Evaluation of supercritical fluid chromatography coupled to tandem mass spectrometry for pesticide residues in food

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Introduction

Supercritical fluid chromatography coupled to triple quadrupole mass spectrometry (SFC-MS/MS, Nexera UC with LCMS-8060, Shimadzu Corporation, Kyoto, Japan) has been evaluated for pesticide residues in food. In order to check its advantages and limitations it was developed a method to identify and quantify 164 pesticides in three different matrices (tomato, orange and leek).

Materials and Methods

A carbon dioxide gradient with methanol (containing 1 mM ammonium formate) was used allowing a flow rate of 1.5 mL/min that made the total run time of 12 min without any problem of overpressure. Addition of a post column flow 150 µL/min of methanol with ammonium formate / formic acid was necessary to improve the ionization (Figure 2).

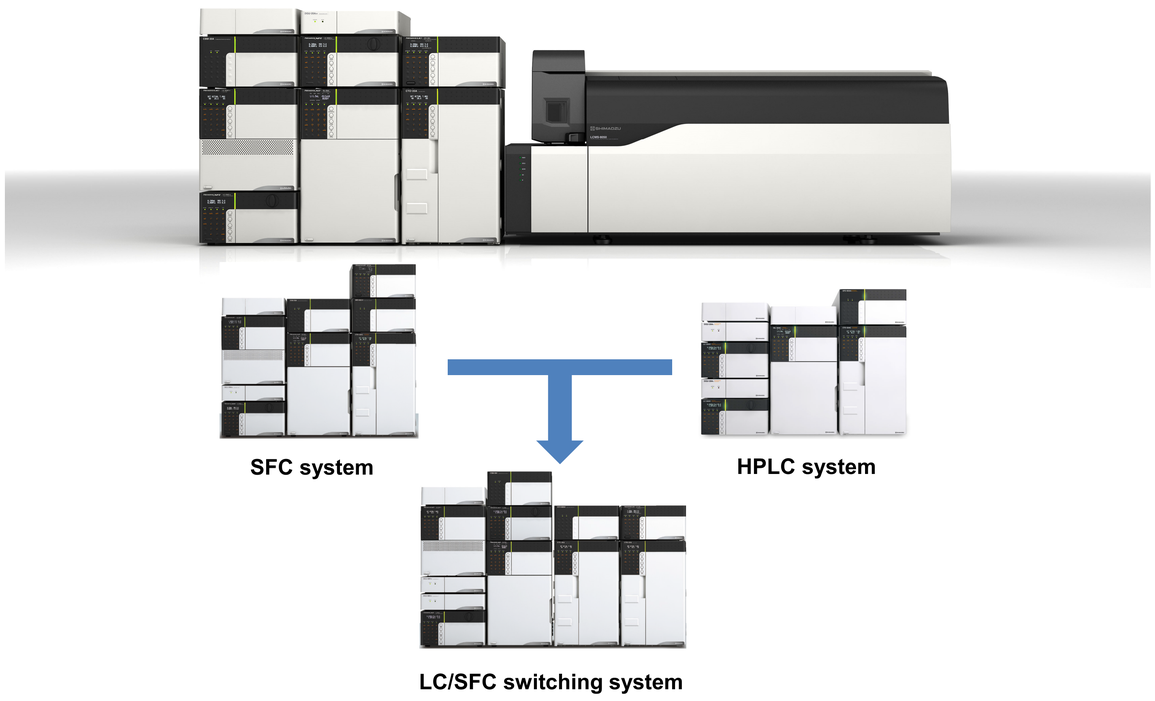

Figure 1: Top: Shimadzu Nexera UC with triplequadrupole mass spectrometer Shimadzu LCMS-8050. Bottom: LC/SFC-MS/MS switching system for automatic change between LC- and SFC-MS/MS.

