Extraction of pesticides from cereals: combining maximum extraction efficiency with minimum degradation

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NRL pesticides CF, AO

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<table>
<thead>
<tr>
<th>EUPT-C1 2007</th>
<th>pesticide</th>
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<th>assigned</th>
<th>recov</th>
<th>reported</th>
<th>method</th>
<th>rec%</th>
<th>correct?</th>
<th>µg/kg</th>
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<td>LC</td>
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<tr>
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<td>Spiroxamine</td>
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<tr>
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<td>659</td>
<td>EtAc</td>
<td>LC</td>
<td>77</td>
<td>432</td>
<td>-0.1</td>
</tr>
</tbody>
</table>
Routine method-1 (feedstuff)

1. Ethyl acetate
   • Sample: 2.5 g
   • Fortification: ISTD (REC-std) [wait 30 min]
   • Wetting: 7.5 ml water, shake, soak until wetted
   • Extraction: 20 ml ethyl acetate, shake 1 hr
   • Phase separation: 10 g Na₂SO₄, vortex, centrifuge
   • Clean up: concentrate: 16 ml -> 1 ml (TurboVap)
     GPC: EnviroGel, 450 x 19 mm ID; 5 ml/min
     collect fraction

Gas chromatography
30 ml -> 0.5 ml
Clean up: PSA 100 mg
  vortex, centrifuge

10 µl GCxGC-TOF-MS (1 g/ml)

Liquid chromatography
15 ml -> just dry
Reconstitute: 0.1 ml acetone, vortex
  0.4 ml methanol, vortex
  0.5 H₂O/1% HAc, vortex

5 µl LC-MS/MS (0.25 g/ml)
Routine method-2 (feedstuff)

1. Acetonitrile (Quechers)
   - Sample: 2.5 g
   - Fortification: ISTD (REC-std) [wait 30 min]
   - Wetting: 7.5 ml water, shake, soak until wetted
   - Extraction: 10 ml acetonitrile/1% HAc, mix by hand
   - Phase separation: 4 g MgSO₄, 1 g NaAc, vortex (3 min), centrifuge

Gas chromatography
- 0.5 ml
- Lacks robustness for feedstuff, but might work with additional clean up*
- 10 µl GCxGC-TOF-MS (0.25 g/ml)

Liquid chromatography
- 0.5 ml filter into autosampler vial
- 5 µl LC-MS/MS (0.25 g/ml)

*Stanisław Walorczyk, J. Chromatogr. 2008 (in press)
Follow up bad Z-score malathion

Possible causes:

• Trivial error (reporting, copy/paste)
• Measurement (interference, integration)
• Calculation (standard solution, linearity, matrix effects, response drift)
• Sample pretreatment (recovery)
Trivial error

- copy/paste: no
- reporting error: no
Measurement (GC-MS)

Interferences frequently observed for malathion in feed (m/z 173) using GC-MS. …

…but less so for wheat and when using GCxGC-MS or MS/MS (LC or GC)

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Calculation

- Standard solution: checked against standard from other laboratory (4-9% diff.)
- Linearity: assigned value within linear range
- Matrix-effect: calibrated using matrix-matched std (CRL control sample)
- Drift: drift: < 10% for subsequent injections of cal. std.
- Calculation error: no
Malathion recovery data

- initial validation (compound feed):
  Average REC 62%; RSD 22% (n=5, 0.1 mg/kg)

- on-going AQC 2008: spikes in different cereals/feed commodities (0.05 mg/kg)
  Results for wheat (n=9):
  Recoveries 51-135%; average 84%
  RSD 30%

=> Analysis lacks robustness but not bad enough to explain bad Z-score:

*Good lab performance with -2<Z<+2 => REC 50-150%*
• Presentation CRL-CF/Mette Poulsen EPRW2008:
  ⇒ water addition prior to extraction results in higher yields
    known also from Fapas PTs, EUPT-C1 (again confirmed)
  ⇒ time between water addition and extraction:
    0 min vs 30 min: no further increase in extraction yield
  ⇒ but: malathion strongly reduced in case of 30 min wetting time

=> Need for more detailed investigation / follow up
1. Literature (search: malathion degradation)

