PESTICIDE RESIDUE RESEARCH GROUP

European Union Reference Laboratory for Pesticide Residues in Fruits and Vegetables
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Supercritical fluid chromatography coupled to tandem mass spectrometry for the analysis of captan and folpet in fruits and vegetables.

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INTRODUCTION

Captan and folpet are pesticides widely used in agriculture practices; however, they present some difficulties to be analyzed. These troublesome compounds are not amenable compounds by liquid chromatography (LC), and, as they are thermally labile pesticides, experience degradation in the source during gas chromatography (GC) injection. Their metabolites phthalimide (PI) and 1,2,3,6-tetrahydrophthalimide (THPI) can be analyzed; nevertheless, the origin of these metabolites can be produced from other sources. As opposed to gas chromatography injection, no degradation is observed in the electrospray (ESI) source during supercritical fluid chromatography (SFC) analysis. The analysis of captan and folpet is necessary to avoid quantitation uncertainties.

EXPERIMENTAL

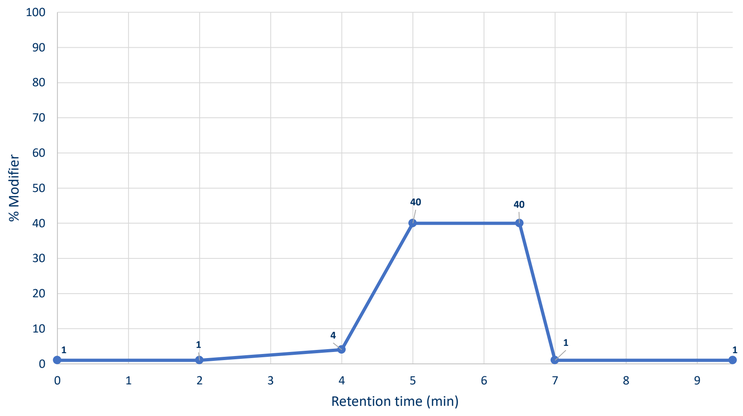
System: Shimadzu Nexera UC coupled to LC-MS 8060

SFC parameters:
- Injection volume: 5µL
- Flow rate: 1,3 mL/min
- Make up flow: 0,08 mL/min
- Oven temperature: 40ºC
- BPR pressure: 150 bar
- BPR Temperature: 50ºC
- Mobile Phases:
  Modifier: MeOH 1mM $HCOONH_4$
  Make up: MeOH 5mM $HCOONH_4$ 0.1% HCOOH

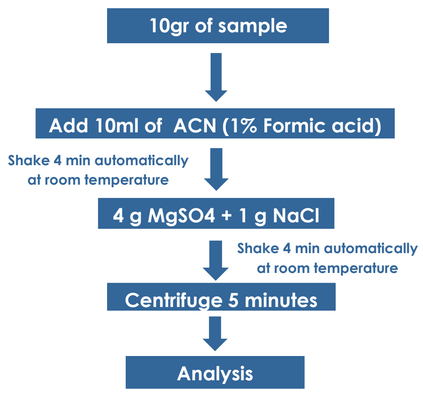
MS parameters:
- Ion source: ESI

Dwell time: 5 ms
Nebulizing Gas Flow: 3 L/min
Heating Gas Flow: 10 L/min
Drying Gas Flow: 10 L/min
Interface temperature: 125ºC
DL temperature: 125ºC
Heat Block Temperature: 150ºC

Gradient



QuEChERS extraction method

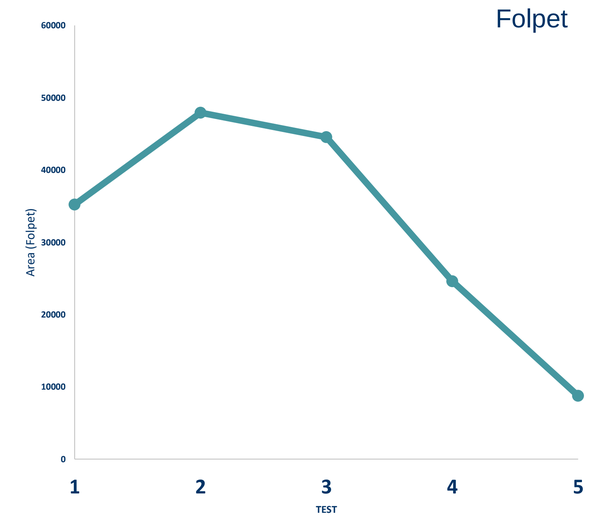


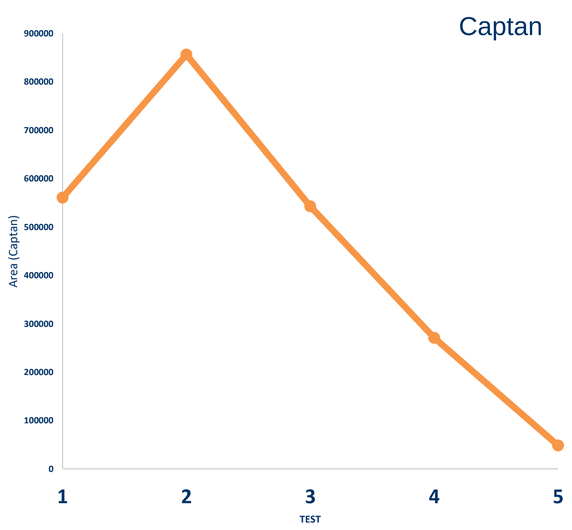
RESULTS AND DISCUSSION

Ion source optimization

The same vial (100 µg/kg) was injected multiple times applying different temperature parameters of the ESI source

