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Analytical Solutions for Food Safety – a Closer Look in the Analytical Toolbox

Uwe Oppermann[1], Stephane Moreau[1], [1]Shimadzu Europa GmbH, 47269 Duisburg, Germany

Introduction

Food safety is a major concern for the European population, with many food scandals being reported in the past few years in Europe and even on a global scale. The growing world population up to 9.7 billion by 2050 will further increase the demand for food. This will require higher crop production globally, by enhancing productivity through optimized methods, fertilizers, agrochemicals and pesticides. Pesticides and their metabolites are of great concern to our society as they are harmful to human health, pollute natural resources and disturb the equilibrium of the ecosystem.

Consequently, stricter food safety regulations are being enforced around the world, placing pesticide analysis laboratories under increasing pressure to expand the list of targeted pesticides and detect analytes at lower and lower levels with high precision. National programs for pesticide monitoring in Europe, the US and Japan have set Maximum Residue Levels (MRL's) or tolerance information (EPA) for monitoring the steadily increasing number of pesticides in food products.

These MRLs are the upper legal levels of a concentration for pesticide residues in or on food to ensure the lowest possible consumer exposure. Commission Regulation (EC) No. 396/2005 lists 320 defined commodities for which 152,000 MRLs have been set. For baby food, the European legislation is even more restrictive as no more than 0.01 mg/kg of any single pesticide residue is permitted in baby food samples.

Reducing Health Risks

The hazardous level of a pesticide depends on its toxicity and a person's exposure to it. Just a single exposure can have acute effects, such as impaired vision. Long-term exposure can lead to more serious illnesses and diseases, including cancer. Because of these risks, the MRLs have been defined for any food or feed where pesticides are applied correctly according to GAP (see Table 1).
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Pesticide	Commodity	Parts per Million
Bromuconazole	Root and tuber vegetables	0.01
Bromuconazole	Bulb vegetables	0.01
Bromuconazole	Fruiting vegetables	0.01
Bromuconazole	Lettuce and salad plants	0.01
Carboxin	Citrus fruits	0.03
Carboxin	Tree nuts	0.05
Carboxin	Pome fruits	0.03
Carboxin	Stone fruits	0.03
Fenpyrazamine	Citrus fruits	0.01
Fenpyrazamine	Tree nuts	0.01
Fenpyrazamine	Pome fruits	0.01
Fenpyrazamine	Root and tuber vegetables	0.01
Pyridaben	Citrus fruits	0.3
Pyridaben	Tree nuts	0.01
Pyridaben	Pome fruits	0.9
Pyridaben	Root and tuber vegetables	0.01

Table 1: MRL´s for pesticides from various commodities

Methods

In order to comply with regulations on food safety, manufacturers of food and beverages must carefully control contaminants such as pesticides, mycotoxins and heavy metals. Shimadzu is supporting these challenges in food analysis and providing the tools for determination of contaminants in food and food packaging according to the European norms and legislations.

The most innovative method for the determination of pesticides in fruit, vegetables and spices is nowadays the supercritical fluid chromatography coupled to tandem mass spectrometry (SFC-MS/MS). The determination of mineral oil hydrocarbons (MOSH/MOAH) in food and food packaging using LC-GC online technique coupled to mass spectrometry and last not least the screening and quantitative analysis of metal impurities in food and drinks is done by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The European Union Reference Laboratories (EURL) are the authorities for pesticide residue analyses (see Regulation (EC) No. 882/2004). Four specialized EURLs are in place all over the continent. The EURL for fruits and vegetables is located in Almeria, Spain (EURL-FV).

