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Evaluation of matrix effects by molecular mapping using liquid chromatography electrospray high resolution mass spectrometry

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INTRODUCTION

The presence of matrix effects is one of the major concerns in food analysis. It presence affect to analyte signal and can lead to errors in the quantification and the detection of the analytes. In this work the relation between matrix suppression and co-extracted matrix components has been investigated. Twenty three different commodities were extracted by various extraction Multi-residue Methods –MRM-, mapping their natural compounds by retention time and accurate mass. Mapping them allow to evaluate the benefit in using one specific method or what can be the main natural compounds that can interact with the target analytes.

EXPERIMENTAL SECTION: SAMPLE TREATMENT AND LC-TOF-MS ANALYSIS

SAMPLE TREATMENT

Extraction of blank matrices
Citrate buffered **QuEChERS** * [1,2]

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Blank extract

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Spiked with 140 pesticides 100 µg/L

* Modified QuEChERS
1 $CaCl_2$ addition in clean-up (0.2 g sample/ml)
2 Additional step of SPE with ZrO_2

LC-QTOF-MS

Operational conditions
Full-scan ESI (+) mode
Nebulizer: 40psi
Gas Temp : 400ºC
Cap. Voltage: 4000 V.
Frag. Voltage: 90 V

Chromatography Agilent 1200 HPLC system

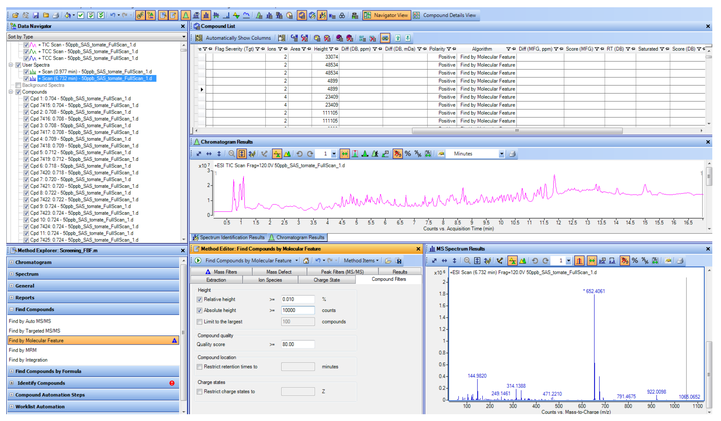
Column: XDB-C18 Agilent. 50mm x 4.6 mm (1.8 µm)

Mobile phase:

AcN (A) (5% water, 0.1% formic acid) and MiliQ Water (B) (0.1 % formic acid)
10% (A) isocratic t=1 min, then to 100 % (A) in 10 min and maintained for 6 min, Flow rate of 0.6 mL/min.

Screening Software

Agilent MassHunter "Molecular Feature Extraction"