• Hits:
  degradation of malathion and phenthoate by glutathione reductase in wheat germ
  Yoshii et al., J. Health Science (2006):
  Malathion residue in wheat kernels is degraded by thion OPP-specific carboxylesterase
  Yoshii et al., J. Health Science (2007):
  Kinetic analysis for hydrolysis of malathion by carboxylesterase in wheat kernels

• findings by Yoshii:
  - carboxylesterase converts malathion into malathion di-carboxylic acid (not malaoxon)
  - only OPP with COOR and P=S are converted (malathion, phenthoate, methacrifos)
  - malathion also converted in oats, barley, rye; but not in corn and rice

=> recommendation: methods should be revised and no water should be added

• contradiction: water needed for efficient extraction but should be avoided to prevent enzymatic conversion
2. Explorative investigations of effect of water

Questions:

• How long do we need to wet?
• How long do we need to extract?
• How much water is needed?

• How to wet the sample and prevent degradation at the same time?

Enzyme activity: pH, organic solvent, water content, temp, time

Hydrolysis: pH, temp, time

to maintain the beneficial effect on extraction efficiency
3. Experiment 1

Set up:

- incurred residues (=> wheat EUPT-C1, EUPT-2)
- “classical” Quechers (no PSA) + LC-MS/MS
- matrix-matched calibration
- test set:

<table>
<thead>
<tr>
<th>Sample</th>
<th>2.5 g wheat (CRL PT samples 2007-2008)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetting</td>
<td>7.5 ml water</td>
</tr>
<tr>
<td>Static wetting time</td>
<td>10 s 3 min 30 min 120 min</td>
</tr>
<tr>
<td>Solvent</td>
<td>10 ml ACN/1% HAc</td>
</tr>
<tr>
<td>Addition of salts</td>
<td>4 g MgSO4/1 g NaAc</td>
</tr>
<tr>
<td>Vortex/shake</td>
<td>3 min</td>
</tr>
<tr>
<td>Addition of salts</td>
<td></td>
</tr>
<tr>
<td>Vortex/shake</td>
<td></td>
</tr>
</tbody>
</table>

- remark: only single analysis, different days
3. Experiment 1: Results

Malathion

<table>
<thead>
<tr>
<th>Wetting time:</th>
<th>10 s</th>
<th>3 min</th>
<th>30 min</th>
<th>120 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition</td>
<td>Water</td>
<td>Water</td>
<td>ACN-1% HAc</td>
<td></td>
</tr>
</tbody>
</table>

Z = -2
- water + > 5-10 min wetting time: unacceptable results
- acidification inhibits degradation
- water/ACN/acid highest results (pos bias)

Z = +2

⇒ water/ACN-1% HAc
3. Experiment 1: Results

Azoxystrobin

- PT-C1 incurred
- PT-C2 spike
- lab QC spike

Wetting time: 10 s      3 min     30 min    120 min
Addition:                        Water                              Water/1% formic acid                  Water/ACN-1% HAc

⇒ Adequate performance in all cases
⇒ water/longer wetting time: neg bias; water/ACN/acid: pos bias

Z = -2
Z = +2
3. Experiment 1: Results

Carbendazim

<table>
<thead>
<tr>
<th>Wetting time:</th>
<th>10 s</th>
<th>3 min</th>
<th>30 min</th>
<th>120 min</th>
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<tbody>
<tr>
<td>Addition:</td>
<td>Water</td>
<td>Water/1% formic acid</td>
<td>Water/ACN-1% HAc</td>
<td></td>
</tr>
</tbody>
</table>

⇒ Adequate performance in all cases
⇒ water/longer wetting time: lowest values;
⇒ water/ACN/acid longer wetting time: highest values
3. Experiment 1: Results

Chlorpyriphos-methyl

- Adequate performance in all cases, except water/120 min
- (acidified) water: neg bias
- water/ACN/acid: highest values
3. Experiment 1: Results

Prochloraz

- Wetting time: 10 s, 3 min, 30 min, 120 min
- Addition: Water, Water/1% formic acid, Water/ACN-1% HAc

Z = -2

Z = +2

⇒ Adequate performance in all cases, except water ≥ 30 min
3. Experiment 1: tentative conclusions

