

# Use of supercritical fluid chromatography coupled to mass spectrometry for the analysis of pesticide residues in fruits and vegetables.

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## INTRODUCTION

Supercritical fluid chromatography coupled to electrospray mass spectrometry (SFC-ESI-MS) has proven to be an alternative to the very well-know reverse-phase liquid chromatography. This type of chromatography has experienced an increment in terms of robustness, providing many advantages for the analysis of pesticide residues in fruits and vegetables. As SFC uses CO<sub>2</sub> as a mobile phase, high flow rates can be applied, providing short run times with good chromatography resolution. The absence of water in the mobile phase and the low flow that reach the ESI source provide an excellent ionization efficiency. This different chromatographic operation allows the possibility to detect and quantify some compounds usually analyzed by gas chromatography (GC) like pyrethroids. Besides, SFC-MS/MS provides the opportunity to perform fast, efficient, and simultaneous chiral separations without changing the mobile phase applied in the multiresidue method.

## EXPERIMENTAL

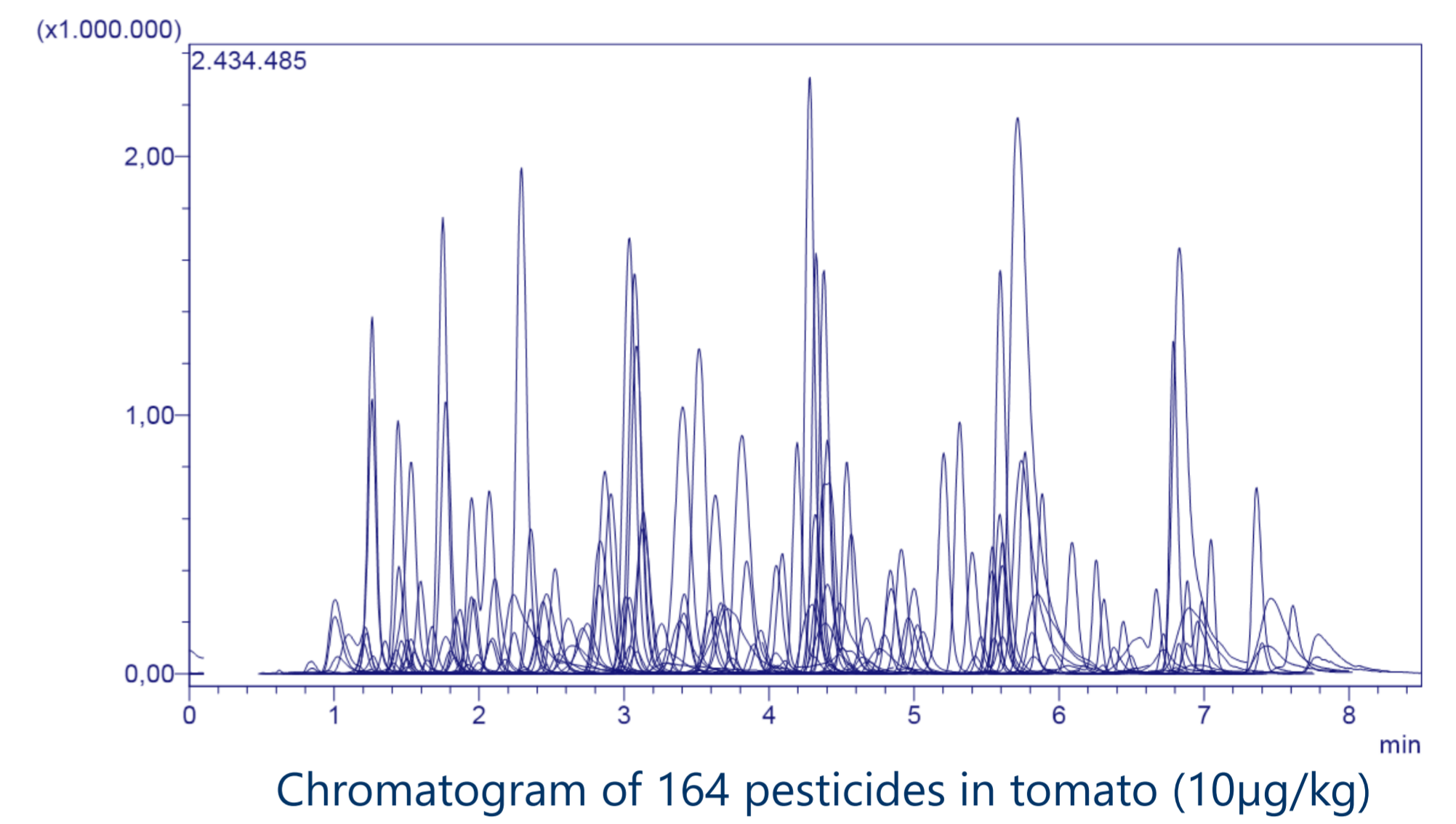
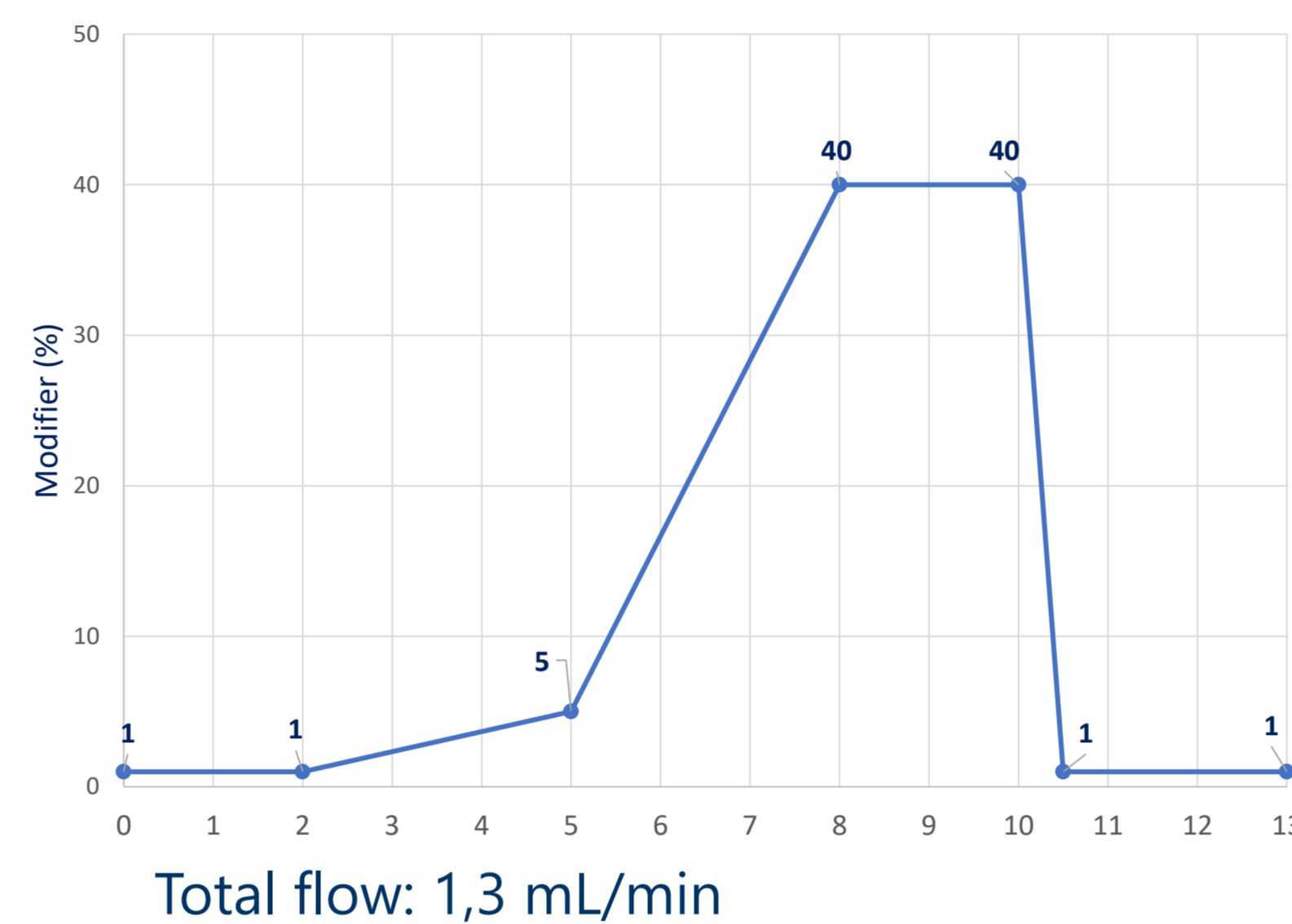
**System:** Shimadzu Nexera UC coupled to LC-MS 8060

### SFC parameters:

- Injection volume: 2µL
- Flow rate: 1,3 mL/min
- Make up flow: 0,08 mL/min
- Oven temperature: 40°C
- BPR pressure: 150 bar
- BPR Temperature: 50°C
- Column: Shim-Pack UC-X RP, 3µm 2.1x250mm
- Mobile Phases:  
Modifier: MeOH 1mM HCOONH<sub>4</sub>  
Make up: MeOH 5mM HCOONH<sub>4</sub> 0.1% HCOOH

