Filtration
   UHPLC-MS/MS

4. Extraction
   2.5 g sample
   5 ml EtOAc:ACN(80:20)
   5 min Spex shaker
   Na₂SO₄
   Centrifugation/filtration
   5 ml EtOAc:ACN(80:20)
   Clean up EMR-Lipid 6 ml
   Elution EtOAc:ACN(20:80)
   Centrifugation/filtration
   Sample conc. 0.2 g/ml
   GC-MS/MS
   UHPLC-MS/MS

10 g/ml (150 g)

0.5 g/ml (10 g)
Participation

Number of participants

EUPTs-FV

European Reference Laboratory - FV
24 EUPTs z-Score Results (47302)
## EUPT-FV1 to EUPT-FV24 in numbers

<table>
<thead>
<tr>
<th>EUPT Nº</th>
<th>Matrices</th>
<th>Nº of Participants</th>
<th>Nº of Possible Pesticides</th>
<th>Nº of pesticides evaluated in test item</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pepper</td>
<td>88</td>
<td>33</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>Apple</td>
<td>85</td>
<td>41</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>Cucumber</td>
<td>116</td>
<td>48</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>Orange</td>
<td>117</td>
<td>57</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>Lettuce</td>
<td>127</td>
<td>57</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>Tomato</td>
<td>130</td>
<td>57</td>
<td>13</td>
</tr>
<tr>
<td>7</td>
<td>Grape</td>
<td>128</td>
<td>65</td>
<td>16</td>
</tr>
<tr>
<td>8</td>
<td>Aubergine</td>
<td>129</td>
<td>68</td>
<td>16</td>
</tr>
<tr>
<td>9</td>
<td>Strawberry</td>
<td>137</td>
<td>82</td>
<td>19</td>
</tr>
<tr>
<td>10</td>
<td>Carrot</td>
<td>132</td>
<td>113</td>
<td>18</td>
</tr>
<tr>
<td>11</td>
<td>Cauliflower</td>
<td>151</td>
<td>128</td>
<td>21</td>
</tr>
<tr>
<td>12</td>
<td>Leek</td>
<td>153</td>
<td>144</td>
<td>17</td>
</tr>
<tr>
<td>13</td>
<td>Mandarin</td>
<td>154</td>
<td>144</td>
<td>19</td>
</tr>
<tr>
<td>14</td>
<td>Pear</td>
<td>167</td>
<td>175</td>
<td>18</td>
</tr>
<tr>
<td>15</td>
<td>Potato</td>
<td>175</td>
<td>175</td>
<td>18</td>
</tr>
<tr>
<td>16</td>
<td>Pepper</td>
<td>183</td>
<td>175</td>
<td>22</td>
</tr>
<tr>
<td>17</td>
<td>Broccoli</td>
<td>185</td>
<td>183</td>
<td>11</td>
</tr>
<tr>
<td>18</td>
<td>Spinach</td>
<td>191</td>
<td>190</td>
<td>16 (14 mandatory + 2 voluntary)</td>
</tr>
<tr>
<td>19</td>
<td>Lemon</td>
<td>174</td>
<td>192</td>
<td>19 (17 mandatory + 2 voluntary)</td>
</tr>
<tr>
<td>20</td>
<td>Green beans</td>
<td>184</td>
<td>195</td>
<td>21 (19 mandatory + 2 voluntary)</td>
</tr>
<tr>
<td>21</td>
<td>Red cabbage</td>
<td>190</td>
<td>205</td>
<td>20 (17 mandatory + 3 voluntary)</td>
</tr>
<tr>
<td>22</td>
<td>Onion</td>
<td>176</td>
<td>208</td>
<td>19 (17 mandatory + 2 voluntary)</td>
</tr>
<tr>
<td>23</td>
<td>Aubergine</td>
<td>182</td>
<td>215</td>
<td>20 (18 mandatory + 2 voluntary)</td>
</tr>
<tr>
<td>24</td>
<td>Tomato</td>
<td>179</td>
<td>215</td>
<td>18 (16 mandatory + 2 voluntary)</td>
</tr>
</tbody>
</table>
EUPTs zScore Results Last Ten Years (9828)

Concentration values below 100 ppb

- 3.7%
- 95.2%
- 1.2%

Number of data
EUPTs zScore Results Last Ten Years (5596)