- Differences are observed when comparing different procedures, but only in few cases this results in unacceptable Z-scores

- Most of the residues in wheat flour stable for > year (freezer)

- Prolonged wetting with water can result in lower values/neg bias

- Acidification of water added prior to extraction inhibits degradation (malathion)

- Water addition prior to extraction vs addition of mixture water/ACN: there is no need to add water first and then acetonitrile; simultaneous wetting/extraction gives highest values/pos bias

⇒ Optimum initial extraction very similar to generic extraction procedure presented at EPRW2008 (Mol et all)
Generic extraction method (pest/nat. toxins/vet. drugs)

1) take 2.5 g
2) add 20 ml extr. solvent*

* water/ACN/FA (25/75/1)

3) shake 1 h (arbitrarily chosen)

4) Centrifuge

5) Inject into UPLC-MS/MS

10 min run time
3. Experiment 2

Goals:

• test extraction efficiency of generic method using samples with incurred residues
• establish required wetting/extraction time

Set up:

• wheat EUPT-C1, EUPT-2
• 2.5 g sample; 10 ml extraction solvent (water/ACN/FA 25/75/1)
• shaking 1 min (hand/vortex); 30 min; 120 min (machine) [triplicates]
• no salts/partitioning; centrifugation and injection into LC-MS/MS
• matrix-matched calibration
3. Experiment 2: Results

**Azoxystrobin**

<table>
<thead>
<tr>
<th>Extraction Time (min)</th>
<th>PT-C1 (incurred)</th>
<th>PT-C2 (spiked)</th>
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<tbody>
<tr>
<td>1</td>
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<td>110</td>
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<td>30</td>
<td>120</td>
<td>130</td>
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<tr>
<td>120</td>
<td>150</td>
<td>160</td>
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</table>

% of assigned value

Z = +2

Z = -2
3. Experiment 2: Results

Carbendazim

PT-C1 (inc+spike)  PT-C2 (incurred)

% of assigned value

<table>
<thead>
<tr>
<th>Extraction Time (min)</th>
<th>1</th>
<th>30</th>
<th>120</th>
<th>1</th>
<th>30</th>
<th>120</th>
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<td>PT-C1 (inc+spike)</td>
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<tr>
<td>PT-C2 (incurred)</td>
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</table>

Z = +2

Z = -2
3. Experiment 2: Results

![Graph showing % of assigned value against extraction time (min) for Malathion and PT-C2 (spiked)]

- **Malathion**
- **PT-C2 (spiked)**

- **Z = +2**
- **Z = -2**
3. Experiment 2: Results

![Graph showing the percent of assigned value vs. extraction time (min) for spiroxamine and trifloxystrobin. The graph includes two sets of data labeled PT-C2 (incurred). The Z values are indicated as Z = +2 and Z = -2.]
3. Experiment 2: Results

MCPA (free) and Mecoprop (free)

PT-C1 (incurred) PT-C1 (spiked)

Z = +2
Z = -2

% of assigned value vs. extraction time (min)
3. Experiment 2: conclusions

- 1 min extraction time is not sufficient in all cases (significant?)
- beyond that: extraction time has little effect / is not a critical parameter
  - no increase (improvement in extraction efficiency)
  - no decrease (degradation of pesticides)
- Extraction with water/ACN/FA (25/75/1) is efficient and robust
- Results for malathion now significant higher than assigned value (Z>2)!
3. Experiment 3

How much water is needed for efficient extraction?

- acetonitrile based method
  - % water, ratio of water and solvent to sample

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<tr>
<th>sample</th>
<th>extraction solvent</th>
<th>ratio</th>
<th>ratio</th>
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<td></td>
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<td>water</td>
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<td>2.5 g EUPT-C</td>
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<td>100</td>
<td>0</td>
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<tr>
<td>2.5 g EUPT-C</td>
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<tr>
<td>2.5 g EUPT-C</td>
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<td>5</td>
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<tr>
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<td>2.5 g EUPT-C</td>
<td>10*</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>2.5 g EUPT-C</td>
<td>20*</td>
<td>75</td>
<td>25</td>
</tr>
</tbody>
</table>

* containing 1% FA

Extraction time 30 min

Matrix-matched calibr.