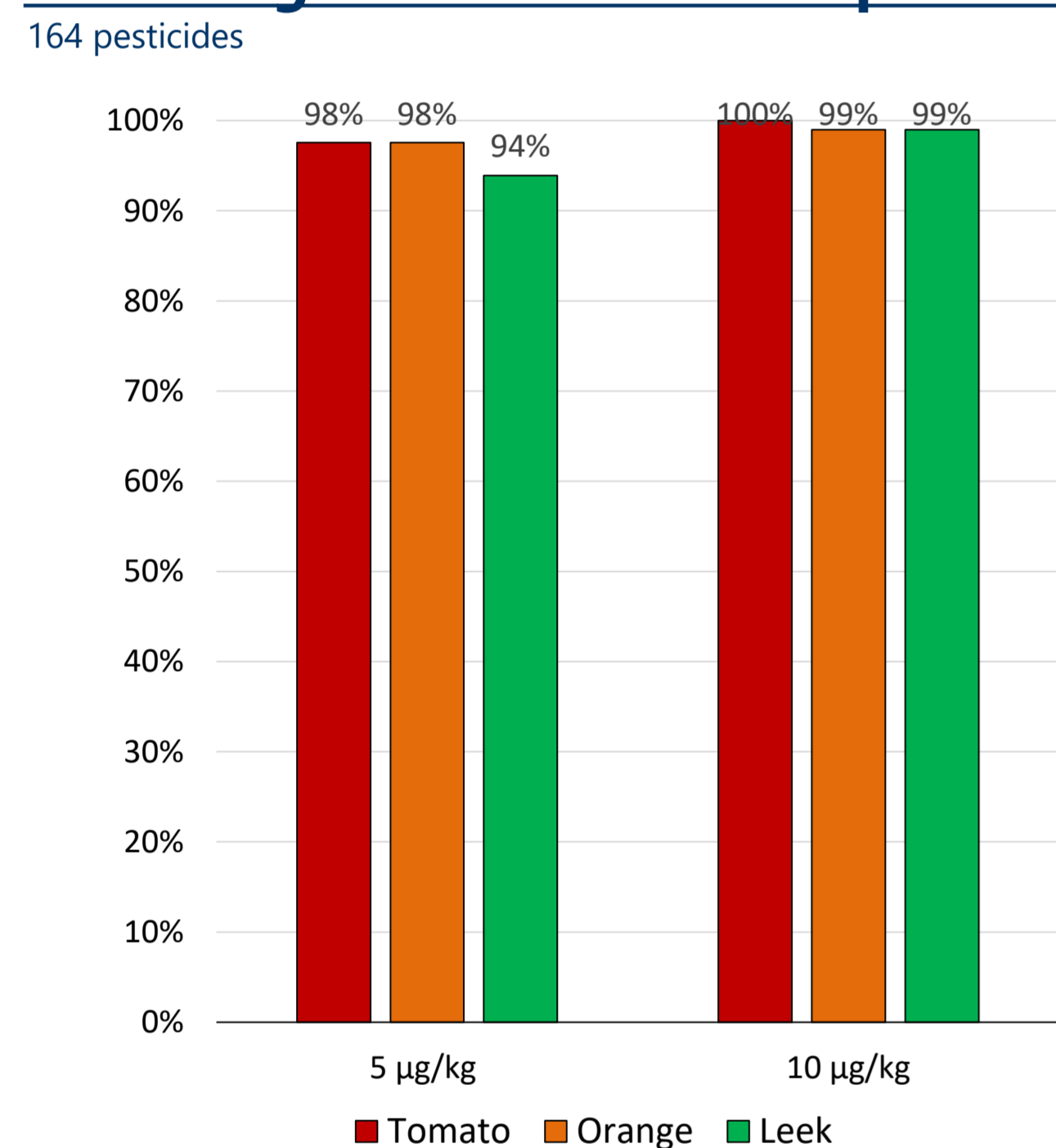
### MS parameters:

- Ion source: ESI
- Polarity: Positive and negative
- Schedule MRM software features
- Dwell time: 5 ms