Concentration values over 500 ppb

- 3.2%
- 94.0%
- 2.8%

Number of data
European Reference Laboratory - FV

LC-ESI

HUNDREDS OF COMPOUNDS

GC-EI
Degradation - Alanycarb

Alanycarb
(Mix - 10 mg/L)

Alanycarb
(Stock solution - 10 mg/L)
Degradation - Alanycarb

Methomyl

(Mix 2 – 10 mg/L)

2.1 ppm of methomyl in mix 4?
Degradation - Alanycarb

Alanycarb
t_R = 12.19 min
Chemical Formula: C_{17}H_{25}N_{3}O_{2}S_{2}
Exact Mass: 399.1286

(Z)-Methomyl
t_R = 2.98 min
Chemical Formula: C_{6}H_{10}N_{2}O_{2}S
Exact Mass: 162.0463

Cocktail effect

thiodicarb

methomyl

methomyl
Potential false positives and negatives: common mass transitions

Aldicarb-sulfone monitored MRM transitions

Butoxy carboxim monitored MRM transitions

240 > 223
240 > 86
240 > 166
Signal supression due to matrix effects

Injection 1g matrix/ml

Concentration level: 100 ppb
EIC: \textit{m/z} 253.0092

Demeton-S-Methyl
EUPTs zScore Results Last Ten Years (26178)

94.8%
EUPTs zScore Results Last Ten Years (26178)

- Number of data
- zScore value

92.1%
EUPTs zScore Results Last Ten Years (26178)

Number of data

zScore value

0 600 1200 1800 2400

95.2%
Global improvements
Quantification

Dispersion of results EUPT-FV1-FV24
(1996-2022)

25% FFP-RSD
Global improvements
Quantification

Dispersion of results EUPT-FV1-FV24
(1996-2022)

25% FFP-RSD
Global improvements
Quantification

Dispersion of results EUPT-FV1-FV24
(1996-2022)

25% FFP-RSD
Global improvements
Quantification

Number of pesticides with CV > 25%
Laboratories with False Negatives
NEW TECHNOLOGIES

High sensitive LC/GC-TQ-MS/MS
High Resolution Mass Espectrometry
Automation
High sensitive LC/GC-TQ-MS/MS
Calibration

Area

Conc. (ppb)

5 ppb  10 ppb  300 ppb
Signal supression due to matrix effects
Injection 1g matrix/ml (5μL-5 mg)
LC-MS

EFFECT OF DILUTION IN “EASY-MEDIUM” COMPLEX MATRICES

% Pesticides Suppression >50%

Total amount of sample injected

Leek
Orange
Broccoli
Tomato
Pepper
Grape
Cucumber

5 mg 1 1 mg 0.5 mg 0.25 mg
<table>
<thead>
<tr>
<th>Injection volume</th>
<th>Matrix injected in column</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC: 5 µL</td>
<td>5 mg</td>
</tr>
<tr>
<td>GC: 1 µL</td>
<td>1 mg</td>
</tr>
</tbody>
</table>

Green Tea

Dilx0  
1 g/mL

Dilx2  
0.5 g/mL

Dilx5  
0.2 g/mL

Dilx10  
0.1 g/mL

Dilx20  
0.05 g/mL
# Matrix effect of leek matrix over tomato matrix (250 compounds)

<table>
<thead>
<tr>
<th>Relative matrix effect</th>
<th>Leek/Tomato (2.5 µL)</th>
<th>Leek/Tomato (5.0 µL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average (%)</td>
<td>-6.6 %</td>
<td>-19.4 %</td>
</tr>
<tr>
<td>Median (%)</td>
<td>-7.3 %</td>
<td>-20.9 %</td>
</tr>
<tr>
<td>&lt;=</td>
<td>20 %</td>
<td>(%)</td>
</tr>
<tr>
<td>&gt;</td>
<td>20 %</td>
<td>&amp; &lt;=</td>
</tr>
<tr>
<td>&gt;</td>
<td>50 %</td>
<td>(%)</td>
</tr>
<tr>
<td>&lt;=</td>
<td>20 %</td>
<td>(%)</td>
</tr>
<tr>
<td>&gt;</td>
<td>20 %</td>
<td>&amp; &lt;=</td>
</tr>
<tr>
<td>&gt;</td>
<td>50 %</td>
<td>(%)</td>
</tr>
</tbody>
</table>

