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Determination of pyrethroids in animal fat and milk using LC-MS/MS

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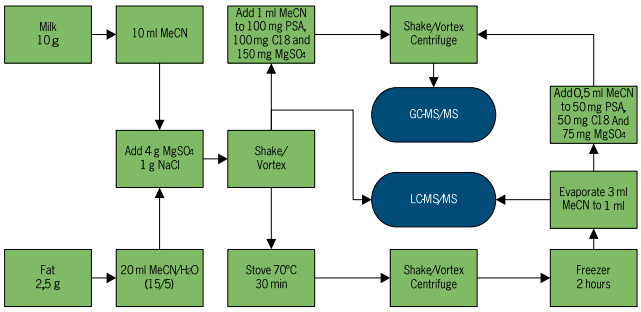
Introduction

Pyrethroids are used against a broad range of ectoparasites in large and small animals, including food animals. MRLs have been established for products of animal origin in 396/2005 and 37/2010. Pyrethroids are typically determined by GC-MS(/MS). In this work the use of LC-MS/MS as alternative and/or complementary analysis method for the determination of pyrethroids in products of animal origin (fat and milk) has been investigated.

Experimental

- Analytes: 9 pyrethroids spiked to the following matrix sets:
- raw cow's milk, 2 blank, 5 spiked at 10 ng/g and 50 ng/g
- animal fat: sheep, pig-1, pig-2, calf, cow; blank and spikes at 10, 50 and 250 ng/g

Sample preparation:
Based on acetonitrile partitioning (QuEChERS [1])



Instrumental analysis:

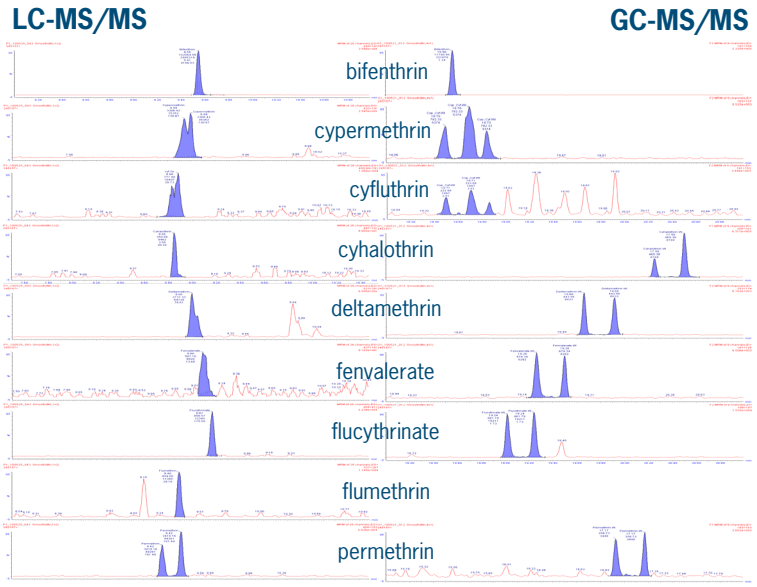
- LC-MS/MS (Waters Quattro Premier XE), 20 µl injection column 100x2.1 mm ID, Acquity UPLC HSS T3 1.8 µm gradient water/MeOH (10 mM NH_4 formate, formic acid).
- GC-MS/MS (Waters Quattro micro), 10 µl injection column 15m x 0.25 mm ID, 0.25 µm Rtx-CLPesticides
- Quantification: 1-point calibration on matrix-matched standard (for animal fat: matrix was a mixture of the 5 fat extracts).

Results

Average recoveries and RSDs were determined for milk and the different fat samples.

		Fat					Milk				
		LC			GC		LC			GC	
Nb	Compound	Rec(%)	RSD (%)	Matrix Effect	Rec(%)	RSD (%)	Rec(%)	RSD (%)	Matrix effect	Rec(%)	RSD (%)
1	Bifenthrin	43	15	0.85	71	15	41	31	0.43	50	18
2	Cyfluthrin	84	16	0.79	76	15	60	17	0.76	72	15
3	Cyhalothrin	76	14	0.90	83	16	103	22	1.00	74	12
4	Cypermethrin	84	11	0.89	76	15	55	18	0.94	72	15
5	Deltamethrin	91	28	0.81	77	17	60	23	0.86	69	12
6	Fenvalerate	128	34	0.31	80	9	57	24	0.77	70	20
7	Flucythrinate	96	20	0.84	89	11	62	12	1.15	86	10
8	Flumethrin	64	29	0.97	nd	nd	50	29	0.64	nd	nd
9	Permethrin	42	25	0.77	63	15	45	30	0.69	56	14

nd = flumethrin could not be detected at lower levels by GC-MS/MS



Comparison of extracted ion chromatograms of pyrethroids in fat extract at the 10 ng/g level.

Discussion

- In the fat-water-acetonitrile extraction mixture, most pyrethroids partition favorably into the acetonitrile phase
- For LC-MS/MS analysis, sample preparation is more straightforward and faster than for GC-MS/MS
- Overall, the S/N in GC-MS/MS is better than for LC-MS/MS except for flumethrin which could not be detected by GC
- GC analysis resulted in more pyrethroid peaks due to i) partial isomer conversion upon introduction of acetonitrile extracts in the GC injector and ii) better separation efficiency in GC.

Note: for pyrethroids included in 37/2010 the residue is defined as the sum of all isomers while in 396/2005 the residue for deltamethrin applies to the cis-isomer and for fenvalerate different MRLs apply for the SR/RS and SS/RR isomers

- In GC-MS/MS matrix-effects for different types of fat were similar, allowing to use one generic blank fat-extract for matrix-matched calibration
- In LC-MS/MS matrix effects for fat were species dependent. Using one generic blank (mixed)fat-extract for quantification may have affected the average recovery and contributed to a higher RSD compared to GC-MS/MS

Conclusion

➢ Acetonitrile partitioning based sample preparation is suited for pyrethroids in animal fats and milk and a much faster alternative for traditional GPC-based methods
➢ LC-MS/MS analysis of pyrethroids is faster and more straightforward (sample prep and data interpretation) but quantitative performance is worse compared to GC-MS/MS. LODs are sufficient for verification of MRLs.
➢ LC-MS/MS is an attractive option for initial screening, followed by GC-MS/MS analysis for confirmation and more accurate quantification of any screening detects.

References

[1] S. Lehotay, K. Mastovska, J. AOAC 88 (2005) 630-638

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Acknowledgement

This research was (partly) financed by the Dutch Ministry of Agriculture, Nature and Food Quality