Hay for livestock feeding – Method validation

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Background:
Hay and grass may account for up to 100% of the feed for dairy and beef cattle. Thus hay may be of high importance for the pesticide residue exposure of livestock. Hay was therefore chosen as test material for EUPT-CF12 carried in January/February 2018. Method performance using QuEChERS according to EN 15662 and dSPE employing three different kits (Table 1) were studied for a selection of analytes (Figure 1). Using 1 gram of sample QuEChERS (EN 15662) performed equally well or better than when modifying the method by using one of the three other dSPE kits. 402 pesticides and metabolites of pesticides were therefore validated on hay using QuEChERS extraction according to EN 15662 and analysis by LC-MSMS and GC-MSMS. The pesticides and metabolites validated are listed in Table 3. The validation was performed in accordance with the requirements outlined in SANTE/11813/20173.

Analytical procedure:

Homogenisation of test material

Chopping and Milling (same size 0.1 mm)

Table 1: Test of dSPE procedure for clean-up of QuEChERS hay extracts

<table>
<thead>
<tr>
<th>dSPE kit</th>
<th>Super™ QuE ChErs (51228-d)</th>
<th>Super™ QuE ChErs (55446-d)</th>
<th>Super™ QuE ChErs (55333-d)</th>
<th>Super™ QuE ChErs Verde (55444-d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>200 mg Supelclean PSA 900 mg MgSO4</td>
<td>15 mg Supelclean ENVI-carb 600 mg MgSO4</td>
<td>45 mg Supelclean PSA 25 mg Supelclean ENVI-carb 900 mg MgSO4</td>
<td>25 mg Supelclean ENVI-carb 50 mg MgSO4</td>
</tr>
<tr>
<td>Suitability according to provider</td>
<td>Samples low in fat, chlorophyll and carotenoids</td>
<td>Samples with moderate levels of chlorophyll and carotenoids</td>
<td>Samples with higher levels of chlorophyll and carotenoids</td>
<td>Providing high recovery of all pesticides, including problematic planar pesticides, in samples containing high levels of chlorophyll</td>
</tr>
</tbody>
</table>

Recoveries following dSPE proc. 1-4

Figure 1: Recoveries of selected pesticides spiked into blank hay samples (0.05 mg/kg) using QuEChERS extraction with dSPE according to proc. 1-4.

Results:

Table 2: Overall results for validation performed on hay using QuEChERS (EN 15662) with sample size reduced to 1 gram. * recoveries for chlorothalonil were 47%.

<table>
<thead>
<tr>
<th>LOQ (mg/kg)</th>
<th>Recoveries</th>
<th>RSDr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025</td>
<td>0.05</td>
<td>0.5</td>
</tr>
<tr>
<td>GC-MSMS</td>
<td>219</td>
<td>39</td>
</tr>
<tr>
<td>LC-MSMS</td>
<td>214</td>
<td>58</td>
</tr>
</tbody>
</table>

Total no. of validated compounds excluding duplicates: 402

Table 3: Pesticides and metabolites validated on hay using QuEChERS method

Analytical setup

GC/ES-MSMS: 5 µl injection on a TG-5MSLMS (30mm x 0.25 mm ID, 0.5 µm film thickness) column, detection in SRM mode with 70 eV ionisation, source temp at 180°C and transfer line at 250°C.

LC/ES-MSMS: 1 µl injection separated on a Agilent UPLC, BEH C18 (1.7 µm, 2 x 150 mm) column, Gradient elution going from 98% water + 0.1% formic acid and 0.02% ammonium hydroxide solution to 98% methanol in 10 min. Ionisation in both positive and negative mode and detection in SRM mode.

Conclusion: QuEChERS (EN 15662) gave satisfactory extraction of analytes from hay (Figure 1, Table 2). In total 402 pesticides and metabolites of pesticides were validated. 296 were GC-MSMS amenable compounds and 297 were LC-MSMS amenable. An LOQ of 0.025 mg/kg were obtained for majority of the pesticides and metabolites (see Table 2).

From inspection of GC-MS full scan chromatogram the hay extract obtained with QuEChERS (EN 15662) was found to be relatively low compared to the amount of co-extract observed for oat (Figure 2).