0.2 mg 0.5 mg
Many commodities

- **Co-extracted matrix components of Black Pepper**
  - Citrate QuEChERS+EMR clean-up

- **Co-extracted matrix components of Orange LC-TOF-MS, Citrate**
  - QuEChERS+PSA clean-up
**Epoxiconazole**

**High Sensitive TQ**
Spiked standard 10 µg/kg
Total injected amount: 0.066 mg Paprika

**Regular**
Spiked standard 10 µg/kg
Total injected amount: 0.13 mg Paprika

**Qualifier transition:**
- High Sensitive TQ: 330 - > 101
- Regular: 330 - > 101
High sensitive TQ
Spiked standard 10 µg/kg
Total injected amount: 0.066 mg Tea

Qualifer transition: 235 -> 136

Lenacil
Spiked standard 10 µg/kg
Total injected amount: 0.13 mg Tea

Qualifer transition: 235 -> 136
High Resolution Mass Spectrometry
Comparison of cycle times

Full scan MS @60K + AIF @60K + 10 tMS2 @15K (Exploris 240)

Full scan MS @70K + 10 tMS2 @ 17.5K (QExactive)

Orbitrap Exploris 240 MS

Vs

Thermo Scientific™ Q Exactive™ Hybrid Quadrupole-Orbitrap™ MS systems
(Classic & Plus)
Parallel Reaction Monitoring (PRM) ≡ Target MS2 (tMS2)
Increasing the scope
Identified pesticides/10ppb in Orange