Duplicate analysis
3. Experiment 3: Results

Azoxystrobin

- PT-C1 incurred
- PT-C2 spike

% of assigned value vs. % water in acetonitrile

$Z = +2$

$Z = -2$
3. Experiment 3: Results

![Graph showing Carbendazim stability with different concentrations of water in acetonitrile.](image)

- **Z = -2**
- **Z = +2**

**Carbendazim**

- PT-C1 inc+spike
- PT-C2 incurred

% of assigned value vs. % water in acetonitrile (20 ml)
3. Experiment 3: Results

The bar chart illustrates the results of the experiment with different water percentages in acetonitrile. The x-axis represents the percentage of water in acetonitrile, ranging from 0 to 25% in increments of 5% and two additional points at 25% with and without FA (20 ml). The y-axis shows the % of assigned value, ranging from 0 to 200.

The compounds and their respective concentration increments are as follows:
- Malathion (inc)
- Chlorpyrifos-me (inc)
- Iprodion (inc)
- Difenoconazole (inc/spi)
- Prochloraz (inc/spi)

Three $Z$ values are highlighted on the chart:
- $Z = +2$ is indicated by a red arrow on the right side of the chart.
- $Z = -2$ is indicated by a red arrow on the left side of the chart.
3. Experiment 3: conclusions

- at least 15% water in acetonitrile (10 ml) = [1.5 ml per 2.5 g sample] is required for efficient extraction of several pesticides from wheat flour
- more water does not further increase extraction efficiency
- for some pesticides (iprodion, difenoconazole) values significantly higher than the assigned value are obtained
## Comparison original results with results new method