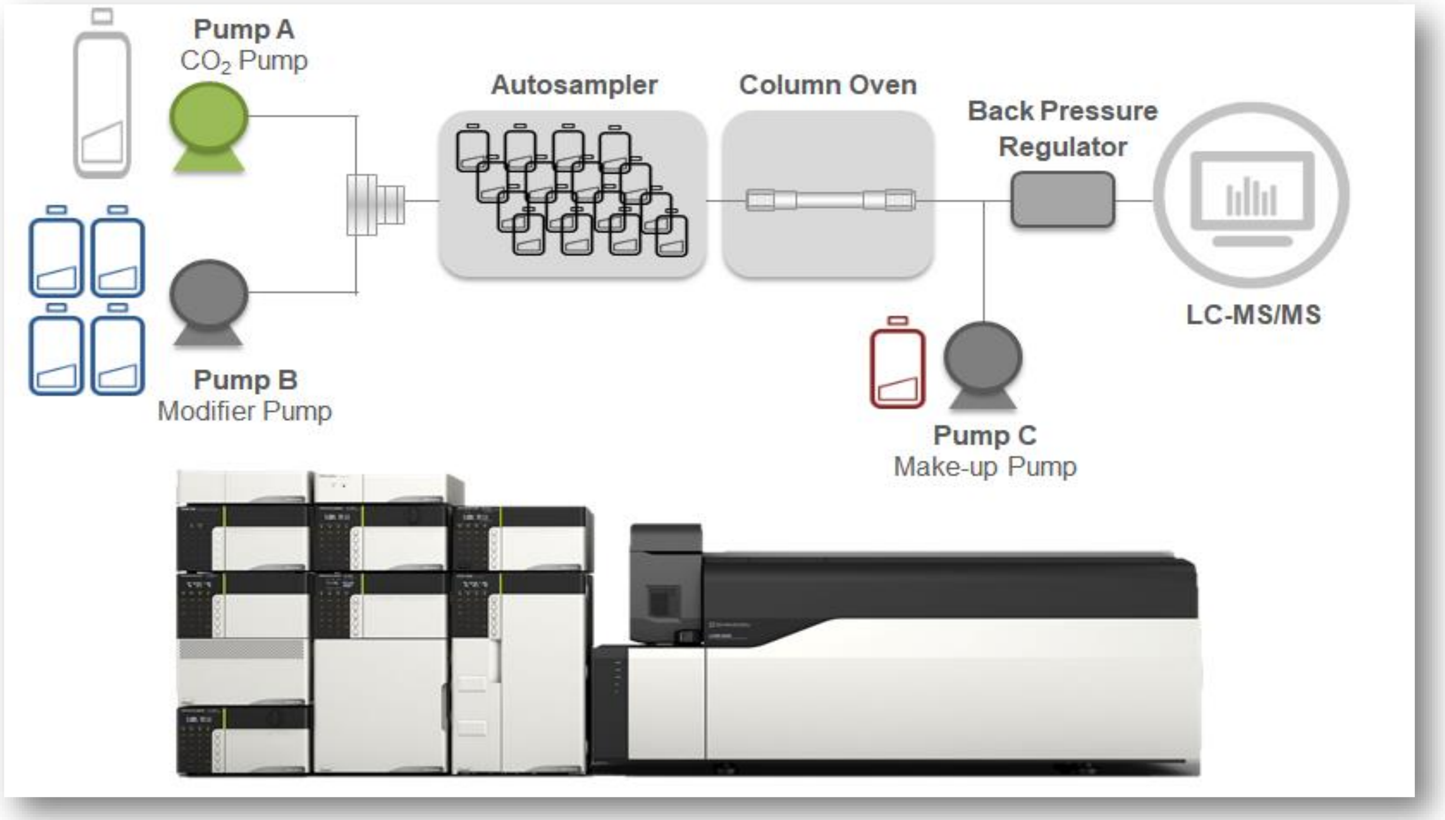

Figure 1: Shimadzu SFC-MS/MS system Nexera UC

Analytical Challenges

Pesticides are complex substances, with multiple pesticide residues belonging to multiple classes. Depending on their characteristics, such as the polarity, volatility, thermal stability and ionization efficiency, the type of instrument is chosen. A liquid chromatograph- or SFC tandem mass spectrometer (LC-MS/MS or SFC-MS/MS) or a gas chromatograph tandem mass spectrometer (GC-MS/MS). These instruments are referred to as triple quadrupole MS.

Advantages of SFC-MS/MS

The Nexera UC triple quadrupole MS solution specializes on quantitative applications requiring the highest sensitivity and robustness while delivering reliable data for routine food analyses. SFC-MS/MS can be used to separate numerous pesticides with different polarities, and it also achieves a marked increase in sensitivity for lots of compounds. Combining the specificity of the Nexera UC and the versatility of SFC-MS/MS technique is an appealing alternative to the conventional LC-MS/MS approach. The EURL-FV in Almeria, Spain, applies SFC-MS/MS for the determination of pesticide residues in food samples with fruit/ vegetable matrix such as tomato, leek and orange or spices like red and black pepper following the identification requirements of DG SANTE/11813/2017.