Acquisition modes: QE Focus (FS/AIF), Orbitrap Exploris 240 MS (FS/AIF/tMS2)
<table>
<thead>
<tr>
<th>Compound 1</th>
<th>Compound 2</th>
<th>Compound 3</th>
<th>Compound 4</th>
<th>Compound 5</th>
<th>Compound 6</th>
<th>Compound 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acephate</td>
<td>Chlorpyrifos</td>
<td>Fenamidone</td>
<td>Iprovalicarb</td>
<td>Paraoxon methyl</td>
<td>Quinoxyfen</td>
<td></td>
</tr>
<tr>
<td>Acetamiprid</td>
<td>Chromafenozide</td>
<td>Fenamiphos</td>
<td>Isocarbophos</td>
<td>Penconazole</td>
<td>Quinoxyfen</td>
<td></td>
</tr>
<tr>
<td>Alachlor</td>
<td>Clothianidin</td>
<td>Fenamiphos-sulfone</td>
<td>Isoprocarb</td>
<td>Pencycuron</td>
<td>Rotenone</td>
<td></td>
</tr>
<tr>
<td>Aldicarb</td>
<td>Cyazofamid</td>
<td>Fenamiphos-sulfoxide</td>
<td>Isoprothiolane</td>
<td>Pendiethalin</td>
<td>Simazine</td>
<td></td>
</tr>
<tr>
<td>Aldicarb-sulfone</td>
<td>Cyamaphos</td>
<td>Fenarimol</td>
<td>Isopropurotan</td>
<td>Penfluifen</td>
<td>Spinosyn A</td>
<td></td>
</tr>
<tr>
<td>Aldicarb-sulfoxide</td>
<td>Cyamaphos</td>
<td>Fenazaquin</td>
<td>Isoxafutolate</td>
<td>Penthiopyrad</td>
<td>Spinosyn D</td>
<td></td>
</tr>
<tr>
<td>Ametocrotacin</td>
<td>Cyflufenamid</td>
<td>Fenbendazole</td>
<td>Kresoxim-methyl</td>
<td>Permethrin, trans-</td>
<td>Spinosyn J</td>
<td></td>
</tr>
<tr>
<td>Anilofos</td>
<td>Cyhalofop-butyl</td>
<td>Fenbuconazole</td>
<td>Lenacil</td>
<td>Phenthoate</td>
<td>Spinosyn L</td>
<td></td>
</tr>
<tr>
<td>Atrazine</td>
<td>Cyoxamnial</td>
<td>Fenhexamid</td>
<td>Linuron</td>
<td>Phosalone</td>
<td>Spirodicolen</td>
<td></td>
</tr>
<tr>
<td>Avermectin B1a</td>
<td>Cyproconazole</td>
<td>Fenobucarb</td>
<td>Malaoxon</td>
<td>Phosmet</td>
<td>Spiromesifen</td>
<td></td>
</tr>
<tr>
<td>Azinphos-ethyl</td>
<td>Cypridinil</td>
<td>Fenoxyxcarb</td>
<td>Malathion</td>
<td>Phoxim</td>
<td>Spirotetramat</td>
<td></td>
</tr>
<tr>
<td>Azinphos-methyl</td>
<td>Cyromazine</td>
<td>Fenpropidin</td>
<td>Manidropamid</td>
<td>Pirimicarb</td>
<td>Siproximate</td>
<td></td>
</tr>
<tr>
<td>Azoxyostrobin</td>
<td>DEET</td>
<td>Fenpropimorph</td>
<td>Mepanipyrim</td>
<td>Pirimicarb, desmethyl</td>
<td>Sulfoxaflor</td>
<td></td>
</tr>
<tr>
<td>BAC10</td>
<td>Demeton-S-methyl</td>
<td>Fenpyrazamine</td>
<td>Metamitron</td>
<td>Pirimiphos-methyl</td>
<td>Tebuconazole</td>
<td></td>
</tr>
<tr>
<td>BAC8</td>
<td>Demeton-S-Methyl-Sulfone</td>
<td>Fenpyroximate</td>
<td>Metconazole</td>
<td>Propargite</td>
<td>Thiabendazole</td>
<td></td>
</tr>
<tr>
<td>Benalaxyl</td>
<td>Demeton-S-methylsulfone</td>
<td>Fenthion</td>
<td>Methamidophos</td>
<td>Propazine</td>
<td>Thiacyclorid</td>
<td></td>
</tr>
<tr>
<td>Bendiocarb</td>
<td>Diazonin</td>
<td>Fenthion-sulfone</td>
<td>Methidathion</td>
<td>Propiconazole</td>
<td>Thiamethoxam</td>
<td></td>
</tr>
<tr>
<td>Bifenazate</td>
<td>Dichlorvos</td>
<td>Fenthion-sulfide</td>
<td>Metiocarb</td>
<td>Propoxur</td>
<td>Thibencarb</td>
<td></td>
</tr>
<tr>
<td>Bifenthrin</td>
<td>Dicrotophos</td>
<td>Fenuron</td>
<td>Methiocarb-sulfone</td>
<td>Propyzamide</td>
<td>Thiocarb</td>
<td></td>
</tr>
<tr>
<td>Bietranol</td>
<td>Diethofencarb</td>
<td>Fipronil_POS</td>
<td>Methiocarb-sulfide</td>
<td>Proquinoxazid</td>
<td>Thiodicarb</td>
