PESTICIDE RESIDUE RESEARCH GROUP

European Union Reference Laboratory for Pesticide Residues in Fruits and Vegetables
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APPLICATION OF SUPERCRITICAL FLUID CHROMATOGRAPHY COUPLED TO TANDEM MASS SPECTROMETRY FOR PESTICIDE ANALYSIS IN FRUITS AND VEGETABLES

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INTRODUCTION

Supercritical fluid chromatography (SFC) uses carbon dioxide (CO_2) as a component of the mobile phase. The CO_2 when is put through specific conditions of temperature (31,1°C) and pressure (73 bar) acts as a solvent. This type of mobile phase provides different separation than combination of water and an organic solvent.

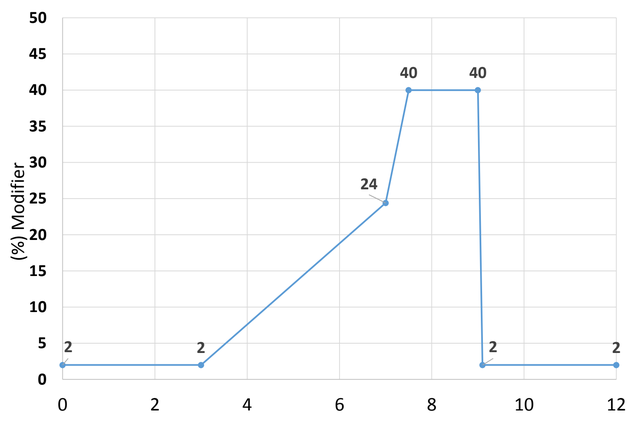
A fast analytical method with supercritical fluid chromatography coupled to triple quadrupole mass spectrometry was validated to quantify 164 pesticides in three different matrices (tomato, orange and leek). A CO_2 gradient with MeOH as co-solvent was employed. Methanol was used also as post-column solvent (added after the chromatographic column).The duration of the method of analysis was 12 minutes eluting the last compound at the minute 7.3.

EXPERIMENTAL

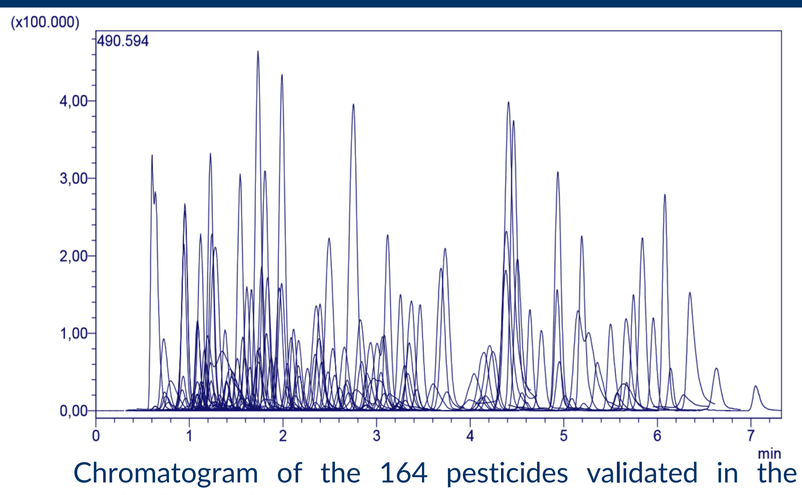
System: Nexera UC coupled to a Shimadzu LC-MS 8060

SFC parameters:
- Injection volume: 2µL
- Flow rate: 1,5 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 $HCOONH_4$
  Make up: MeOH 5mM $HCOONH_4$ 0.1% HCOOH
- Gradient time: 9 min + 3 min reequilibration

