Screening & Quantitation of 250 Pesticides in Fruit/Vegetable Juice using the eXtreme|FV® by LC/MS/MS

Abstract
A study was conducted using the Bruker EVOQ for the analysis of 250 pesticides in apple, orange, cranberry, white grape and vegetable juices using only one method in store-bought juice and simple sample preparation using the Thomson eXtreme (FV) in a dilute-and-shoot approach without sample enrichment. LC-MS/MS operated in Multiple Reaction Monitoring (MRM) mode with dual scan Electrospray ionization (ESI) is widely used for polar, semi-volatile, and thermally labile pesticides in food testing. The Bruker EVOQ Elite LC-Triple Quadrupole System provides fast positive/negative switching, allows for simultaneous determination of hundreds of positive and negative co-eluting compounds numbering in the hundreds. Simple sample preparation is explored using Thomson eXtreme (FV) for sample cleanup instead of lengthy alternatives like SPE or centrifugation followed by liquid-liquid extraction.

Results

Table 1: Store bought fruit juice test results.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Apple Juice</th>
<th>Orange Juice</th>
<th>Cranberry Juice</th>
<th>White Grape Juice</th>
<th>Vegetable Juice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pirimiphos</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Bucral</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Carbaryl</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<tr>
<td>Benthiocarb</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Thabendazole</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

Fig 1: Chromatogram of a 0.25ppb standard containing the compounds listed in Table 1. This is equivalent to 0.1ppb in juice.

Equipment
- EVOQ Elite Triple Quadrupole Mass Spectrometer
- Bruker UNILC
- CTC Autosampler
- Source: HESI
- Spray Voltage Positive: 4000V
- Spray Voltage Negative: 4000V
- Column: YMC-Aqua C18 2.5μm 4.6 x 100mm
- Column Temperature: 40°C
- Injection Volume: 30μL
- Flow Rate: 0.2μm PDA
- Mobile Phase: 0.1% Formic Acid in Water: Acetonitrile (90:10) 0.1% Formic Acid

Sample Preparation
1. Pipette 50μL of store-bought apple juice and 450μL of solvent (10% Methanol:90% Water) directly into the outer shell of Thomson eXtreme® (FV). 0.2μm PDA.
2. Partially depress the extreme® (FV) plungers and vortex.
3. Depress the completely and load onto the autosampler.

Conclusion
- The calibration on triplicate injections showed excellent linearity and response factor RSD over 3 orders, range using the Thomson eXtreme® (FV) for sample preparation.
- Good linearity, sensitivity and response factor, RSD for positive and negative co-eluting pesticides.
- Pesticides were detected in store-bought apple, orange, cranberry and vegetable juices.

Comparison of eXtreme|FV® vs SPE for Improved Pesticide Recovery in Orange Juice by GC/MS

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Abstract
Pesticide residues are toxic when found in sufficient quantities in food. This is of particular importance for orange juice because it is consumed in large quantities. In order to reduce the risk to consumers, sensitive, rapid, and cost-effective analytical methods are required. The pesticides in orange juice testing shown below compares recoveries for samples prepared using SPE versus Thomson eXtreme (FV).

Equipment
- Agilent Technologies GC/MS, 7000 Triple Quad System
- Agilent 7890A GC System
- Agilent 7695 Autosampler

Sample Preparation
1. Spite 10 mL of commercially available High Pulp Orange Juice with 1 mL of 1 ppm pesticide standard mix containing 87 pesticides in a 40 mL vial.
2. Add one pack (approximately 0.5 g of Restek Extraction Salts (Restek catalog # 7890A) to 400μL of the reagent to the SPE cartridge.
3. Extract the orange juice with 10 mL of acetonitrile.
4. Concentrate to dryness using a Turbovap II concentrator.
5. Dissolve the residue in approximately 10 mL of acetonitrile.
6. Vortex and sonicate the re-suspended residue with frequent swirling.
7. Split the re-suspended residue into two 5 mL portions.
8. Dilute each 5 mL portion with acetonitrile to 10 mL using a volumetric flask.
9. Label one flask ‘for SPE’ and the other ‘for Thomson extreme (FV)’.

Filter Vial Cleanup Prior to Analysis - Thomson eXtreme® (FV)
1. Add 40μL of the re-suspended residue from the flask labeled ‘for Thomson extreme (FV)’ to the shell of one Thomson extreme® (FV) 0.45μm,
2. Insert plungers completely.

SPE Cleanup Prior to Analysis - 6 mL Combo SPE Cartridge
1. Wash one 6 mL Combo SPE cartridge (packed with 200 mg Carboprep 200 and 400mg PSA) with acetonitrile.
2. Add the 10μL portion of the re-suspended residue from the flask labeled ‘for SPE’ to the SPE cartridge.
3. Elute the sample from the cartridge with 50mL of acetonitrile.
4. Concentrate the eluted sample to 10mL using a Turbovap II concentrator.
5. Filter sample with a syringe filter filter, PTFE 0.45µm and elute into autosampler vial

Conclusion
- The Thomson extreme® 0.45µm, PTFE Filter Vials yielded 26% higher recoveries on average when tested with 87 different common pesticides.
- In the case of Hexachlorobenzene, no pesticide was detected in the sample prepared by SPE and 0.019 ppm was detected in the sample prepared with the extreme® (FV).
- The results show Thomson extreme® (FV) offer a viable alternative with higher recovery and less preparation time compared to SPE for the preparation of juice, and specifically orange juice samples prior to pesticide analysis.
- Conforms to USP 561