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Validation of a GC-extension of a generic extraction method for the determination of pesticides and contaminants in feed commodities

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Introduction

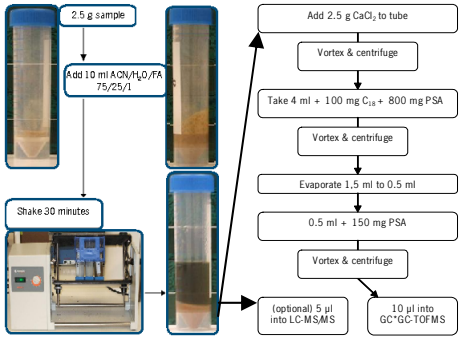
In previous work a very easy and fast sample preparation procedure for LC-MS based screening of pesticides, natural toxins and veterinary drugs was developed [1]. Samples are extracted using a mixture of acetonitrile/water/formic acid (75/25/1) which is directly analyzed. In this work, to extend and/or complement the LC-MS based method, the raw extract was further processed to facilitate GC analysis. The extracts obtained were analyzed by GCxGC-TOF-MS [2].

The method was validated according to SANCO/10684/2009 with emphasis on analytes not, or less, amenable to LC-MS including organochlorine pesticides, certain organophosphorus pesticides, pyrethroids, indicator PCBs and PAHs.

Experimental

Horse feed and wheat samples were spiked with 54 compounds at the 10 ng/g and 100 ng/g level.

Extraction and clean-up procedure



GCxGC-TOFMS parameters

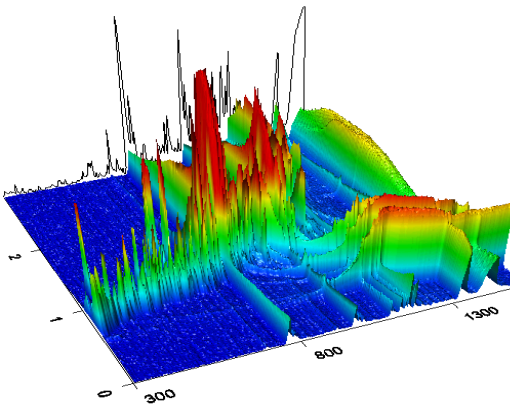
10 µl injection (1 g matrix equivalent/ml). First Column; 10 m; 0.25 mm ID, 0.25 µm RTX-CLpestides. Second Column; 1 m; 0.1mm ID, 0.1µm BPX-50. 26 min run time. Acquisition: m/z 50 – 600, 200 Hz. Datahandling: ChromaTOF 4.21

References

[1] H.G. J. Mol, P. Plaza-Bolanõs, P. Zomer, T.C. de Rijk, A.A.M. Stolker, P.P. J. Mulder, Anal.Chem., 80 (2008) 9450–9459
[2] M.K. van der Lee, G. van der Weg, W.A. Traag, H.G.J. Mol, J. Chromatogr. 1186 (2008) 325–339

Results Wheat

GCxGC-TOF-MS 3D image of a blank.

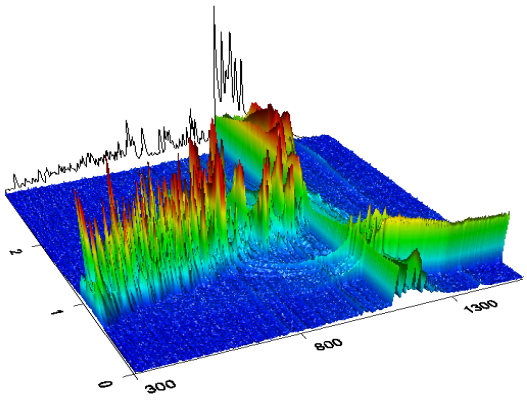


Average recovery and RSD at 10 and 100 ng/g level (n=5).