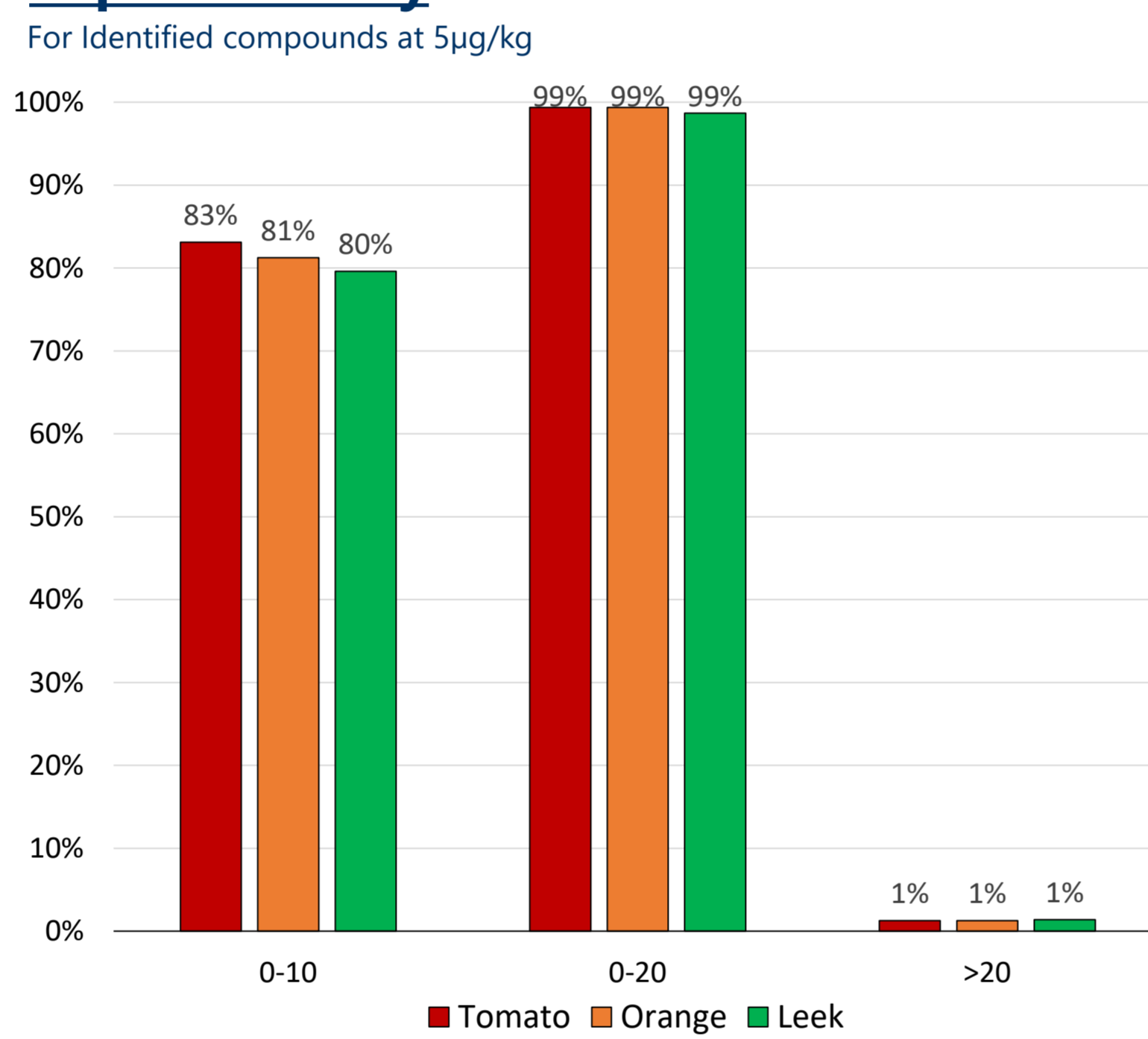


## RESULTS AND DISCUSSION

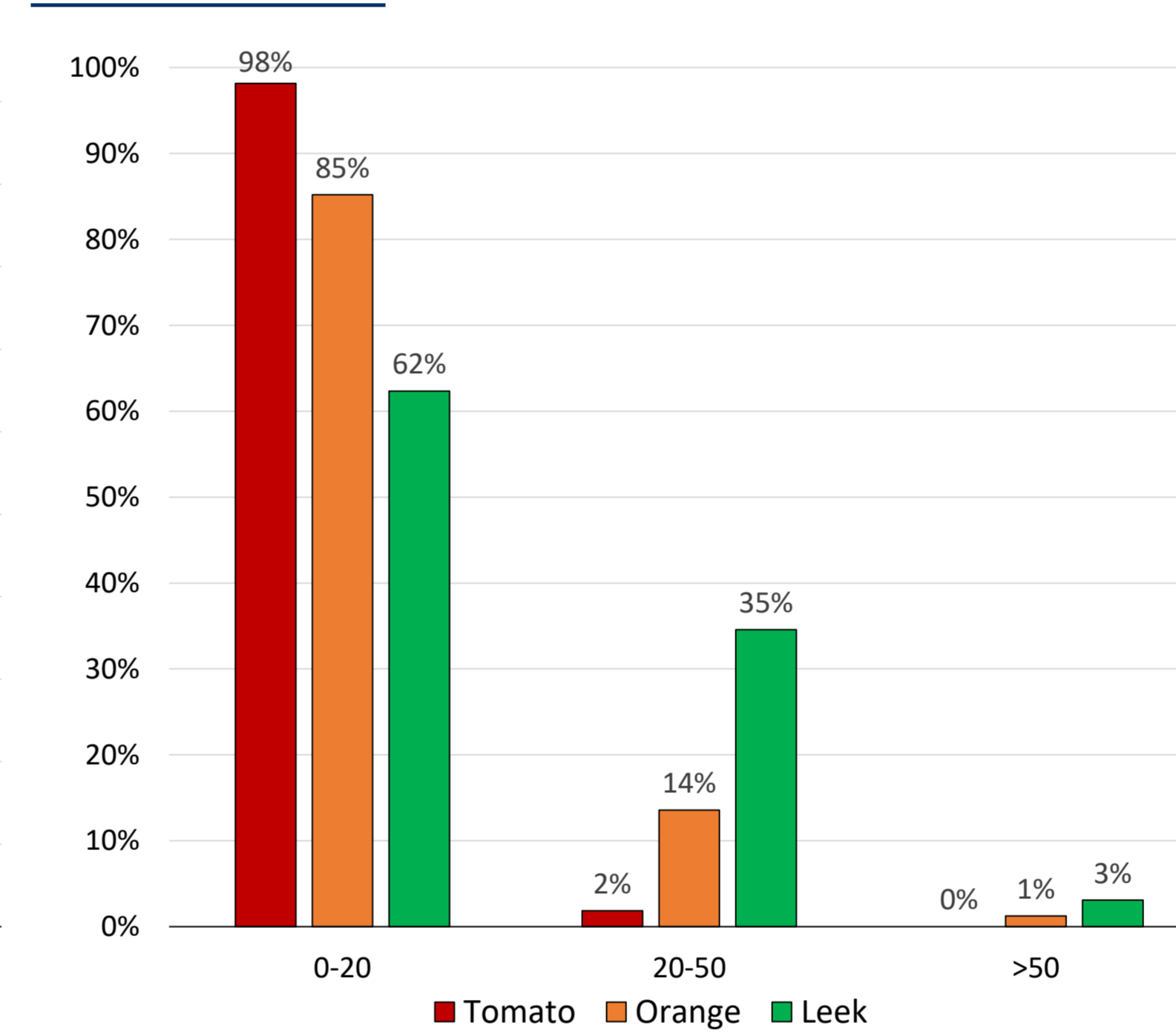
