Analysis of highly polar pesticides using QuPPe and LC-MS/MS or SFC-MS/MS in the ESI-pos. mode

H. Dias, A. Wachtler, E. Scherbaum and M. Anastassiades
E-Mail: Hanna.Dias@cvuas.bwl.de

Introduction

Highly polar cationic or potentially cationic pesticides and metabolites are commonly analysed by LC-MS/MS. SFC-MS/MS was tested as an alternative measurement technique. For comparison, spiked commodities of plant and animal origin were extracted using the QuPPe method - developed by the EURL-SRM – and the extracts were analysed by both techniques with focus on measurement repeatability and matrix effects.

Analytical method

LC Instrument parameters	
Instrument	Acquity UPLC H-Class System plus
Column/Temp.	BEH Amide 2.1 x 100 mm, 1.7 µm; 40 °C
Eluent A	50 mmol NH_4-formate in water (adjust to pH 3 with formic acid)
Eluent B	Acetonitrile
Injection volume	0.5 µl
Gradient:	See QuPPe V12, method 4.2

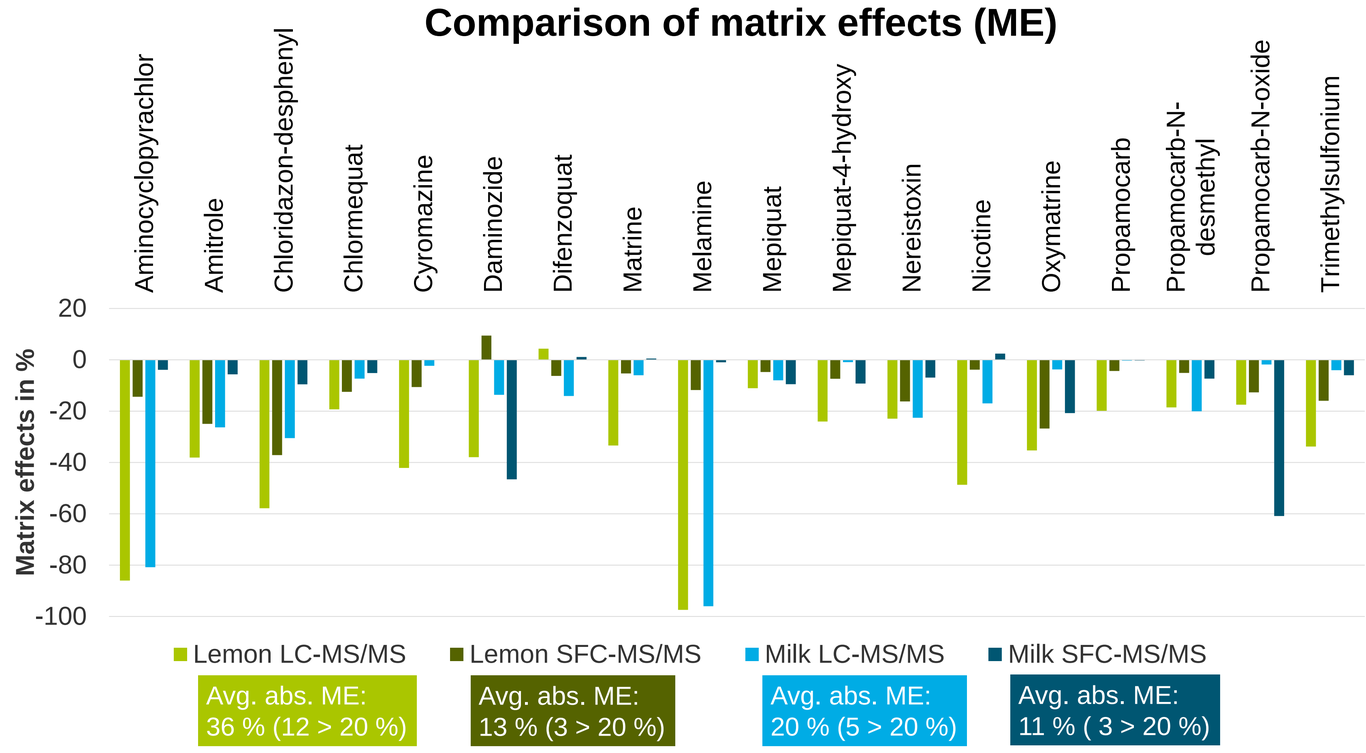
SFC Instrument parameters			
Instrument	Acquity UPC² System		
Column/Temp.	Viridis BEH Column 3.0 x 100 mm, 1.7 µm; 55 °C		
Eluent A	CO_2		
Eluent B	MeOH/H_2O 95:5 with 20 mmol NH_4-formate		
Make-Up Solvent/Flow	MeOH/H_2O 90:10 with 0.1 % formic acid; 0.3 ml/min		
ABPR	124 bar		
Injection volume	0.5 µl		
Gradient	%A	Flow [ml/min]	Time [min]
	95	1.5	0
	95	1.5	1.0
	50	1.5	8.0
	50	1.5	12.0
	95	1.5	12.2
	95	1.5	14.2

MS Instrument parameters			
Instrument	Waters Xevo TQ-Sµ		
Ionisation mode	ESI pos.	Source Temp.	150 °C
Desolvation Temp.	600 °C	Desolvation Gas Flow	1000 L/h
Cone Gas Flow	150 L/h	Capillary	0.5 kV