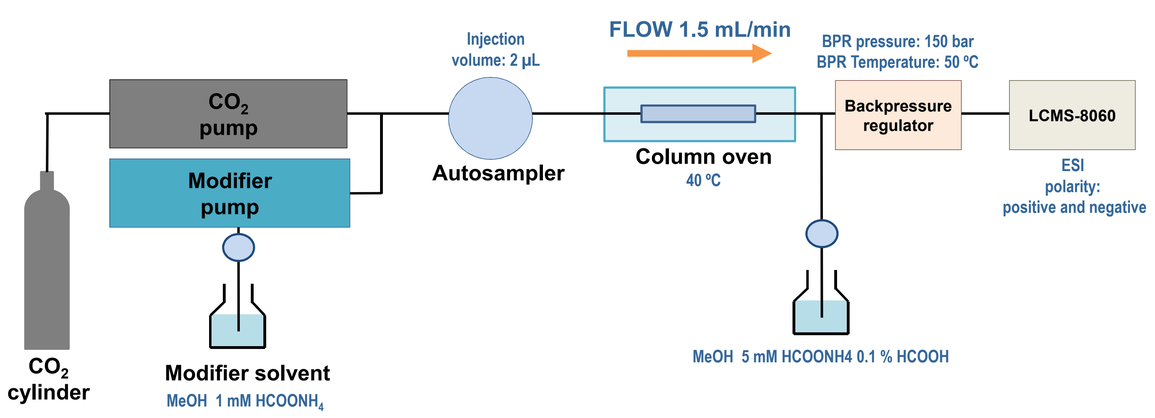

Figure 2: SFC-MS/MS conditions and system configuration

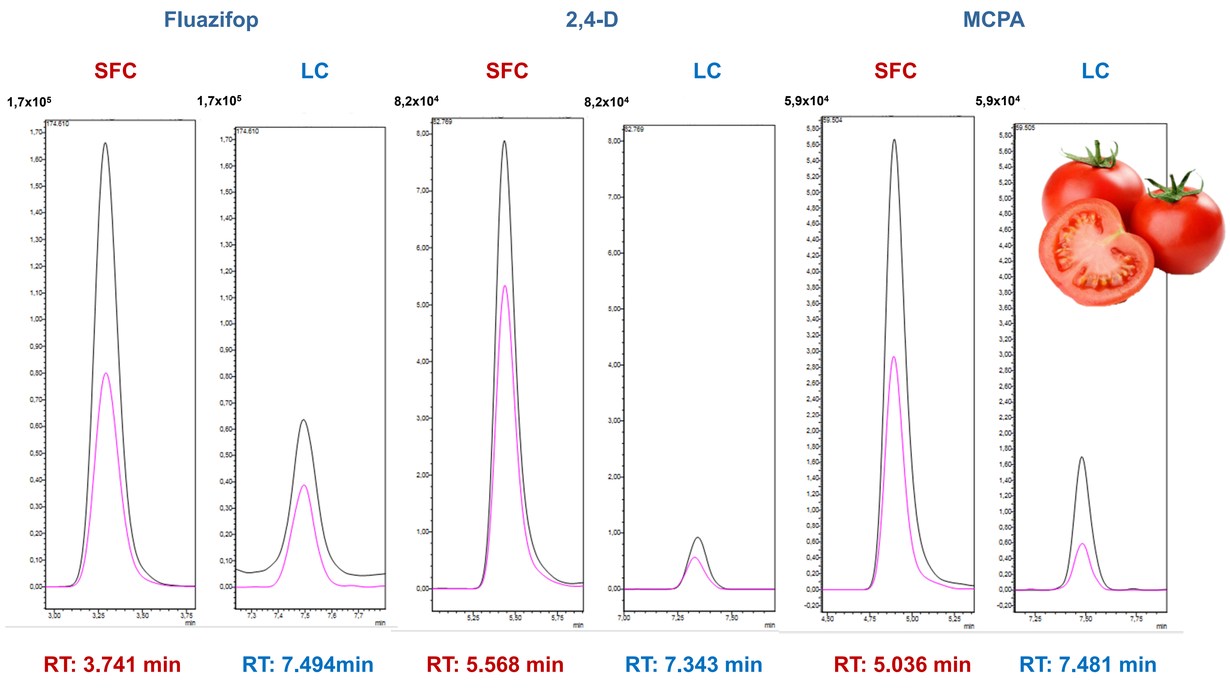

Figure 3: Examples of some compounds that increase their sensitivity using SFC-MS/MS. 100 µg/kg tomato.

Results and discussion

The matrix effect study revealed that the percentages of pesticides with irrelevant matrix effect (suppression lower than 20 %) was 99 % in tomato, 87 % in orange and 62 % in leek, whereas significant suppression (higher than 50 %) was not found in tomato and only 1 % of the compounds in orange and 3 % in leek (Figure 4). These results compare favorably with that typically obtained in LC–MS/MS.