### Percentage of identified compounds



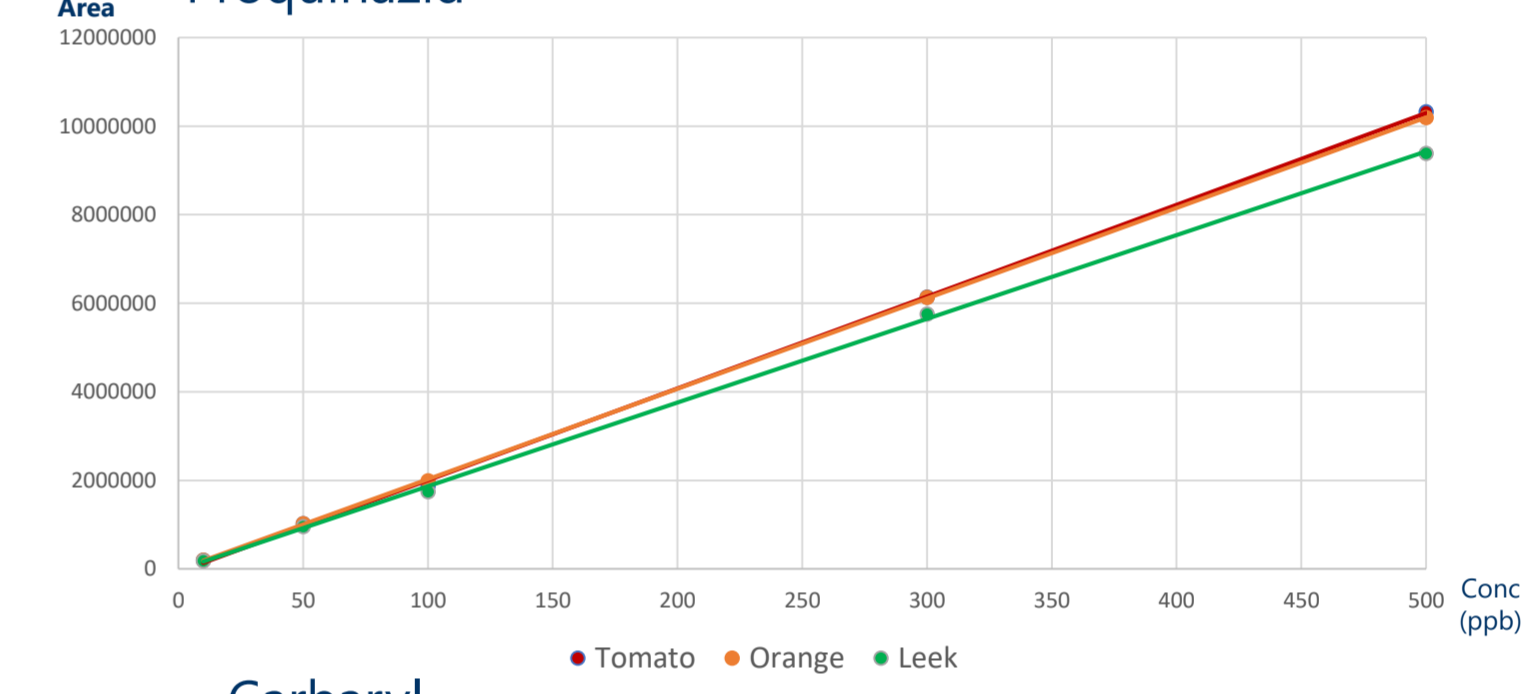
### Reproducibility



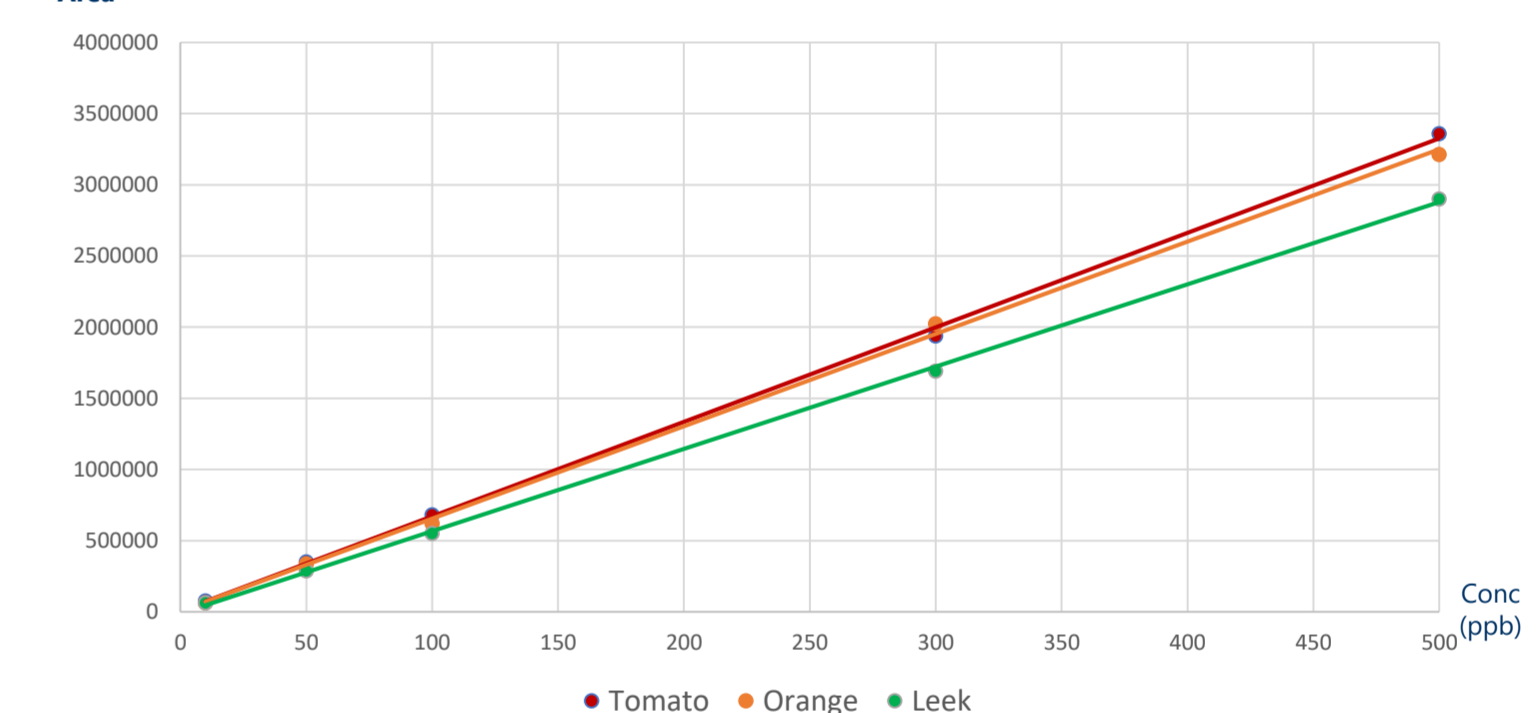