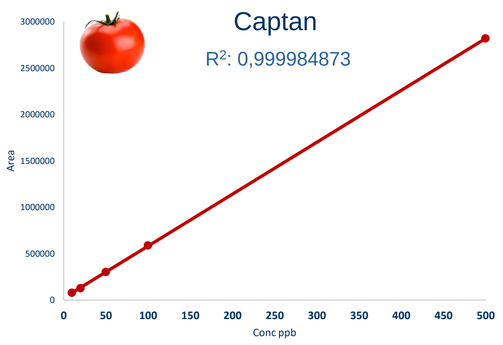
Temperature test ESI	Interface (C°)	DL (C°)	Heat block (C°)
T1	100	100	150
T2	125	125	200
T3	150	150	300
T4	200	200	300
T5	300	250	400

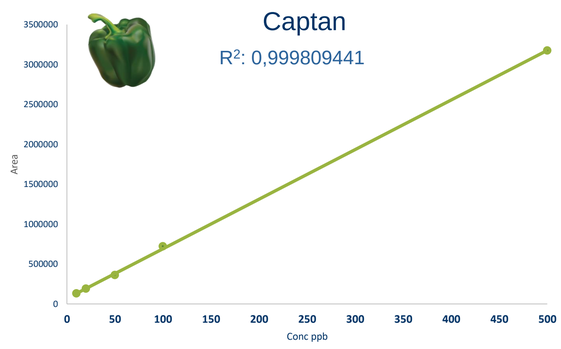


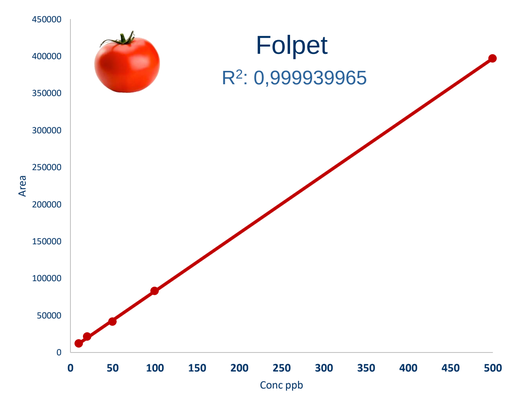


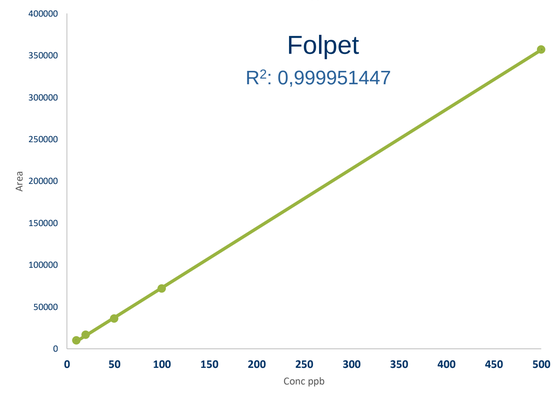
Linearity

Calibration curves were prepared at 5 different concentration levels (10,20,50,100,500 µg/kg)



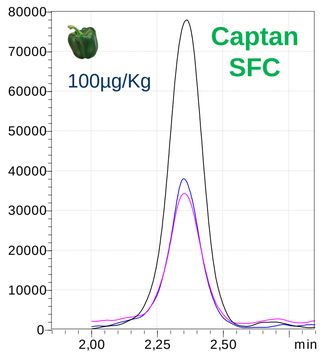


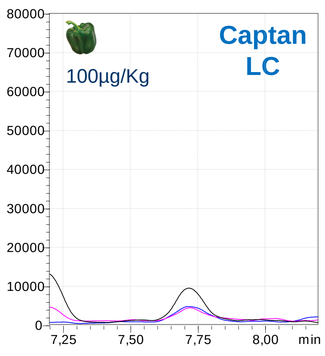


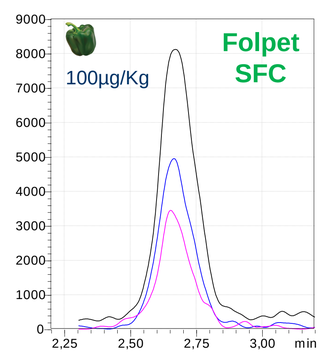


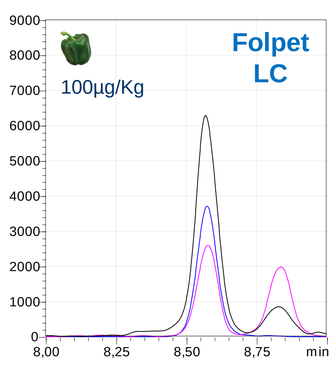
SFC vs LC

The same vial injected changing the type of chromatography (ESI parameters maintained).