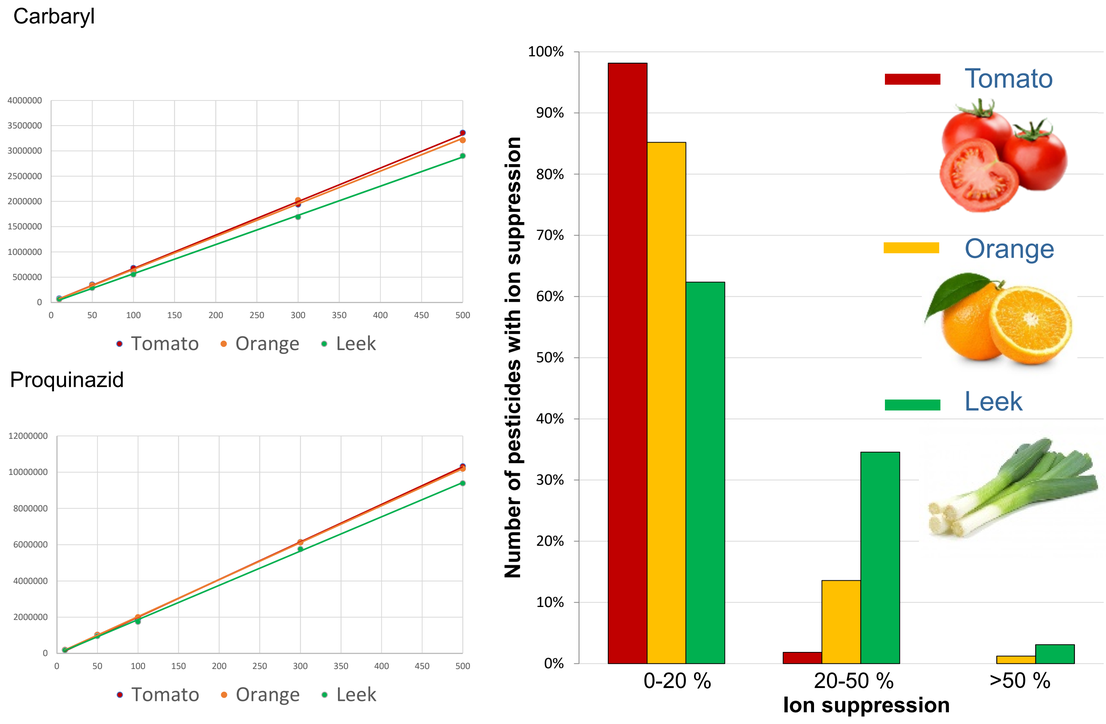

Figure 4: Matrix-effect (164 pesticides).

The absence of water in the mobile phase also provided some important advantages regarding LC–MS/MS as (i) higher retention of polar compounds in the column, which elute with high sensitivity and good peak shape and (ii) a general increase of the sensitivity of the analysis, consequence of the high ionization and ion extraction efficiency (Figure 3). Pesticides evaluated were identified following the SANTE/11813/2017. At the spiking concentration of 5 µg/kg, 98 % of the pesticides were identified in tomato, 98 % in orange and 94 % in leek, whereas for the concentration of 10 µg/kg all the compounds were identified in tomato and only spiromesifen was not identified in orange and leek. At the concentration of 20 µg/kg, spiromesifen was also identified in these two matrices. The linearity and reproducibility of the method were evaluated with results which guarantee high quality in the analytical measurements. Even though only 2 µL of final extract were injected, the sensitivity of the SFC method was enough to achieve stringent LOQs. Real samples, including 6 different fruits and vegetables, were analyzed by the SFC-MS/MS proposed method, the results being similar to those obtained by LC–MS/MS.

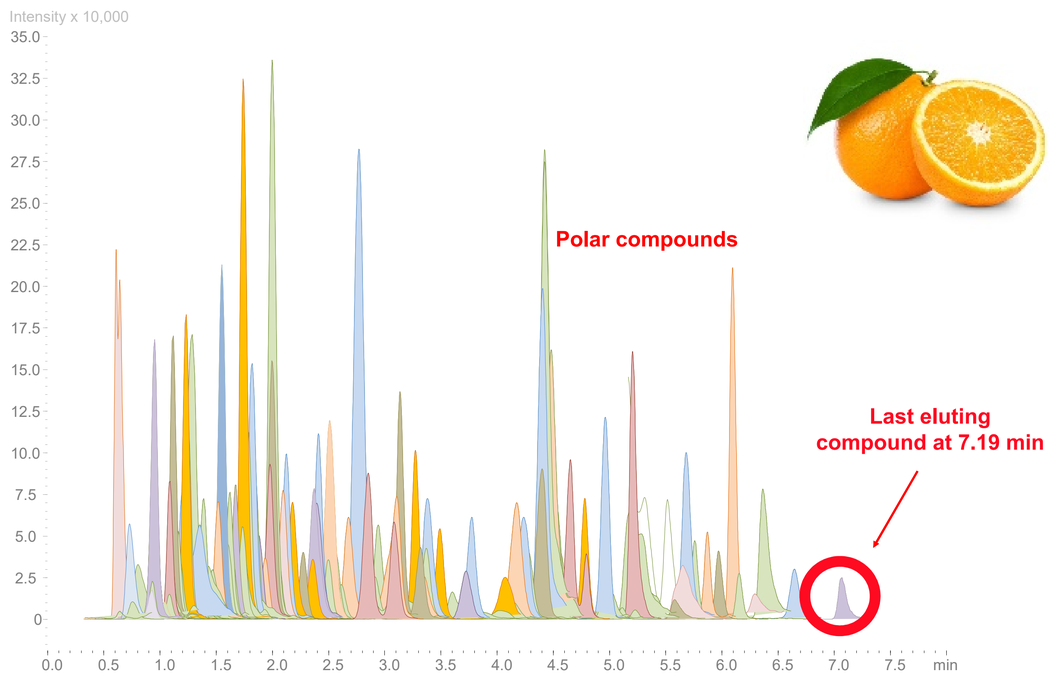

Figure 5: 164 pesticides spiked at the default MRL of 0.01 mg/kg (orange matrix).Quantifier ion is shown.

Conclusion

Carbon dioxide as mobile phase with methanol as modifier can represent a good alternative to LC-MS/MS with reduction of matrix effects and shorter run times.

Reference

V. Cutillas, M. M. Galera, Ł. Rajski, A. R. Fernández-Alba, J. Chrom. A, 2018, 1545, 67-74