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



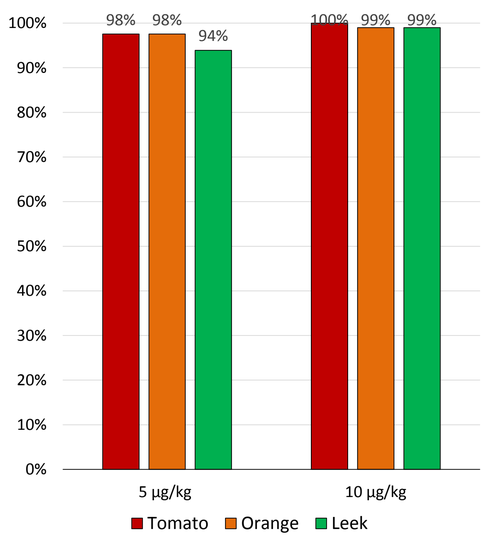
Total flow: 1,5 mL/min



Chromatogram of the 164 pesticides validated in the method spiked at the concentration of 10µg/Kg in tomato.

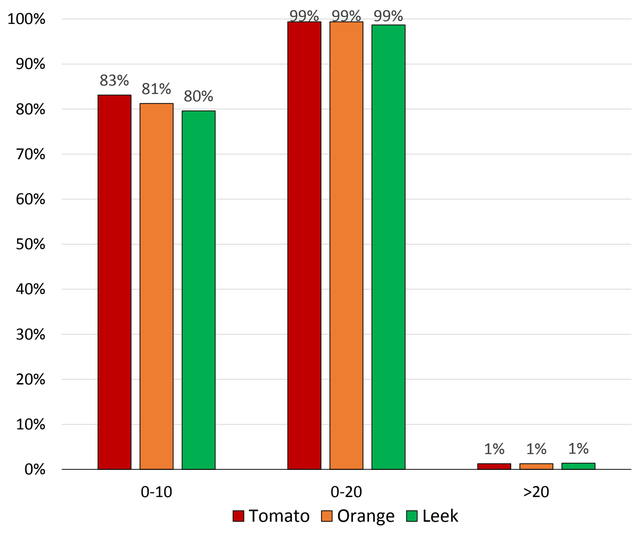
RESULTS AND DISCUSSION

Percentage of identified compounds

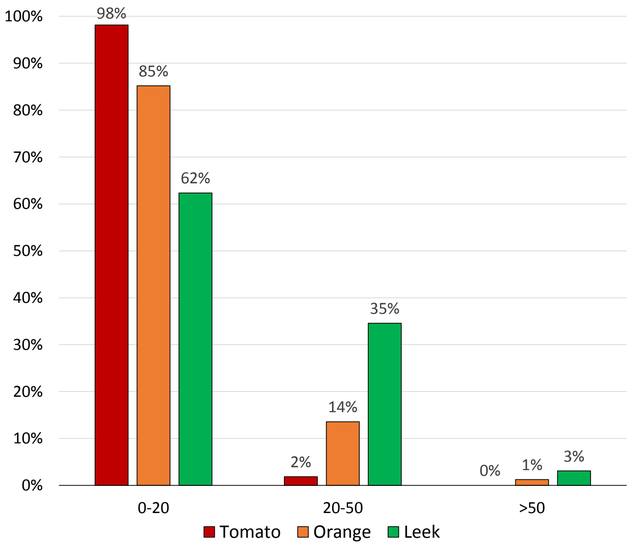


Reproducibility