<table>
<thead>
<tr>
<th>pesticide</th>
<th>residue</th>
<th>assigned</th>
<th>reported</th>
<th>method</th>
<th>Z-score</th>
<th>method</th>
<th>set-1 av (n=3)</th>
<th>calc. Z-score</th>
<th>set-2 av (n=2)</th>
<th>calc. Z-score</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Azoxystrobin</strong></td>
<td>inc</td>
<td>240</td>
<td>234</td>
<td>ACN</td>
<td>LC</td>
<td>-0.1</td>
<td>generic</td>
<td>LC</td>
<td>316</td>
<td>1.3</td>
</tr>
<tr>
<td><strong>Carbendazim</strong></td>
<td>inc/spi</td>
<td>126</td>
<td>113</td>
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<td><strong>Deltamethrin</strong></td>
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<tr>
<td><strong>Propiconazole</strong></td>
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<td>ACN</td>
<td>LC</td>
<td>-0.4</td>
<td>generic</td>
<td>LC</td>
<td>484</td>
<td>1.5</td>
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<tr>
<td><strong>Endosulfan</strong></td>
<td>inc</td>
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<td>35</td>
<td>EtAc</td>
<td>GC</td>
<td>n.a.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Azoxystrobin</strong></td>
<td>spi</td>
<td>239</td>
<td>234</td>
<td>EtAc</td>
<td>LC</td>
<td>-0.1</td>
<td>generic</td>
<td>LC</td>
<td>291</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>Bifenthrin</strong></td>
<td>inc</td>
<td>87</td>
<td>94</td>
<td>EtAc</td>
<td>GC</td>
<td>0.3</td>
<td>generic</td>
<td>LC</td>
<td>602</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>Carbendazim</strong></td>
<td>inc</td>
<td>570</td>
<td>709</td>
<td>EtAc</td>
<td>LC</td>
<td>1.0</td>
<td>generic</td>
<td>LC</td>
<td>568</td>
<td>0.0</td>
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<tr>
<td><strong>Chlorpyrifos-methyl</strong></td>
<td>inc</td>
<td>130</td>
<td>141</td>
<td>EtAc</td>
<td>GC</td>
<td>0.3</td>
<td>generic</td>
<td>LC</td>
<td>118</td>
<td>-0.4</td>
</tr>
<tr>
<td><strong>Cypermethrin</strong></td>
<td>inc</td>
<td>98</td>
<td>76</td>
<td>EtAc</td>
<td>GC</td>
<td>-0.9</td>
<td>generic</td>
<td>LC</td>
<td>118</td>
<td>-0.4</td>
</tr>
<tr>
<td><strong>Difenoconazole</strong></td>
<td>inc/spi</td>
<td>169</td>
<td>171</td>
<td>EtAc</td>
<td>LC</td>
<td>0.0</td>
<td>generic</td>
<td>LC</td>
<td>250</td>
<td>1.9</td>
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<tr>
<td><strong>Epoxyconazole</strong></td>
<td>inc</td>
<td>176</td>
<td>187</td>
<td>EtAc</td>
<td>LC</td>
<td>0.3</td>
<td>generic</td>
<td>LC</td>
<td>266</td>
<td>2.3</td>
</tr>
<tr>
<td><strong>Iprodione</strong></td>
<td>inc</td>
<td>289</td>
<td>355</td>
<td>EtAc</td>
<td>LC</td>
<td>0.9</td>
<td>generic</td>
<td>LC</td>
<td>623</td>
<td>4.6</td>
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<tr>
<td><strong>Malathion</strong></td>
<td>inc/spi</td>
<td>162</td>
<td>&lt; 50 (0.034)</td>
<td>EtAc</td>
<td>GC</td>
<td>-4.0</td>
<td>generic</td>
<td>LC</td>
<td>275</td>
<td>2.8</td>
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<tr>
<td><strong>Pirimicarb</strong></td>
<td>inc</td>
<td>38</td>
<td>39</td>
<td>EtAc</td>
<td>LC</td>
<td>0.2</td>
<td>generic</td>
<td>LC</td>
<td>44</td>
<td>0.6</td>
</tr>
<tr>
<td><strong>Prochloraz</strong></td>
<td>inc/spi</td>
<td>239</td>
<td>267</td>
<td>EtAc</td>
<td>LC</td>
<td>0.5</td>
<td>generic</td>
<td>LC</td>
<td>233</td>
<td>-0.1</td>
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<tr>
<td><strong>Spiroxamine</strong></td>
<td>inc</td>
<td>75</td>
<td>54</td>
<td>EtAc</td>
<td>LC</td>
<td>-1.1</td>
<td>generic</td>
<td>LC</td>
<td>118</td>
<td>2.3</td>
</tr>
<tr>
<td><strong>Trifloxystrobin</strong></td>
<td>inc</td>
<td>439</td>
<td>432</td>
<td>EtAc</td>
<td>LC</td>
<td>-0.1</td>
<td>generic</td>
<td>LC</td>
<td>562</td>
<td>1.1</td>
</tr>
</tbody>
</table>

?? Improvement or not ??

---

**EUPT-C1 2007**

**EUPT-C2 2008**

RIKILT INSTITUTE OF FOOD SAFETY WAGENINGEN
4. Conclusions

- The reason for the bad Z-score for malathion has been found (enzym. degr.)
- Differences are observed in extraction efficiency of spiked and incurred residues. Recoveries from spiked AQC samples do not always reflect reality.
- Need for addition of water to low-moisture matrices again confirmed.
- Exposure time of sample to water prior to extraction is critical parameter. SOPs adjusted: EtAc method: minimize wetting time. ACN (Quechers): add mixture of water/ACN.
- With water/ACN (FA) mixtures, extraction time is not a critical parameter.
- With water/ACN (FA) mixtures, ratio water:sample should be at least 3:5.
- For several pesticides, extraction with water/ACN (FA) mixtures increased levels of pesticides were found (clearly above the assigned values: propiconazole, difenoconazole, iprodion, malathion, spiroxamine?, trifloxystrobin?)
- A 1-to-1 comparison of the different methods employed needs to be performed to confirm findings and establish significance of differences in extraction efficiency.
Acknowledgement

CRL-CF people

RIKILT colleagues: Annemieke Vos van Avezathe, William Tilburgs, Theo de Rijk

Darinka Stajnbaher (Public Health Institute, Maribor, Slovenia)
Thank you for your attention
Structures OPs

- Malathion
- Phenthoate
- Methacrifos
- Diazinon
- Pirimiphos-methyl
- Chlorpyrifos-methyl
- Pirimiphos-methyl
- Mevinphos