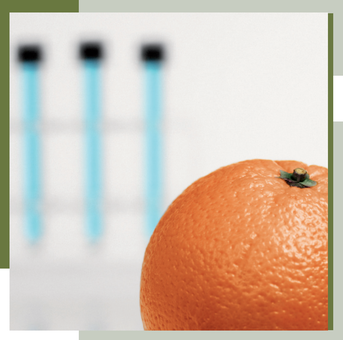

FOOD

S19, QuEChERS, Polar Pesticides – Is There Anything Methodological Left for Research?

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Introduction

The fundamental innovations in the way of multiresidue methods (MRM) in pesticide analysis have been DFG S19 and QuEChERS methodology. Recently for the coverage of polar pesticides (PP) a complementary MRM has been established. Beyond dispute many pesticides of a wide polarity range are covered by these MRMs and valid variants applicable for most of the relevant matrices. Present-day MRMs are characterized by reasonable LOQs, high reproducibility, robustness and analytical speed.

Looking into more detailed data of everyday routine pesticide analysis unfortunately the essential class of "acid" pesticides does not seem to be adequately covered by the methodologies listed above. Prominent members are presented in Table 1. For these pesticides comparatively sparse residue data is available in databases like pesticides online. Reasons for this might probably be the spare usage of these specific pesticides or the deficits in today's MRMs used for generating the residue data of those kinds of pesticides.

Three major analytical problems of these LC-MS-MS amenable pesticides can be noted: often low detector sensitivity, furthermore the susceptibility to differential mass-spectrometric interferences by matrix compounds and finally the low extraction yield and the deficient reproducibility in the extraction recovery strictly depending on the matrix and the pH value during extraction and clean up.

In this study a new kind of MRM is presented suitable for the analysis of a number of 96 pesticides classified into two dozens of pesticide families (Table 1).

Table 1: Acid pesticides tested positively to be amenable to the analysis by the newly generated MRM

Pesticide Class	Pesticide
Aryloxyphenoxypropionic acid	Chlorizafop
	Clodinafop
	Clofop
	Cyhalofop
	Diclofop
	Fenoxaprop
	Fluazifop
	Haloxyfop
	Propaquizafop
	Quizalofop
	Trifop
Auxine	1-Naphthylacetic acid
	2-Naphthoxyacetic acid
Benzoic acid	2,3,6-Trichlorobenzoic acid
	2,4-Dichlorobenzoic acid
	2,5-Dichlorobenzoic acid
	Chloramben
	Dicamba
	Tricamba
Benzothiazole	Benazolin
	Fenthiaprop
Gibberelins	Gibberellic acid
Halogenated aliphatic acid	Alorac
	Chloropon
	Dalapon
	Flupropanate
Hydroxybenzonitrile	Bromoxynil
	Chloroxynil
	Ioxynil
Imidazolinone	Imazamethabenz
	Imazamox
	Imazapic
	Imazapyr
	Imazaquin
	Imazethapyr
Organochlorine	2,4,5-Trichlorophenol
	2,4,6-Tribromophenol
	2,4,6-Trichlorophenol
	2,4-Dichlorophenol
	2,6-dichloro-4-methylphenol
	4-Chlorophenol
	Pentachlorophenol
Oxazol	Hymexazol
Phenoxy acetic acid	2,4,5-T
	2,4-D
	3,4-DA
	4-CPA
	MCPA

Pesticide Class	Pesticide
Phenoxy butyric acid	2,4-DB
	3,4,5-TB
	3,4-DB
	4-CPB
	MCPB
Phenoxy propionic acid	2,4,5-TP
	3,4-DP
	4-CPP
	Cloprop
	Dichlorprop
	MCPP
Phenylpyrazole	Pyraflufen
Phthalic acid	Chlorthal
Picolinic acid	Aminopyralid
	Clopyralid
	Picloram
Pyridinecarboxylic acid	Fluroxypyr
	Triclopyr
Pyrimidinyloxy-/ thiobenzoic acid	Bispyribac
	Pyriminobac
	Pyrithiobac
Pyrimidinylsulfonylurea	Chlorimuron
	Mesosulfuron
	Sulfometuron
Quinolinecarboxylic acid	Oxolinic Acid
	Quinclorac
	Quinmerac
Semi-carbazone	Diflufenzopyr
Sulfonylurea	Bensulfuron
	Flupyrsulfuron
	Halosulfuron
	Iodosulfuron
	Primisulfuron
	Thifensulfuron
	Triflusulfuron
Triazinylsulfonylurea	Ethametsulfuron
	Metsulfuron
	Tribenuron
Triazolone	Carfentrazone
	Thiencarbazone
Triazolopyrimidine	Cloransulam
Unclassified	Chlorfenprop
	Chlorflurenol
	Cloquintocet
	Cyclanilide
	Fenridazon
	Fluthiacet
	Prohexadione

Experimental

- Sample homogenisation
- Alkylation of acid herbicides in an aqueous solvent mixture with TBAOH
- Phase separation by centrifugation
- DSPE cleanup of the organic phase with magnesium sulphate/PSA/GCB
- Direct injection of the organic phase into GC-NCI-MSD and LC-MS-MS and determination of the alkyl derivatives

Results

- Via a single derivatization step in buffered aqueous medium easily to perform the pesticides are transformed into their alkyl derivatives amenable both to LC-MS-MS and GC-MS analysis.
- The sample preparation is accomplished within one hour, just a little more than needed for the QuEChERS process.
- The method is suited to any plant commodity mentioned in document SANCO/10684/2009, especially for "difficult and unique" commodities like tea, spices and dried herbs (see Fig. 1).
- The most prominent 33 of 96 pesticides amenable to the newly generated MRM have been validated.
- The LOQs determined according to document SANCO/10684/2009 are in the low ppb range (Table 2).