<td></td>
</tr>
<tr>
<td>Boscalid</td>
<td>Difenoconazole</td>
<td>Flazasulfuron</td>
<td>Methoxyfenoide</td>
<td>Proquinazid</td>
<td>Thiophanate-methyl</td>
<td></td>
</tr>
<tr>
<td>Bromacil</td>
<td>Difenoxuron</td>
<td>Flonicamid</td>
<td>Methoxyfenoide</td>
<td>Prosolufcar</td>
<td>Tolfenpyrad</td>
<td></td>
</tr>
<tr>
<td>Bromuconazole</td>
<td>Diflubenzuron</td>
<td>Fluyarpym</td>
<td>Metromuron</td>
<td>Promecarb</td>
<td>Triadimefon</td>
<td></td>
</tr>
<tr>
<td>BTS_4459s</td>
<td>Dimethoate</td>
<td>Fluacrypyrin</td>
<td>Metothoate</td>
<td>Prometyn</td>
<td>Triadimenol</td>
<td></td>
</tr>
<tr>
<td>BTS_44596</td>
<td>Dimethomorph</td>
<td>Fluazifop</td>
<td>Metolachlor</td>
<td>Propamocarb</td>
<td>Tryptamine</td>
<td></td>
</tr>
<tr>
<td>BTS-40348</td>
<td>Dimethylvinphos, Z-</td>
<td>Flufenacet</td>
<td>Metolcarb</td>
<td>Terbutyn</td>
<td>Tryptamine</td>
<td></td>
</tr>
<tr>
<td>Bupirimate</td>
<td>Diniconazole</td>
<td>Flufenoxuron</td>
<td>Methiocarb-sulfide</td>
<td>Propargite</td>
<td>Turbutylazine-desyethyl</td>
<td></td>
</tr>
<tr>
<td>Buprofezin</td>
<td>Diuron</td>
<td>Flumeturon</td>
<td>Methiocarb-sulfide</td>
<td>Thiabendazole</td>
<td>Terbuthylazine</td>
<td></td>
</tr>
<tr>
<td>Butoxycarboxim</td>
<td>Dodine</td>
<td>Flupicolidine</td>
<td>Monocrotophos</td>
<td>Totienpyrad</td>
<td>Terbuthylazine-desyethyl</td>
<td></td>
</tr>
<tr>
<td>Carbaryl</td>
<td>Edifenphos</td>
<td>Fluopyram</td>
<td>Monolinuron</td>
<td>Pymetrozine</td>
<td>Triazoline</td>
<td></td>
</tr>
<tr>
<td>Carbendazim</td>
<td>Emamectin B1a</td>
<td>Flusilazole</td>
<td>Monuron</td>
<td>Pyraclostrobin</td>
<td>Triallate</td>
<td></td>
</tr>
<tr>
<td>Carbofuran</td>
<td>Epoxiconazole</td>
<td>Fluxapyroxad</td>
<td>Myclobutanil</td>
<td>Pyrethrin</td>
<td>Triazolophos</td>
<td></td>
</tr>
<tr>
<td>Carbofuran, 3OH-</td>
<td>Ethifencarb</td>
<td>Formetanae</td>
<td>Neburon</td>
<td>Pyrethrinii</td>
<td>Trichloroform</td>
<td></td>
</tr>
<tr>
<td>Chlorantraniliprole</td>
<td>Ethion</td>
<td>Fosthiazate</td>
<td>Nitenpyram</td>
<td>Pyridaben</td>
<td>Triclocarb</td>
<td></td>
</tr>
<tr>
<td>Chlorbromuron</td>
<td>Ethiprole</td>
<td>Haloxynidol</td>
<td>Novaluron</td>
<td>Pyridalyl</td>
<td>Tricyclazole</td>
<td></td>
</tr>
<tr>
<td>Chlorfenvinphos, B-</td>
<td>Ethirimol</td>
<td>Hexaconazole</td>
<td>Oxadiargyl</td>
<td>Pyridaphenthion</td>
<td>Trifloxystrobin</td>
<td></td>
</tr>
<tr>
<td>Chlorfluazuron</td>
<td>Ethoprophos</td>
<td>Hexalumrun</td>
<td>Oxadixyl</td>
<td>Pyridate</td>
<td>Triflumizole</td>
<td></td>
</tr>
<tr>
<td>Chloridazon</td>
<td>Etofenprox</td>
<td>Hexythiazox</td>
<td>Oxamyl</td>
<td>Pyrimethanil</td>
<td>Triflumuron</td>
<td></td>
</tr>
<tr>
<td>Chlorotoluron</td>
<td>Etoxazole</td>
<td>Imazalid</td>
<td>Oxsulfuron</td>
<td>Pyriofenone</td>
<td>Triticonazole</td>
<td></td>
</tr>
<tr>
<td>Chloroxuron</td>
<td>Famoxadone</td>
<td>Imidacloprid</td>
<td>Oxendaolzo</td>
<td>Pyriproxyfen</td>
<td>Tritisulfuron</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Indoxacarb</td>
<td>Paclobutrazol</td>
<td>Quinalphos</td>
<td>XMC</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Quinoclamine</td>
<td>Zoxamide</td>
<td></td>
</tr>
</tbody>
</table>
Increasing the scope

