Pesticide residue analysis using SFC and LC both coupled to mass spectrometry

EPRW 2022 BOLOGNA

Víctor Cutillas[1], Carmen Ferrer[1], Amadeo R. Fernández-Alba[1]

European Union Reference Laboratory for Pesticide Residues in Fruits & Vegetables, University of Almería, Department of Chemistry and Physics. Agrifood Campus of International Excellence (ceiA3), Ctra. Sacramento s/n, La Cañada de San Urbano, Almeria, 04120, Spain. E-mail: **amadeo@ual.es**

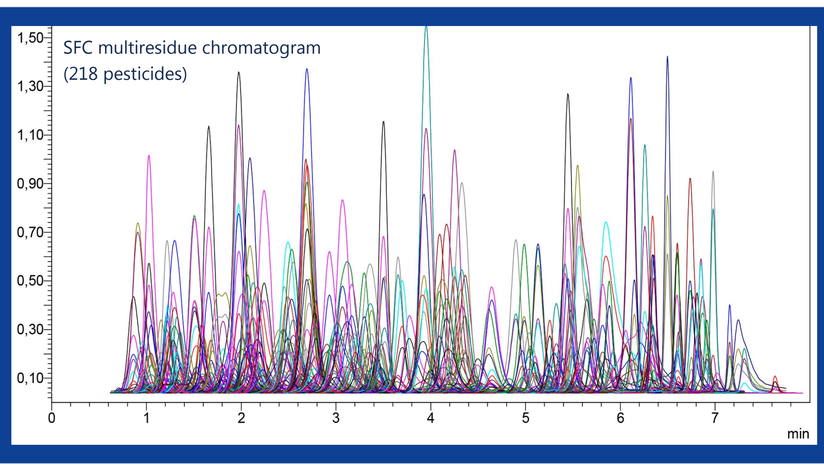
Research paper:

UNIVERSIDAD DE ALMERÍA

Co-funded by the European Union

Overview

Since the introduction of modern mass spectrometer devices, reverse-phase liquid chromatography (LC) has been used as the prevailing technique for the analysis of relatively polar and thermolabile pesticides. The system robustness and the broad scope covered made it one of the preferred approaches to work coupled to mass spectrometry in routine laboratories. On the other hand, the numerous advances and achievements in the last decades provided Supercritical fluid chromatography (SFC) of the necessary quality to be an alternative to the conventional liquid chromatography system.

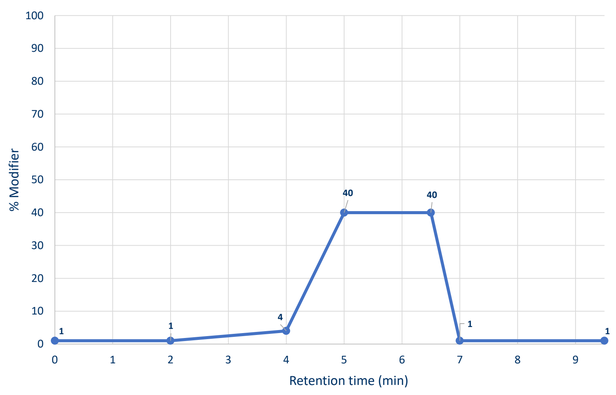


In the present study, a multiresidue method of 215 pesticide was tested using supercritical fluid chromatography (SFC) and liquid chromatography (LC), both coupled to the same triple cuadrupole mass spectrometer (MS/MS). The experiments were carried out using tomato, leek, onion and orange as a representative fruit and vegetables matrices. How the different ion source temperatures affect to the sensitivity of each chromatography was evaluated. Detailed research was performed to the pesticides that presented higher sensitivity in each technic, their chemical groups and octanol/water coefficients were studied. Finally, the impact of the matrix effects using LC or SFC were evaluated.

Methods

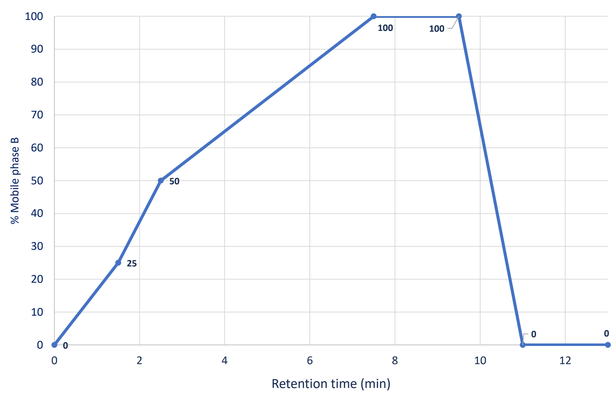
SFC parameters:

- Injection volume: 2µL
- Flow rate: 1,3 mL/min
- Make up flow: 0,08 mL/min
- Oven temperature: 40ºC
- Column: Shimpack UC-X RP C18 2.1x250mm, 3 µm
- BPR pressure: 150 bar
- BPR Temperature: 50ºC
- Mobile Phases:
  Modifier: MeOH 1mM $HCOONH_4$
  Make up: MeOH 5mM $HCOONH_4$ 0.1% HCOOH