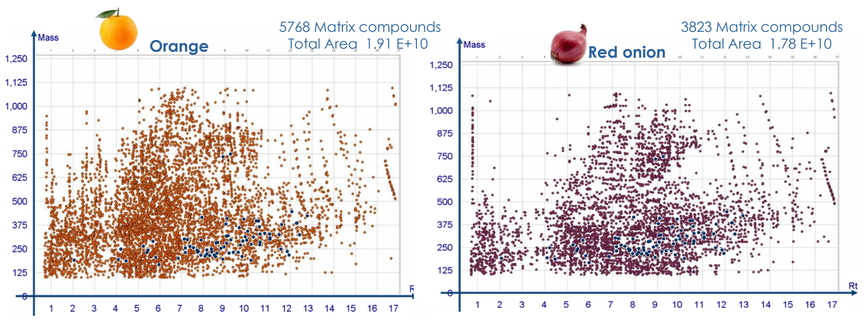


RESULTS

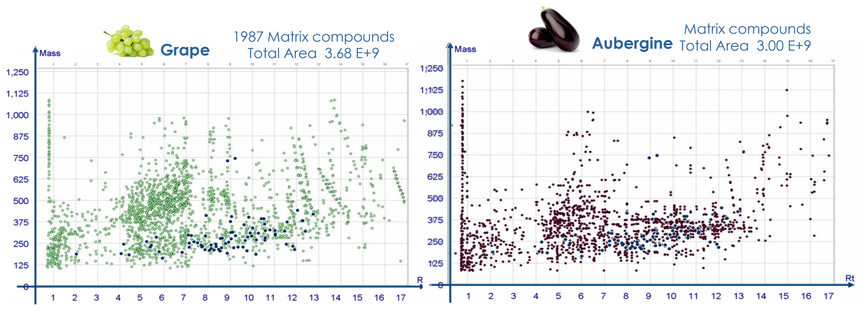
Commodity groups	Matrix	Nº of co-extracted compounds Retention Time: 0-17min	TIC (Counts)
High water content	Papaya	1270	3.70E+09
	Aubergine	1400	3.00E+09
	Plum	2008	3.12E+09
	Lettuce	1586	3.70E+09
	Tomato (Kumato type)	2155	4.18E+09
	Tomato (Cherry type)	2833	5.63E+09
	Pear	2919	3.64E+09
	Apple	3047	4.25E+09
	Mango	2649	3.77E+09
	Pepper	3419	5.51E+09
	Green bean	2398	3.92E+09
	Asparagus	2277	3.33E+09
	Cucumber	2258	5.73E+09
	Cauliflower	2560	3.66E+09
	Zucchini	3115	5.78E+09
	Broccoli	3397	4.58E+09
	Onion (white type)	2925	1.05E+10
	Onion (red type)	3823	1.78E+10
	Leek	4381	8.10E+9
High acid content and high water content	Grape (red type)	1930	3.92E+09
	Grape (white type)	1987	3.68E+09
	Grapefruit	5064	7.20E+09
	Orange	5768	1.91E+10
	Mandarin	6060	1.57E+10
Difficult or unique commodities	Chamomile	3784	1.36E+10
	Black tea	4910	1.18E+10
	Green tea	5793	1.32E+10
	Red tea	4504	1.18E+10

Mapping of Co-extracted matrix compounds-Pesticides

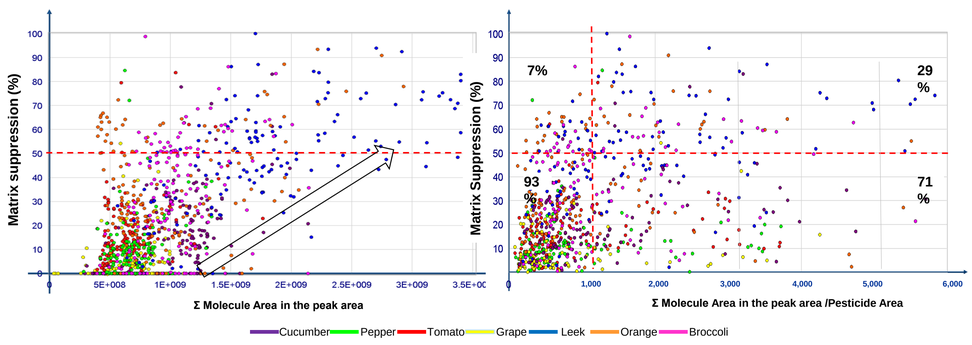
"Difficult" matrices



"Easy" matrices



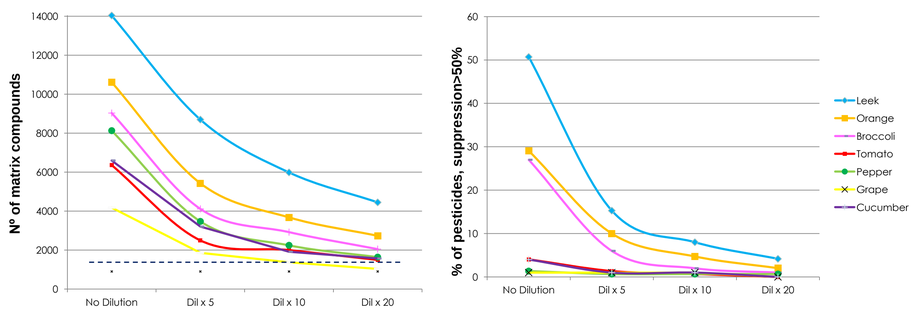
Correlation of signal suppression and co-extracted compounds



An increase of signal suppression is noted when the signal area of matrix components at the same retention time window increase

It can be established a ratio around 1000 between matrix/pesticide area as a prediction of high suppression influence.

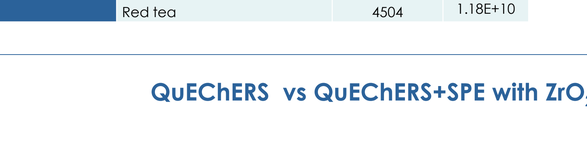
Dilution to overcome matrix effects



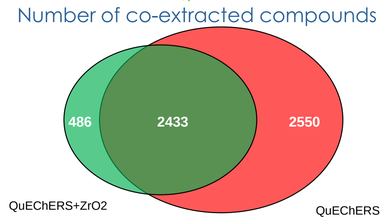
A sample dilution decreases the number of competing molecules and thus the analyte signal increases and matrix effects improved for the majority of pesticides.