Concentration	10 PPB		100 PPB	
Matrix: wheat	recovery	RSD	recovery	RSD
Aldrin	89%	5%	86%	2%
Benzo(a)pyrene	63%	7%	78%	5%
Benzo(b)fluoranthene	77%	6%	83%	6%
Benzo[a]anthracene	82%	3%	81%	4%
Bifenthrin	110%	9%	87%	7%
Bromopropylate	90%	4%	88%	3%
Chlordane cis- (alpha)	87%	4%	100%	3%
Chlordane trans- (gamma)	88%	5%	100%	3%
Chlorfenvinphos	98%	7%	101%	5%
Chlorobenzilate	87%	5%	84%	3%
Chlorpyrifos	96%	3%	96%	3%
Chrysene	Included in Benzo(a)anthracene			
Cyfluthrin	147%	14%	112%	15%
Cyhalothrin	136%	8%	107%	17%
Cypermethrin	98%	16%	115%	4%
DDD op'- [TDE]	98%	5%	87%	5%
DDD pp'- [TDE]	93%	9%	90%	3%
DDE op'-	93%	6%	102%	7%
DDE pp'-	93%	5%	86%	4%
DDT op'-	79%	14%	97%	13%
DDT pp'-	65%	36%	71%	55%
Deltamethrin	115%	14%	114%	5%
Dieldrin	90%	9%	97%	2%
Endosulfan alpha-	84%	18%	104%	4%
Endosulfan beta-	97%	5%	97%	2%
Endosulfan sulphate	74%	43%	85%	24%
Endrin	98%	4%	95%	3%
Fenitrothion	79%	33%	80%	19%
Fenvalerate	110%	6%	102%	5%
Flucythrinate	121%	14%	110%	4%
HCB	83%	3%	79%	2%
HCH alpha-	65%	28%	89%	22%
HCH beta-	89%	5%	93%	3%
HCH gamma- (Lindane)	81%	20%	87%	16%
Heptachlor	95%	9%	98%	3%
Heptachlor epoxide (iso B)	95%	6%	98%	2%
Methoxychlor	86%	14%	105%	14%
Oxychlordane	94%	5%	99%	2%
Parathion-ethyl	111%	6%	95%	2%
Parathion-methyl	63%	30%	74%	23%
PCB 101	81%	7%	84%	11%
PCB 118	83%	4%	80%	2%
PCB 138	85%	3%	78%	3%
PCB 153	77%	5%	77%	2%
PCB 180	75%	3%	68%	3%
PCB 28	87%	6%	85%	3%
PCB 52	90%	4%	91%	2%
Permethrin	119%	13%	95%	6%
Pirimiphos-methyl	97%	6%	89%	5%
Procymidone	103%	4%	105%	2%
Toxaphene Parlar 26	86%	7%	91%	6%
Toxaphene Parlar 50	67%	26%	86%	17%
Toxaphene Parlar 62	24%	139%	76%	43%
Vinclozolin	96%	5%	96%	3%

Results Horse Feed

GCxGC-TOF-MS 3D image of a blank.



Average recovery and RSD at 10 and 100 ng/g level (n=5).

Concentration	10 PPB		100 PPB	
Matrix: Horse feet	recovery	RSD	recovery	RSD
Aldrin	98%	7%	84%	2%
Benzo(a)pyrene	63%	7%	67%	6%
Benzo(B)fluoranthene	77%	7%	81%	2%
Benzo[a]anthracene	77%	6%	85%	5%
Bifenthrin	114%	10%	94%	4%
Bromopropylate	78%	9%	82%	5%
Chlordane cis- (alpha)	96%	3%	90%	6%
Chlordane trans- (gamma)	103%	3%	96%	2%
Chlorfenvinphos	107%	11%	96%	3%
Chlorobenzilate	90%	5%	82%	2%
Chlorpyrifos	104%	3%	95%	3%
Chrysene	89%	6%	90%	3%
Cyfluthrin	104%	12%	100%	15%
Cyhalothrin	103%	8%	100%	9%
Cypermethrin	418%	25%	56%	13%
DDD op'- [TDE]	100%	5%	88%	4%
DDD pp'- [TDE]	94%	7%	89%	8%
DDE op'-	91%	11%	87%	10%
DDE pp'-	99%	3%	97%	2%
DDT op'-	50%	82%	148%	27%
DDT pp'-	57%	138%	185%	58%
Deltamethrin	78%	11%	84%	9%
Dieldrin	102%	5%	93%	2%
Endosulfan alpha-	110%	11%	105%	4%
Endosulfan beta-	97%	6%	93%	7%
Endosulfan sulphate	93%	32%	89%	24%
Endrin	52%	138%	149%	20%
Fenitrothion	122%	15%	86%	15%
Fenvalerate	110%	16%	95%	10%
Flucythrinate	107%	35%	91%	8%
HCB	92%	6%	73%	3%
HCH alpha-	85%	8%	79%	13%
HCH beta-	90%	10%	93%	6%
HCH gamma- (Lindane)	85%	9%	86%	12%
Heptachlor	85%	7%	95%	7%
Heptachlor epoxide (iso B)	101%	4%	89%	2%
Methoxychlor	77%	61%	208%	49%
Oxychlordane	94%	5%	95%	5%
Parathion-ethyl	99%	6%	92%	3%
Parathion-methyl	121%	14%	81%	21%
PCB 101	96%	3%	89%	2%
PCB 118	117%	4%	105%	3%
PCB 138	97%	2%	90%	2%
PCB 153	91%	3%	80%	3%
PCB 180	81%	6%	75%	3%
PCB 28	106%	9%	85%	3%
PCB 52	100%	6%	90%	2%
Permethrin	91%	12%	92%	6%
Pirimiphos-methyl	103%	11%	87%	7%
Procymidone	105%	6%	98%	2%
Toxaphene Parlar 26	82%	25%	99%	12%
Toxaphene Parlar 50	76%	38%	127%	25%
Toxaphene Parlar 62	28%	224%	137%	129%
Vinclozolin	105%	3%	90%	3%

Conclusion

A GC-based method for quantitative analysis of pesticides and contaminants, including indicator PCBs and indicator PAHs was successfully validated for most of the compounds investigated in wheat and a complex compound feed.

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Acknowledgement

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