LC parameters:

- Injection volume: 2µL
- Flow rate: 0,3 mL/min
- Oven temperature: 40ºC
- Column: Shimpack UC-X RP C18 2.1x150mm, 3 µm
- Mobile Phases:
  A: 98% H_2O 2% MeOH 5mM $HCOONH_4$ 0.1% HCOOH
  B: 98% MeOH 2% H_2O 5mM $HCOONH_4$ 0.1% HCOOH



MS parameters:

- Ion source: ESI
- Interface temperature: 350ºC
- Desolvation line temperature: 200ºC
- Heated block temperature: 400ºC
- Nebulizing Gas flow: 3 L/min
- Heating Gas flow: 3 L/min
- Drying Gas flow: 3 L/min
- Working mode: MRM
- Dwell time: 4ms
- Voltage: 4 kV
- Switching polarity time: 5msec

Figure 1. Shimadzu UC – LCMS 8060

Results

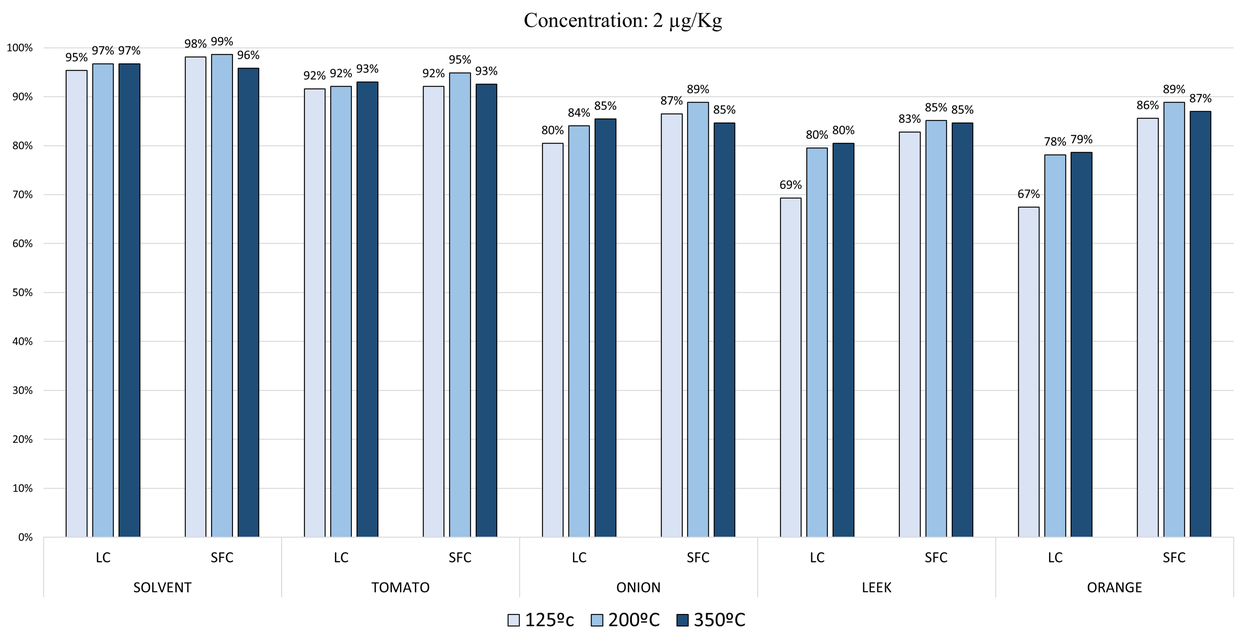


Figure 2. Percentage of identified compounds at the three ion source temperatures tested. The 215 pesticides were evaluated in solvent and tomato, onion, leek, and orange matrices by both techniques.