Evaluation of Multi-Residue Extraction Methods

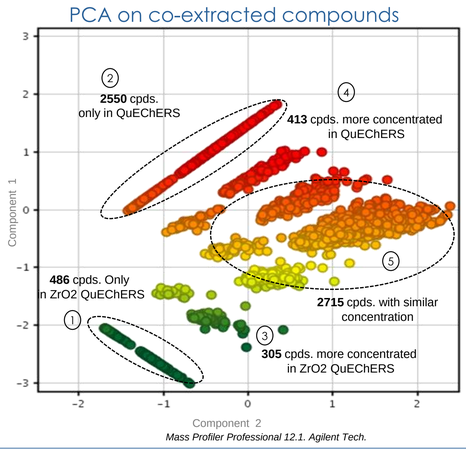
QuEChERS vs QuEChERS+SPE with ZrO_2 in Parsley matrix



Number of co-extracted compounds

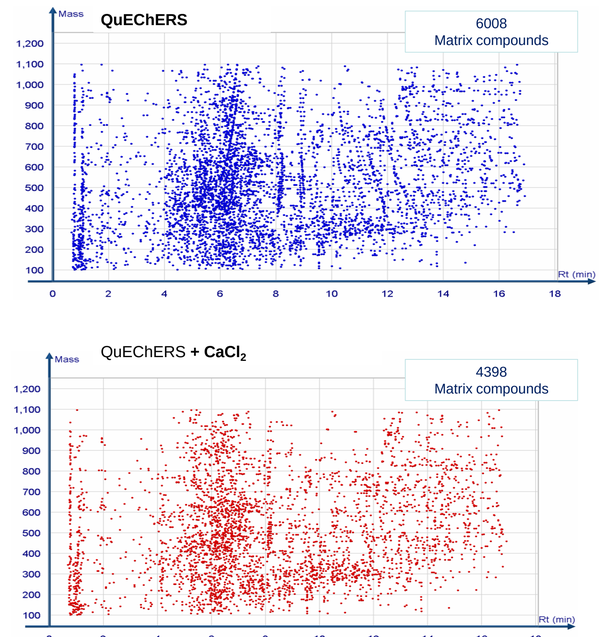


PCA on co-extracted compounds

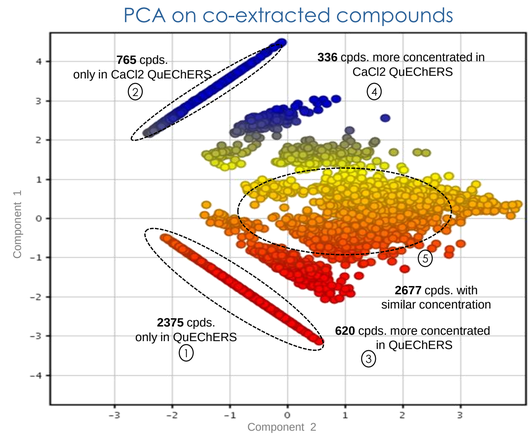


Mass Profiler Professional 12.1. Agilent Tech.

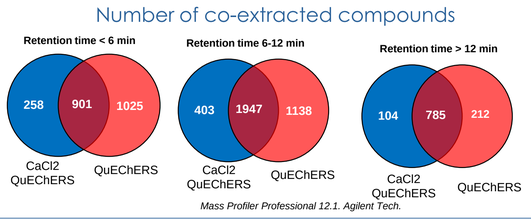
QuEChERS vs QuEChERS+$CaCl_2$ in Green tea matrix



PCA on co-extracted compounds



Number of co-extracted compounds



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CONCLUSION

Molecular mapping of matrix components by molecular weight and retention time is a very effective approach for assessing matrix difficulty, risk of matrix suppression effects and evaluation of sample preparation methods. The number and distribution of co-extracted compounds, vary much depending on vegetable matrix even those included in the same commodity group according to EU SANTE/11945/2015 guidance document. "Difficult" matrices providing a high number and concentration of natural components have associated a high suppression. Dilution of the extracts was shown as an effective method to reduce the interfering compounds and to diminish the signal suppression for the majority of the pesticides in all commodities. In tea and parsley matrices the he use of $CaCl_2$ and ZrO_2 respectively, in the clean-up step, showed to be much more efficient removing interfering compounds than the original QuEChERS clean-up.

The authors acknowledge funding support from the European Commission, DG SANCO (Specific Agreement No. 5 to Framework Partnership Agreement No. SANCO/2005/FOOD SAFETY/0025-Pesticides in fruit and vegetables)