**Targeted Pesticides database + Libraries**

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Acquisition modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>139 (84% of 166)</td>
<td>Q Exactive Focus hybrid quadrupole-Orbitrap MS</td>
</tr>
<tr>
<td>158 (95% of 166)</td>
<td>Orbitrap Exploris 240 MS</td>
</tr>
<tr>
<td>231 (94% of 246)</td>
<td>Orbitrap Exploris 240 MS</td>
</tr>
<tr>
<td>1500</td>
<td>Orbitrap Exploris 240 MS</td>
</tr>
</tbody>
</table>

Acquisition modes:
- QE Focus (FS/AIF), Orbitrap Exploris 240 MS (FS/AIF/tMS2), Orbitrap Exploris 240 MS (FS/AIF/tMS2/ Data Dependent)
<table>
<thead>
<tr>
<th>Database: 1500 compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>European Reference Laboratory - FV</td>
</tr>
</tbody>
</table>
Full scan MS
EIC 399.1681 ± 5ppm
Mass error 0.05 ppm

Valifenalate in avocado
(2 peaks)

Fragment ion present in the database

Spectral library
False Positives
Spinetoram J
LC-MS/MS

Standard 0.1 mg/kg
(aubergine blank matrix)

SRM 1: 748.3>142.1
SRM 2: 748.3>98.1
Ion ratio: 0.2125

FV23 Sample

SRM 1: 748.3>142.1
SRM 2: 748.3>98.1
Ion ratio: 0.1922
False Positives

European Reference Laboratory - FV

Standard 0.1 mg/kg (aubergine blank matrix)

Spinetoram J
LC-MS/MS

FV23 Sample

- **Spinetoram**
  - SRM 1: 748.3 > 142.1
  - SRM 2: 748.3 > 98.1
  - Ion ratio: 0.2125

  - SRM 1: 746.2 > 142.0
  - SRM 2: 746.2 > 98.2
  - Ion ratio: 0.1915

- **Spinosad**
  - SRM 1: 748.3 > 142.1
  - SRM 2: 748.3 > 98.1
  - Ion ratio: 0.1922

  - SRM 1: 746.2 > 142.0
  - SRM 2: 746.2 > 98.2
  - Ion ratio: 0.1813
False Positives

FV23 Sample

Spinetoram J
LC-MS HRMS

Spinetoram J
C_{42}H_{69}NO_{10}
748.49942 ± 5ppm

Spinosyn D
C_{42}H_{67}NO_{10}
746.48377 ± 5ppm

^{13}C C_{41}H_{67}NO_{10}
747.48716 ± 5ppm

^{13}C_2 C_{40}H_{67}NO_{10}
748.49031 ± 5ppm

Common fragment ions of spinosyn A, spinosyn D, spinetoram J, and spinetoram L

m/z 98.09643  m/z 142.12264
False Positives

FV23 Sample

Spinetoram J
LC-MS HRMS

Spinetoram J  m/z 748.49942 ± 5ppm

Spinetoram J  m/z 748.49942 ± 15ppm

Spinosyn D  m/z 746.48377 ± 5ppm

13C2 Spinosyn D  m/z 748.49031 ± 5ppm

Spinetoram J m/z 748.49942

13C2 Spinosyn D m/z 748.49031

Difference  -12.2 ppm
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>MATRIX</th>
<th>TARGET/QUANTITATIVE</th>
<th>SCREENING</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>Kiwi</td>
<td>Phosmet</td>
<td></td>
</tr>
<tr>
<td>002</td>
<td>Kiwi</td>
<td>Phosmet</td>
<td></td>
</tr>
<tr>
<td>003</td>
<td>Kiwi</td>
<td>Phosmet</td>
<td></td>
</tr>
<tr>
<td>004</td>
<td>Kiwi</td>
<td>Phosmet</td>
<td></td>
</tr>
<tr>
<td>005</td>
<td>Kiwi</td>
<td>Phosmet</td>
<td></td>
</tr>
<tr>
<td>006</td>
<td>Kiwi</td>
<td>Phosmet</td>
<td></td>
</tr>
<tr>
<td>007</td>
<td>Kiwi</td>
<td>Phosmet</td>
<td></td>
</tr>
<tr>
<td>008</td>
<td>Kiwi</td>
<td>Phosmet</td>
<td></td>
</tr>
<tr>
<td>009</td>
<td>Kiwi</td>
<td>Phosmet</td>
<td></td>
</tr>
<tr>
<td>010</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>011</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>012</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>013</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>014</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>015</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>016</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>017</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>018</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>019</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>020</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>021</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>022</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>023</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>024</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>025</td>
<td>Onion</td>
<td>Boscalid</td>
<td></td>
</tr>
<tr>
<td>026</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>027</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>028</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>029</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>030</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>031</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>032</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>033</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>034</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>035</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>036</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>037</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>038</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>039</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>040</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>041</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>042</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>043</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>044</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>045</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>046</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>047</td>
<td>Orange</td>
<td>Acetamiprid</td>
<td></td>
</tr>
<tr>
<td>048</td>
<td>Pineapple</td>
<td>Famoxadone; Fluxapyroxad; Indoxacarb; Mandipropamid; Metalaxyl; Methoxyfenozide; Metrafenone; Penconazole; Proquinazid; Pyrimethanil; Sulfoxaflor; Tebuconazole; Zoxamide</td>
<td></td>
</tr>
<tr>
<td>049</td>
<td>Raisins</td>
<td>Famoxadone; Fluxapyroxad; Indoxacarb; Mandipropamid; Metalaxyl; Methoxyfenozide; Metrafenone; Penconazole; Proquinazid; Pyrimethanil; Sulfoxaflor; Tebuconazole; Zoxamide</td>
<td></td>
</tr>
<tr>
<td>050</td>
<td>Strawberries</td>
<td>Boscalid; Fluopyram</td>
<td></td>
</tr>
</tbody>
</table>
Screening (non regulated compounds)