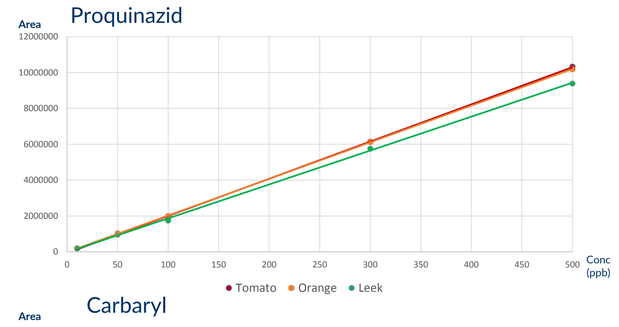
For Identified compounds at 5µg/kg



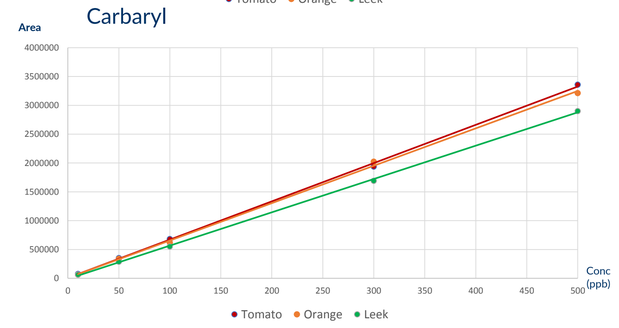
Matrix Effect



Proquinazid

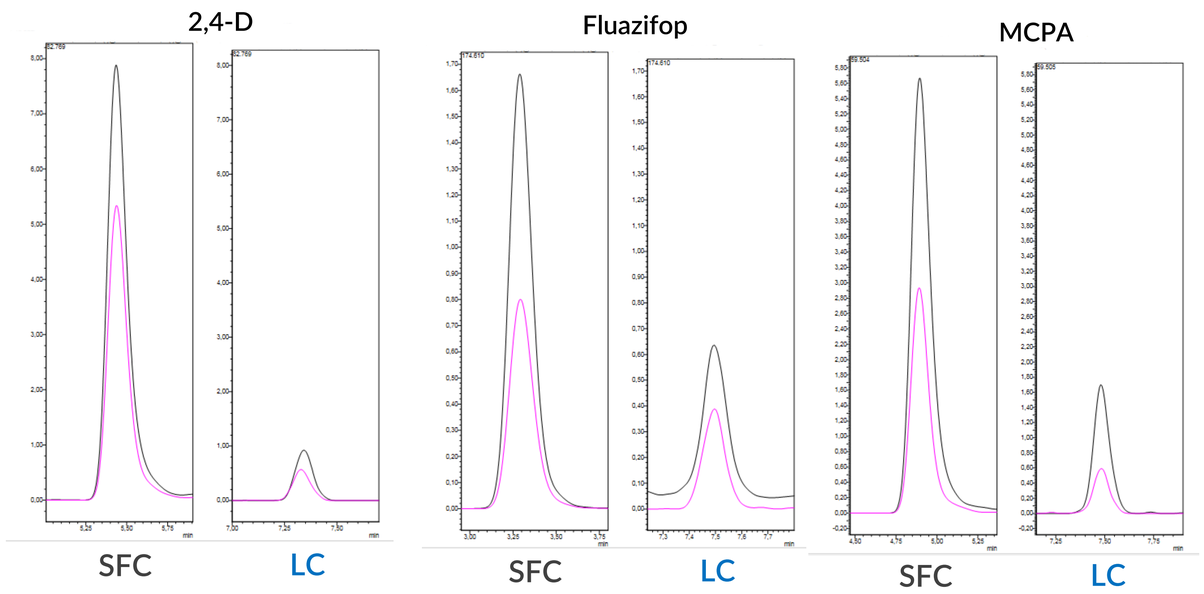


Carbaryl



Sensitivity of some acidic/polar compounds

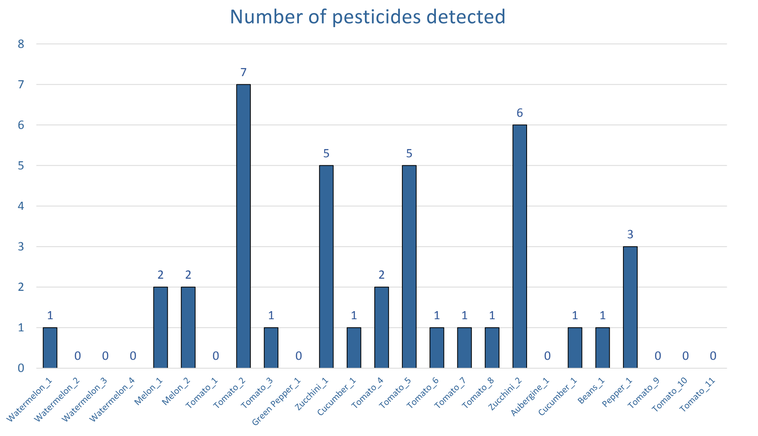
Comparison of the sensitivity for the same compounds in liquid and critical fluid chromatography.



