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

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Publication date:
2016

Document Version
Publisher's PDF, also known as Version of record

DTU Food
National Food Institute

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

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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 91/414/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 Though extracts were withdrawn prior to dSPE in order to determine if specific analytes were adsorbed by the PSA.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 10 ml acetonitrile and shake vigorously by hand for 1 min. *(1. extraction)*

Add 4 g $MgSO_4$, 1 g NaCl, 1 g Na_3 citrate dihydrate and 0.5 g Na_2H citrate sesquihydrate.
Shake vigorously for 1 min. *(2. Extraction with phase separation)*.
Centrifuge for 10 min at 4500 rpm.

Store 8 ml of the supernatant in the freezer
(-80˚C for 1 hour or over night).
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 $MgSO_4$.
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

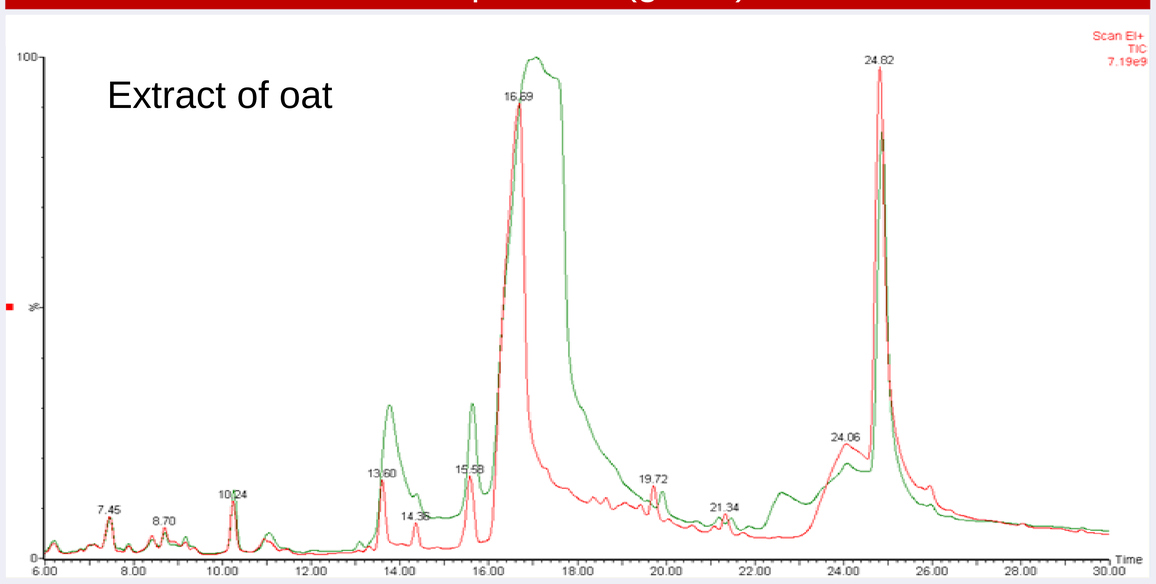
Conclusion

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_r and RSD_R 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 RSD_R for several analytes considerately.

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



Validation results

LC-MS/MS	Spike level mg/kg **0.01** with PSA clean-up Recovery %	RSDr %	RSDR %	Spike level mg/kg **0.01** no clean-up Recovery %	RSDr %	RSDR %	LOQ w. cleanup/ no cleanup
6-benzylaminopurine / 6-benzyladenine	85	6	6	85	6	6	0.01
Amisulbrom (+GC)	97	40	44	93	18	19	n.a./0.01
Carbetamide (+GC)	112	6	6	104	6	6	0.01
Cyflufenamide (+GC)	109	6	6	103	7	9	0.01
Difenacoum	112	9	29	96	11	10	0.02/0.01
Ethirimol	85	5	9	91	6	6	0.01
Fenpyrazamine (+GC)	106	7	11	98	8	10	0.01
Novaluron (+GC)	102	10	13	106	12	11	0.01
Penoxsulam	98	9	8	109	7	8	0.01
Profoxydim	88	26	26	82	19	20	0.02/0.01
Propaquizafop (+GC)	101	5	6	94	10	10	0.01
Pyridalyl (+GC)	78	12	19	20	73	147	0.01/n.a.
Quizalofop (free acid)	43	19	52	107	8	9	n.a./0.01
Spinetoram	111	7	8	98	8	11	0.01
Spirotetramat cis-enol	66	11	62	119	7	7	n.a./0.01
Spirotetramat cis-keto-hydroxy (+GC)	104	8	10	105	7	7	0.01
Spirotetramat enol-glucoside	75	11	14	90	10	12	0.01
Spirotetramat mono-hydroxy	104	7	9	105	6	6	0.01
Tembotrione	91	15	16	111	12	11	0.01
Thiencarbazone-methyl (+GC)	107	12	11	107	8	7	0.01
Triazoxide	100	18	19	90	18	17	0.01
Triflusulfuron-methyl (+GC)	99	6	10	111	7	6	0.01
Mean (accepted only)	98	9	11	100	9	10	
Maksimum (accepted only)	112	18	19	119	19	20	
Minimum (accepted only)	75	5	6	82	6	6	

GC-MS/MS	Spike level mg/kg **0.01** with PSA clean-up Recovery %	RSDr %	RSDR %	Spike level mg/kg **0.02** with PSA clean-up Recovery %	RSDr %	RSDR %	LOQ (mg/kg)
Amisulbrom (+LC wo. clean-up)	94	16	16	96	13	12	0.01
Cyflufenamide (+LC)	112	8	8	105	5	5	0.01
Fenpyrazamine (+LC)	107	10	16	108	7	12	0.01
Novaluron (+LC)	87	14	24	85	12	18	0.01
Propaquizafop (+LC)	93	8	20	99	9	20	0.01
Pyridalyl (+LC w. clean-up)	80	7	32	82	11	24	0.02
Spirotetramat cis-keto-hydroxy (+LC)	106	31	29	110	11	15	0.02
Thiencarbazone-methyl (+LC)	83	22	22	81	15	14	0.01
Triflusulfuron-methyl (+LC)	87	16	28	91	8	11	0.02

EURL-CF: EU Reference Laboratory for pesticide Residues in Cereals and Feeding stuff, DTU National Food Institute, Moerkhoej Bygade 19, DK-2860 Soeborg, Denmark
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