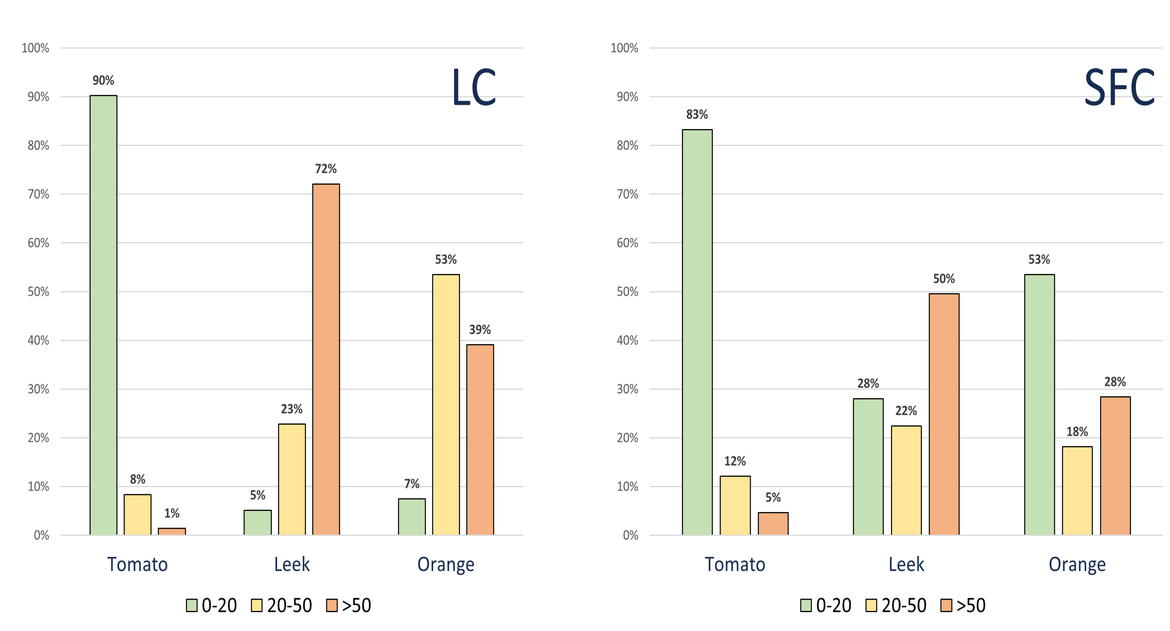


Figure 4. Matrix effects were calculated by comparing the slope values of the calibration curves in solvent with those values of the matrix-matched calibration curves. Matrix effects between 0 and 20% were considered low or non-existent (Green); however, modifications of the signal between 20 and 50% (Yellow) and >50% (Orange) were considered as medium and strong matrix effects, respectively.

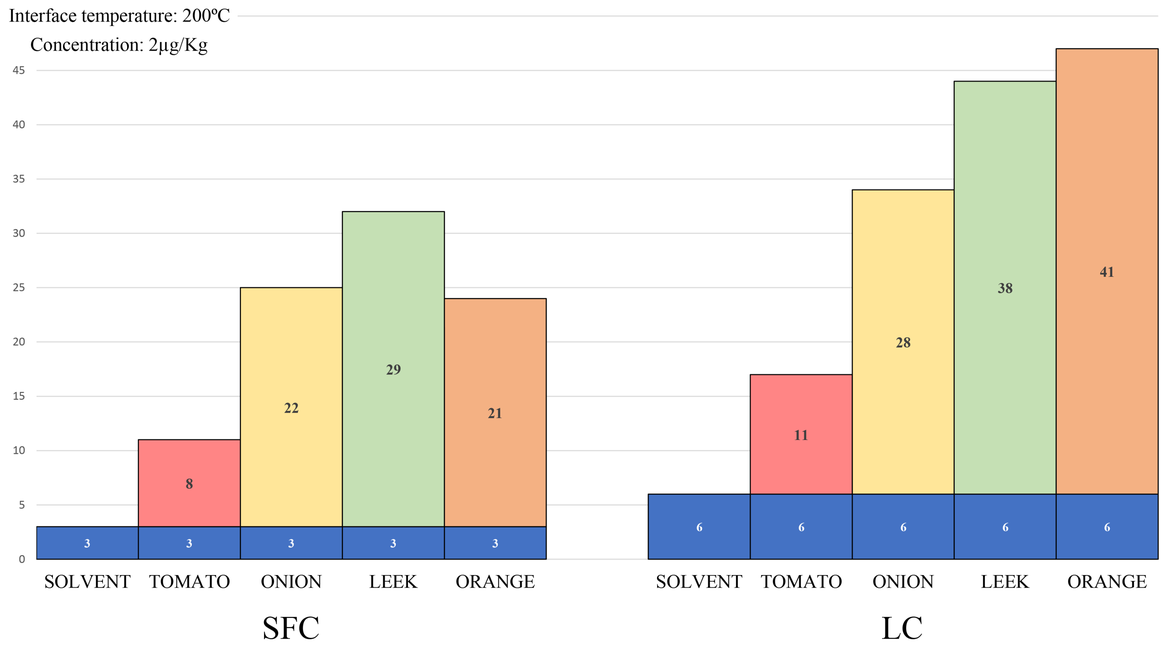


Figure 3. Number of non-identified compounds by SFC and LC in solvent and four different matrices at the concentration level of 2 µg/kg.

Conclusions

- LC needed the highest temperature tested (350 °C) to achieve the highest sensitivity. However, in SFC, the sensitivity differences were much lower between the higher and the lower temperatures tested.
- Focusing on the compounds that presented higher sensitivity in each technic, it was observed that triazoles were the chemical group whose sensitivity was higher in SFC, followed by organophosphates. In LC, a majority correspond to organophosphates.
- These pesticides were also studied in terms of their octanol/water partition coefficient and the values were similar in both cases, concluding that this parameter did not work as a tool for predicting which chromatography will show higher sensitivity for each pesticide.
- Higher ion suppression was observed in LC when complex matrices were analyzed.

Co-funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Health and Digital Executive Agency (HaDEA). Neither the European Union nor the granting authority can be held responsible for them.