Real Samples

Fruits and vegetables

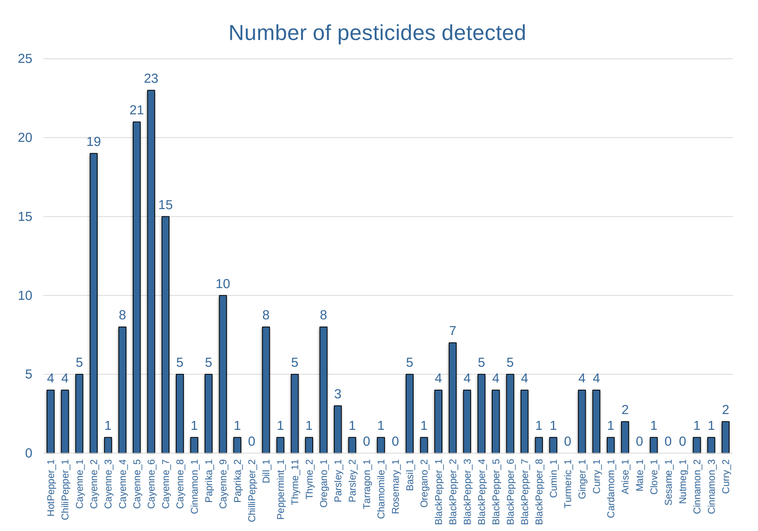
Number of samples analyzed	25
Samples with pesticides	18 (72%)
Range of pesticides detected per sample (LOQ: 5 µg/kg)	0 -7
Samples with pesticides above MRL	1 (4%)
Most detected pesticides	Chlorantraniliprole (3) Cyprodinil (3) Fenpyroximate (3) Fluopyram (3)



Real Samples

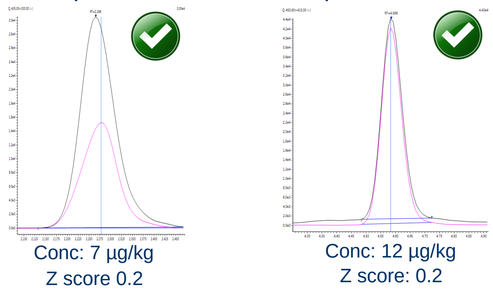
Spices

Number of samples analyzed	50
Samples with pesticides	43 (86%)
Range of pesticides detected per sample (LOQ: 5 µg/kg)	0 -23
Samples with pesticides above MRL	23 (46%)
Most detected pesticides	Carbendazim (21) Imidacloprid (16) Acetamiprid (13)



Proficiency Test

Fipronil in eggs (JRC-GEEL 2017)

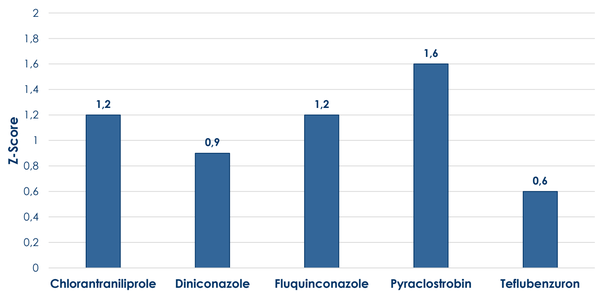


Conc: 7 µg/kg
Z score 0.2

Conc: 12 µg/kg
Z score: 0.2

Proficiency Test

Pesticides Residues in pear purée (FAPAS 2017)



CONCLUSIONS

- Supercritical fluid chromatography facilitates the high flow rates providing short analysis times.
- Despite low injection volume (2µL) the developed SFC-MS/MS method allowed the identification of the majority of 164 target pesticides at the concentration of 5 µg/kg in tomato, orange and leek.
- The majority of the analytes showed no significant matrix effects. For 98% of the study pesticides in tomato, 85% in orange and 62% in leek, the suppression was lower than 20%.
- The absence of water provide better sensitivity of some acidic/polar compounds. Furthermore, the use of 100% organic solvent improves ionization efficiency.

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