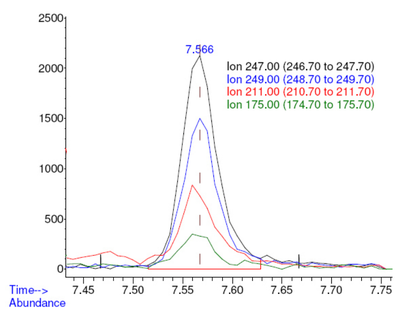

Figure 1: GC-NCI-MSD chromatogram of a peppermint tea sample containing 38 ppb Clopyralid.

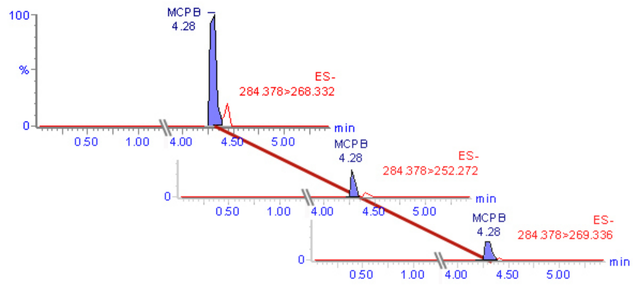

Figure 2: LC-MS-MS chromatogram of a wheat sample containing 63 ppb MCPB.

Table 2: Method LOQs of 33 acid herbicides in different commodities. LOQ levels [µg/kg] were determined at the lowest validated spike level on matrix meeting the method performance acceptability criteria (mean recoveries for each representative commodity in the range 70-120%, with a RSDr ≤ 20%).

Pesticide	Plant Commodity					Test method
	Tomato (high water content)	Wheat flour (high starch and/or high protein content)	Orange (high acid and high water content)	Dried apricot (high sugar and low water content)	Black Tea (difficult commodity)	
	Method LOQ [µg/kg]					
2,4,5-T	5	5	5	5	20	GC-NCI-MS
2,4,5-TP	5	5	5	5	20	GC-NCI-MS
2,4,6-Tribromophenol	1	1	1	1	5	GC-NCI-MS
2,4,6-Trichlorophenol	1	1	1	1	5	GC-NCI-MS
2,4-D	5	5	5	5	10	GC-NCI-MS
2,4-Dichlorophenol	5	5	5	5	10	GC-NCI-MS
4-Chlorophenol	5	5	5	5	10	GC-NCI-MS
4-CPA	10	10	10	10	20	GC-NCI-MS
Aminopyralid	10	10	10	10	20	LC-MS-MS
Bromoxynil	5	5	5	5	10	GC-NCI-MS
Chloramben	5	5	5	5	10	GC-NCI-MS
Chlorflurenol	5	10	10	10	20	GC-NCI-MS
Chlorthal	20	20	20	20	50	LC-MS-MS
Clopyralid	10	10	10	10	20	GC-NCI-MS
Cyclanilide	5	5	5	5	10	GC-NCI-MS
Dicamba	10	20	20	20	20	GC-NCI-MS
Fluazifop	5	5	5	5	10	GC-NCI-MS
Fluroxypyr	5	5	5	5	10	GC-NCI-MS
Haloxyfop	5	5	5	5	10	GC-NCI-MS
Imazamox	10	10	10	10	20	LC-MS-MS
Imazapyr	5	5	5	5	10	LC-MS-MS
Imazaquin	20	20	20	20	20	LC-MS-MS
Imazethapyr	5	5	5	5	10	LC-MS-MS
Ioxynil	5	5	5	5	10	LC-MS-MS
MCPA	5	5	5	5	10	GC-NCI-MS
MCPB	10	10	10	10	20	LC-MS-MS
MCPP	5	5	5	5	10	GC-NCI-MS
Oxolinic Acid	1	5	5	5	5	LC-MS-MS
Pentachlorophenol	1	2	2	2	5	GC-NCI-MS
Picloram	5	5	5	5	10	GC-NCI-MS
Quinclorac	5	5	5	5	10	GC-NCI-MS
Quizalofop	5	5	5	5	10	GC-NCI-MS

Conclusions

- The analysis of acid herbicides is performed by this newly-developed MRM in a fast, easy, sensitive and selective way.
- This MRM is suited for the analysis of any plant commodity mentioned in document SANCO/10684/2009, especially for matrices like tea, spices and dried herbs.
- The application of this MRM will be complementary to S19, QuEChERS and PP and will give new insights into the true residue situation of acid pesticides in any plant-derived material.
- The analysis of the remaining 63 pesticides is going to be validated in the next months.