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Supercritical fluid chromatography coupled to tandem mass spectrometry for the analysis of pesticide residues in dried spices

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INTRODUCTION

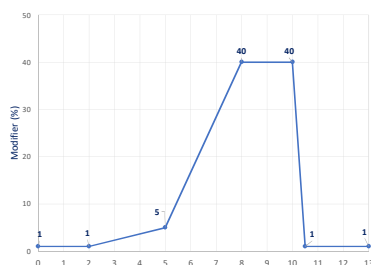
In the last decade, the production and consumption of spices in Europe have doubled in terms of area harvested and production quantity. Similar trends are observed worldwide during the same period. Spices are complex matrices that contain large amounts of essential oils, plant nutrients and secondary metabolites such as flavonoids, terpenes and alkaloids. These interfering matrix components produce ion enhancement or suppression which can be very strong and depend on the origin of the sample. This study describes the improvement of sensitivity and the reduction of the ion suppression that can be achieved by supercritical fluid chromatography (SFC) in the analysis of dried spices as difficult matrices.

EXPERIMENTAL

System: Shimadzu Nexera UC coupled to LC-MS 8060

SFC parameters:

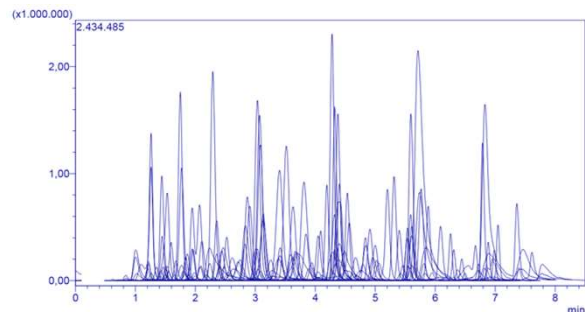
- Injection volume: 2µL
- Flow rate: 1,3 mL/min
- Make up flow: 0,08 mL/min
- Oven temperature: 40°C
- BPR pressure: 150 bar
- BPR Temperature: 50°C
- Column: Shim-Pack UC-X RP, 3µm 2.1x250mm
- Mobile Phases:
 - Modifier: MeOH 1mM HCOONH₄
 - Make up: MeOH 5mM HCOONH₄ 0.1% HCOOH



Total flow: 1,3 mL/min

MS parameters:

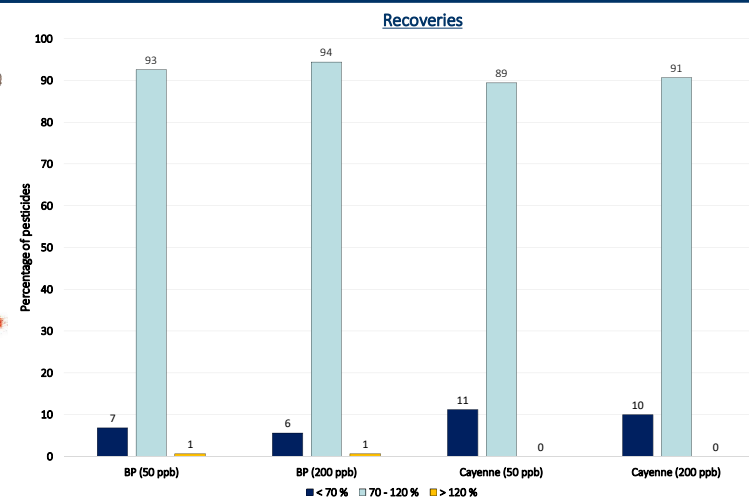
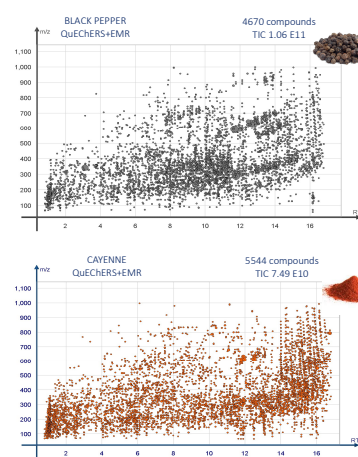
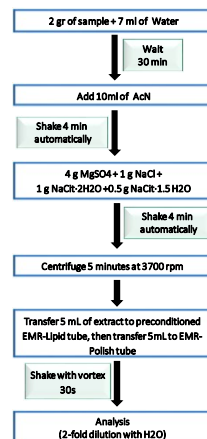
- Ion source: ESI
- Polarity: Positive and negative
- Schedule MRM software features
- Dwell time: 5 ms



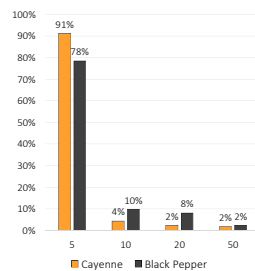
Chromatogram of the 162 pesticides validated in the method spiked in the vial at the concentration of 5µg/kg in Cayenne.

RESULTS AND DISCUSSION

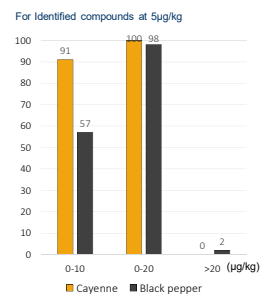
Extraction method



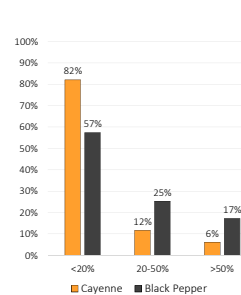
Percentage of identified compounds



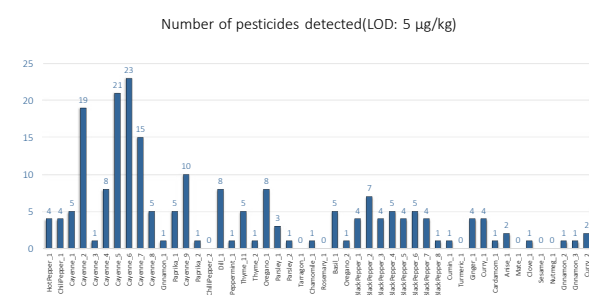
Reproducibility



Matrix Effect



Real Samples



CONCLUSIONS

- Supercritical fluid chromatography facilitates the high flow rates providing short analysis times.
- Increased ionization efficiency consequence of the low flow reaching the ESI source and the absence of water in the mobile phase.
- At least 95% of the compounds showed good recoveries for both matrices at the selected concentration levels (50 µg kg⁻¹ and 200 µg kg⁻¹).
- Regarding matrix effect, only 6% of the compounds in cayenne and 17% in black pepper showed strong signal suppression.
- Most of the pesticides studied met the requirements to be identified at the lowest concentration level of 5 µg kg⁻¹ in both matrices.