### Matrix Effect



### Proquinazid

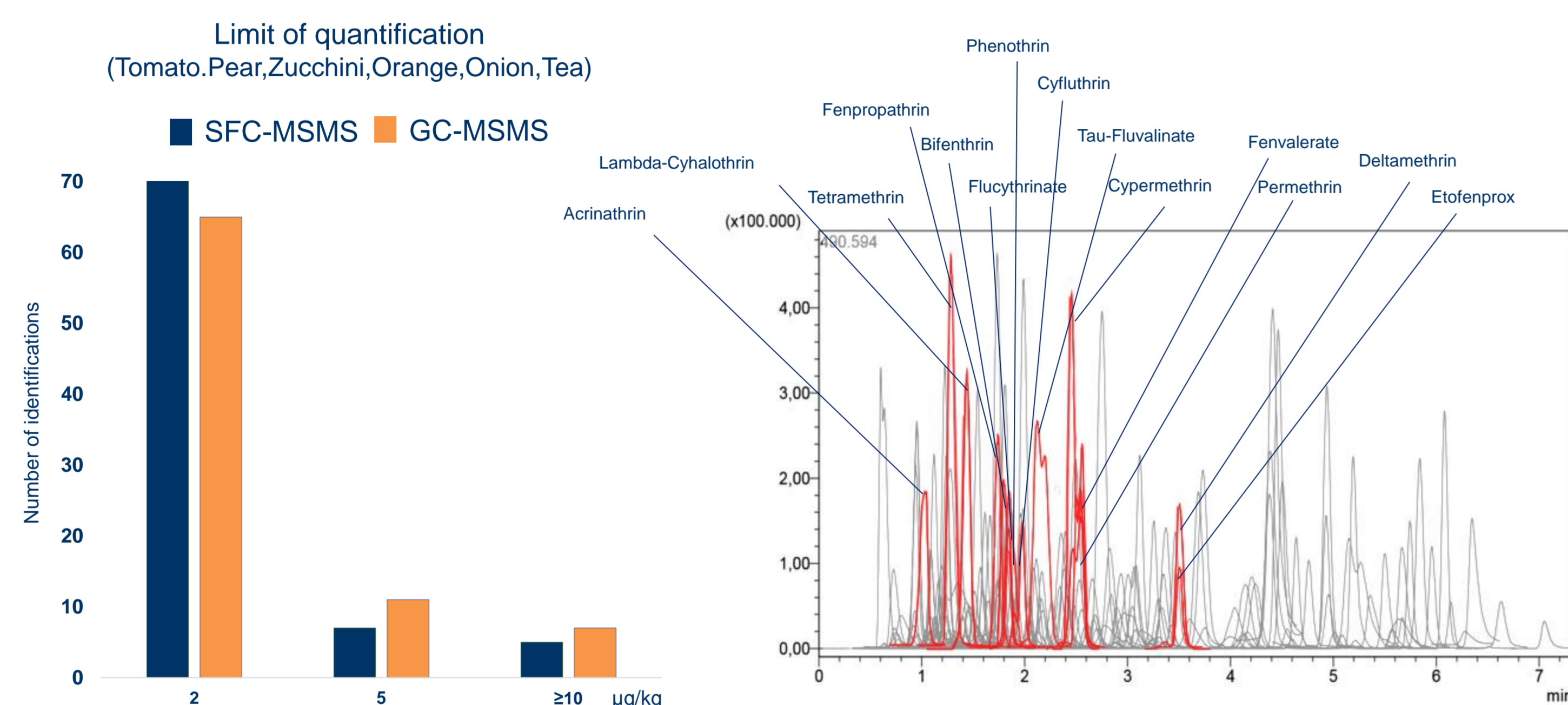


### Carbaryl



### Pyrethroid analysis

Fourteen pyrethroids were included in the SFC multiresidue method. An evaluation was performed comparing SFC-MS/MS with GC-MS/MS.