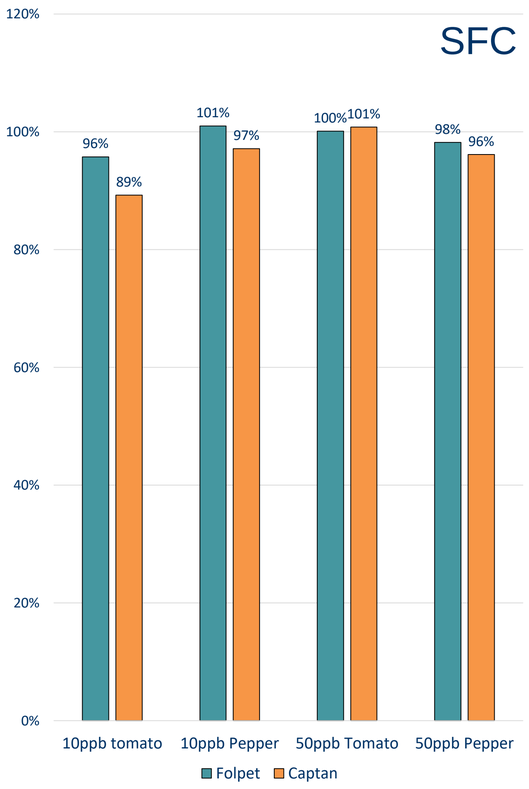


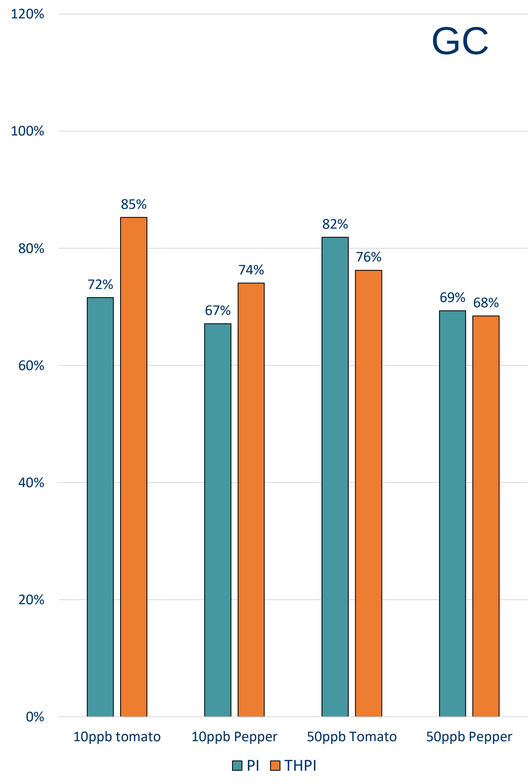




Recoveries

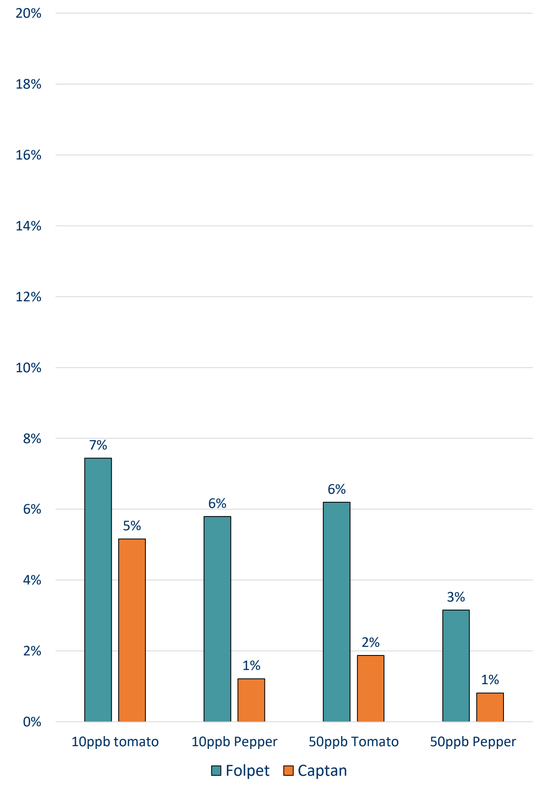
Tomato and pepper samples were spiked at 10 and 50 µg/kg . The recoveries were studied by SFC and GC.





Reproducibility SFC

3 replicates.



CONCLUSIONS

- The ion source optimization proves that the optimum temperatures for captan and folpet are 125, 125 and 200ºC for interface, DL and heat block, respectively.
- A direct comparison between SFC and LC demonstrates that higher sensitivity can be obtained for captan and folpet using supercritical fluid chromatography.
- The recoveries of both compounds using SFC were between the 70-120% range for tomato and pepper matrices at 10 and 50 µg/Kg concentration levels.
- The reproducibility results were below 10% in all the studied cases.

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