Expansion of cereal multi residue method with pesticides planned for review under regulation No 396/2005 Article 12

Herrmann, Susan Strange; Hajeb, Parvaneh; Poulsen, Mette Erelius

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Expansion of cereal multi residue method with pesticides planned for review under regulation No 396/2005 Article 12

Herrmann, S.S., Hajeb, P. and Poulsen, M.E.
National Food Institute, Technical University of Denmark, Mørkhøj Bygade 19, DK-2860 Søborg, Denmark. e-mail : sher@food.dtu.dk

Introduction

Article 12 in Regulation No. 396/2005 states that assessment of existing MRLs should be performed by the Authority within a period of 12 months from the date of the inclusion or non-inclusion of an active substance in Annex I to Directive 91/141/EEC. All compounds included in the present validation are included in the so-called MRL progress list, which lists the active compounds coming up for review under article 12 in Regulation No. 396/2005. In connection with the review, information on the availability of methods for enforcement, availability of standards and achievable LOQs are needed. In order to obtain this information the present validation work was performed.

Validation, of the 22 pesticides or metabolites of pesticides, was performed on oat, rye and wheat samples spiked with 0.01, 0.02 and 0.1 mg/kg using QuEChERS extraction according to CEN method 15662 for dry matrices. Though extracts were withdrawn prior to dSPE in order to determine if specific analytes were adsorbed by the PSA.

Extraction method

Shake 5 g (±0.05 g) of flour, 10 g of cold water and a ceramic homogenizer briefly by hand

Add 4 g MgSO4, 1 g NaCl, 1 g Na3 citrate dihydrate and 0.5 g Na2H citrate sesquihydrate. Shake vigorously for 1 min. (2. Extraction with phase separation).

Centrifuge for 5 min. while extract is cold at 4500 rpm.

Take aliquot of supernatant for LC-MS/MS analysis with out clean-up

Clean-up by transferring 6 ml of the supernatant to a tube containing 150 mg PSA and 900 mg MgSO4
Close the tube and shake vigorously for 30 seconds. Centrifuge for 5 min. at 4500 rpm.

Withdraw 4 ml of the supernatant and pH adjust with 40 µl 5% formic acid in acetonitrile
Dilute the extract 1:1 with acetonitrile in the auto sampler vial

Analyse by LC-MS/MS and/or GC-MS/MS

Conclusion

All 22 analytes were LC-MS/MS amenable, and 9 also GC-MS/MS amenable. Using the QuEChERS CEN method 15662 for cereals, including the dSPE with PSA, 17 analytes were validated at 0.01 mg/kg using LC-MS/MS.

If the results for oat were excluded the RSD, and RSDR would for several analytes be reduced, e.g. for difenacoum (LC) and spirotetramat-keto-hydroxy (GC).

21 analytes were amenable to QuEChERS without dSPE clean-up and detection by LC-MS/MS. Only for pyridalyl were the inclusion of the dSPE step required. Excluding the dSPE step reduced the RSDR for several analytes considerably.

Validation results

MS Chromatogram of flour stored at -20°C (red) and room temperature (green)

Extract of oat

<table>
<thead>
<tr>
<th>Spike level mg/kg</th>
<th>LOQ in clean-up</th>
<th>LOQ w. cleanup</th>
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LC-MS/MS

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<th>Spike level mg/kg</th>
<th>Recovery %</th>
<th>RSDr %</th>
<th>RSDR %</th>
<th>Recovery %</th>
<th>RSDr %</th>
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GC-MS/MS

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<th>RSDR %</th>
<th>Recovery %</th>
<th>RSDr %</th>
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EURL-CF: EU Reference Laboratory for pesticide Residues in Cereals and Feeding stuff, DTU National Food Institute, Moerkhoj Bygade 19, DK-2860 Soeborg, Denmark.
email: eurl-cf@food.dtu.dk, www.eurl-pesticides.eu