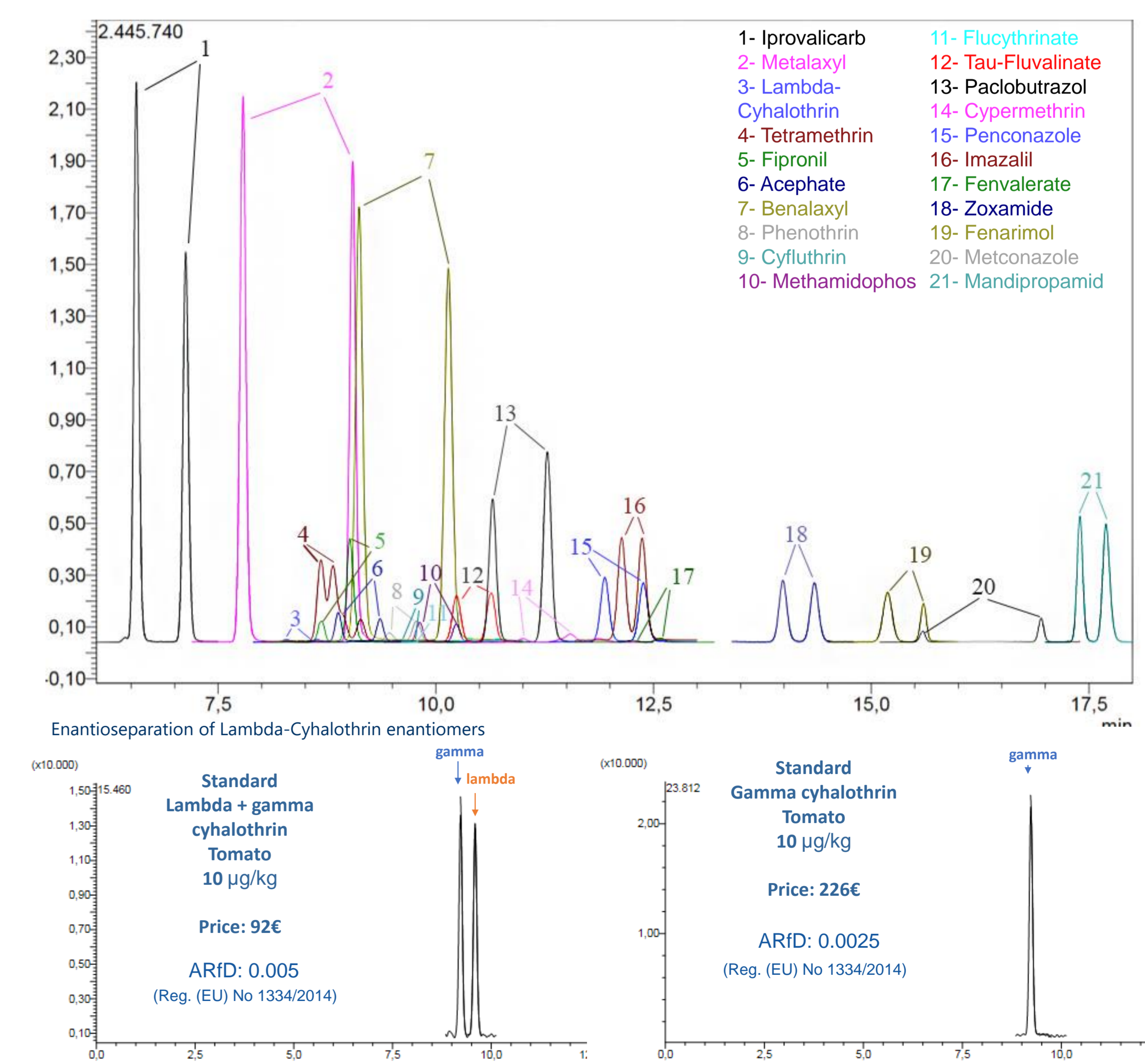


Matrix Effect	Pear		Zucchini		Orange		Onion		Tea	
	SFC	GC	SFC	GC	SFC	GC	SFC	GC	SFC	GC
Achrinathrin	5	10	5	7	0	94	0	44	-22	52
Bifenthrin	10	4	8	8	-7	33	-24	28	-3	5
Cyfluthrin	10	0	15	-1	-4	40	-2	23	-57	-5
Cypermethrin	-2	1	4	-2	-8	43	-17	26	-32	3
Deltamethrin	1	11	3	-3	-14	23	-63	15	-18	-
Etofenprox	0	1	-1	0	-8	21	-65	15	-10	-12
Fenprothrin	18	5	20	4	-7	41	-25	30	-1	13
Fenvalerate	0	-1	4	10	-6	24	-40	12	-32	1
Flucythrinate	-5	6	-5	1	-8	52	-37	34	-86	16
Lambda-cyhalothrin	-7	2	-6	2	-9	43	-18	25	-19	18
Permethrin	2	3	8	5	2	48	-11	28	-10	2
Phenothrin	6	9	11	12	-8	53	-17	41	-75	18
Tau-Fluvalinate	6	9	10	-4	-6	62	-12	22	-50	35
Tetramethrin	-3	4	3	6	-4	64	-2	35	-11	-38

Real Samples	Matrix	Conc. (µg/kg)	
		SFC-ESI-MS/MS	GC-EI/MS/MS
Achrinathrin	Pepper	639	633
	Pepper	397	321
Cypermethrin	Potato	135	119
	Mandarin	158	137
Etofenprox	Green Beans	502	516
	Pepper	75	80
Permethrin	Broccoli	228	184
	Mandarin	142	137

### Chiral enantioseparation

Twenty-one chiral pesticides were separated using polysaccharide stationary phase column (Lux Cellulose-1)



## CONCLUSIONS

- Supercritical fluid chromatography provides short run times
- Increased ionization efficiency consequence of the low flow reaching the ESI source and the absence of water in the mobile phase
- Weak matrix effect was observed even in complex matrices like leek and spices
- Pyrethroid analysis can be performed without any disadvantages compared to gas chromatography coupled to mass spectrometry
- Twenty-one chiral pesticides were separated including complex cases like lambda-cyhalothrin