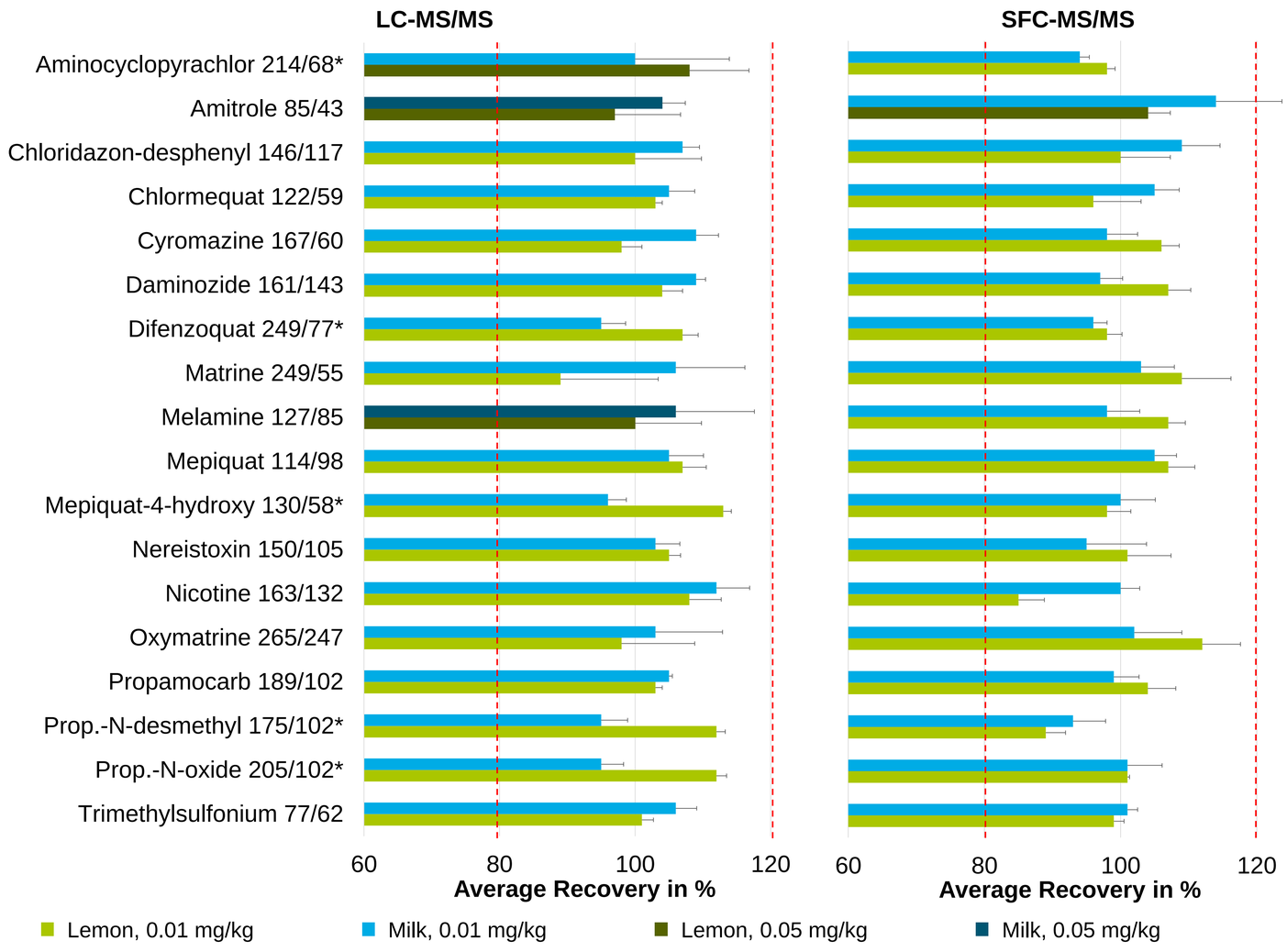
Matrix effects and validation data

Validation was performed using isotopically labelled internal standards (ILISs) and a 2-point matrix matched calibration (n=5). The sample weight was 10 g for both lemon and milk. Two spiking levels (0.01 mg/kg and 0.05 mg/kg) were used for validation.

Comparison of matrix effects (ME)



Validation data



Results shown refer to target MRM. In all cases at least one additional MRM fullfilled the criteria for succesfull validation

*matrix-matched without ILIS

Results

Mean recovery rates and repeatabilities achieved were satisfactory by both techniques on both spiking levels and both matrices with few exceptions where validation was successful only at 0.05 mg/kg (LC: 3x lemon, 2x milk; SFC: 1x lemon). SFC-MS/MS was overall less affected by matrix effects than LC-MS/MS (avg. abs. ME -13 vs. -36% in lemon and -11 vs. -20% in milk). In milk there were a few cases where LC- showed lower MEs than SFC-MS/MS, i.e. daminozide (-47 vs. -14%), oxymatrine (-21 vs. -4%) and propamocarb-N-oxide (-61 vs. -2%).

EPRW 2022
PD - 20

Co-funded by the European Union

Baden-Württemberg