- Full scan MS TIC
- AIF MS2 TIC
- MS spectrum
- MS2 spectrum
Screening using a Target List & Database
Precursor ion (mass tolerance 5 ppm) - 580 hits

Precursor ion (mass tolerance 5 ppm) + 1 fragment ion (5 ppm) + isotopic pattern
6 hits

Precursor ion (mass tolerance 5 ppm) + 1 fragment ion (5 ppm) + isotopic pattern
6 hits

Precursor ion (mass tolerance 5 ppm) + 1 fragment ion (5 ppm) + isotopic pattern
6 hits
mzCloud™

Carbamazepine

Norepinephrine

MS2 spectrum
Screening

Screening with TraceFinder (local data bases and libraries)

237.1022 mass error 0.74 ppm

Carbamazepine

Fragment #2: 194.0961 mass error 1.62 ppm
Screening

Screening with Compound Discoverer (mzCloud™, Chemspider™, etc.)

Carbamazepine
Involuntary human exposure to carbamazepine: A cross-sectional study of correlates across the lifespan and dietary spectrum

Michael Schapira a, Orly Manor a, Naama Golan b, Dorit Kalo c, Yered Mordehay b, Noam Kirshenbaum b, Rebecca Goldsmith a, d, Benny Chefetz b,1, e, Ora Paltiel a,1, e
NEW TECHNOLOGIES

Automation

THEORETICAL IMPLEMENTATION

PRACTICAL IMPLEMENTATION
European Reference Laboratory - FV

Fluazifop-P

Quizalofop

TFNG

TFNA

MgSO₄
CarbonX
C18
PSA

Diclofop

Haloxyfop

Tolylfluanid

Rimsulfuron
New Technologies

Knowledge And skills
No of visits per year

No of visits in **EURLs webpage**: 242,516 pageviews

No of visits in **EURL-FV specific webpages**: 43,285 visits

- 13,886 Main EURL-FV webpage
- 6,434 EURL-FV23
- 5,382 EU Procedures
- 3,398 List of methods FV
- 2,882 Workshops
- 2,782 Last publications
- 1,825 EURL-SM13
- ...
e-Platform

Dear colleagues,

EURL-FV provides a series of formative tutorials related to the difficulties, new MRM approaches, etc.... that can be found in the routine work in the laboratory:

- EURL-FV (2021-T1) Solutions for addressing specific LC-MS problematic pesticide residues in Multi-residue Methods.
- EURL-FV (2021-T2) Solutions for addressing specific LC-MS problematic pesticide residues in Multi-residue Methods. Part II.

If you wish to obtain a certificate of the trainings received in these tutorials, you should register and also fill in the corresponding questionnaire of the content of the tutorials (if you answers are not correct you can fill in the assessment again).
Thank You for Your Attention

"Co-funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Health and Digital Executive Agency (HaDEA). Neither the European Union nor the granting authority can be held responsible for them."