To help reducing the incidence of false positive and negative reporting in pesticide residue monitoring, multiple-reaction monitoring (MRM) methods have been enhanced to monitor a higher number of fragment ion transitions to increase specificity and reporting confidence. Using the Shimadzu Pesticide MRM Library accelerates analysis.

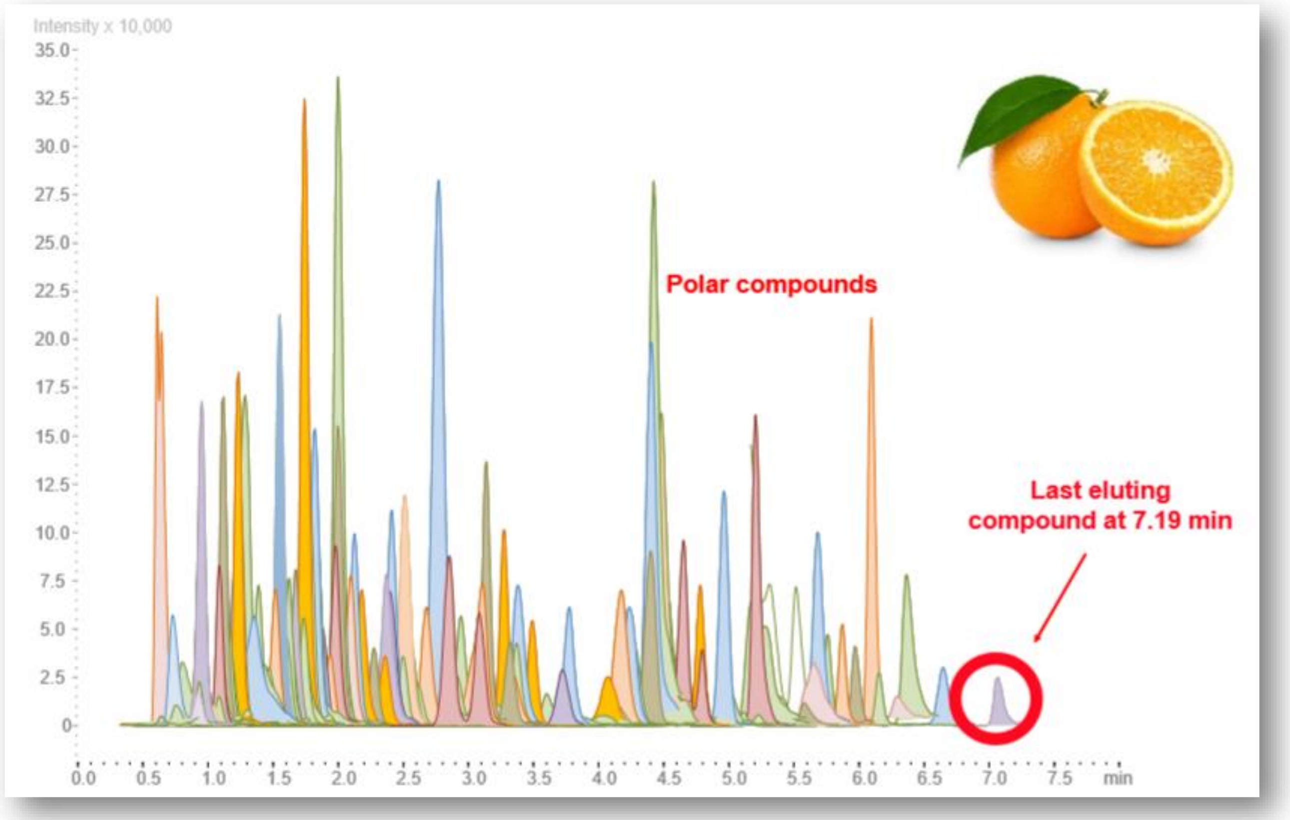

Figure 2: 164 pesticides spiked at the default MRL of 0.01 mg/kg (orange matrix). Quantifier ion is shown

Results and Discussion

The absence of water in the mobile phase provided some important advantages regarding LC–MS/MS such as higher retention of polar compounds in the column, which elute with high sensitivity and good peak shape and furthermore a general increase of the sensitivity of the analysis, consequence of the high ionization and ion extraction efficiency (Figure 3).

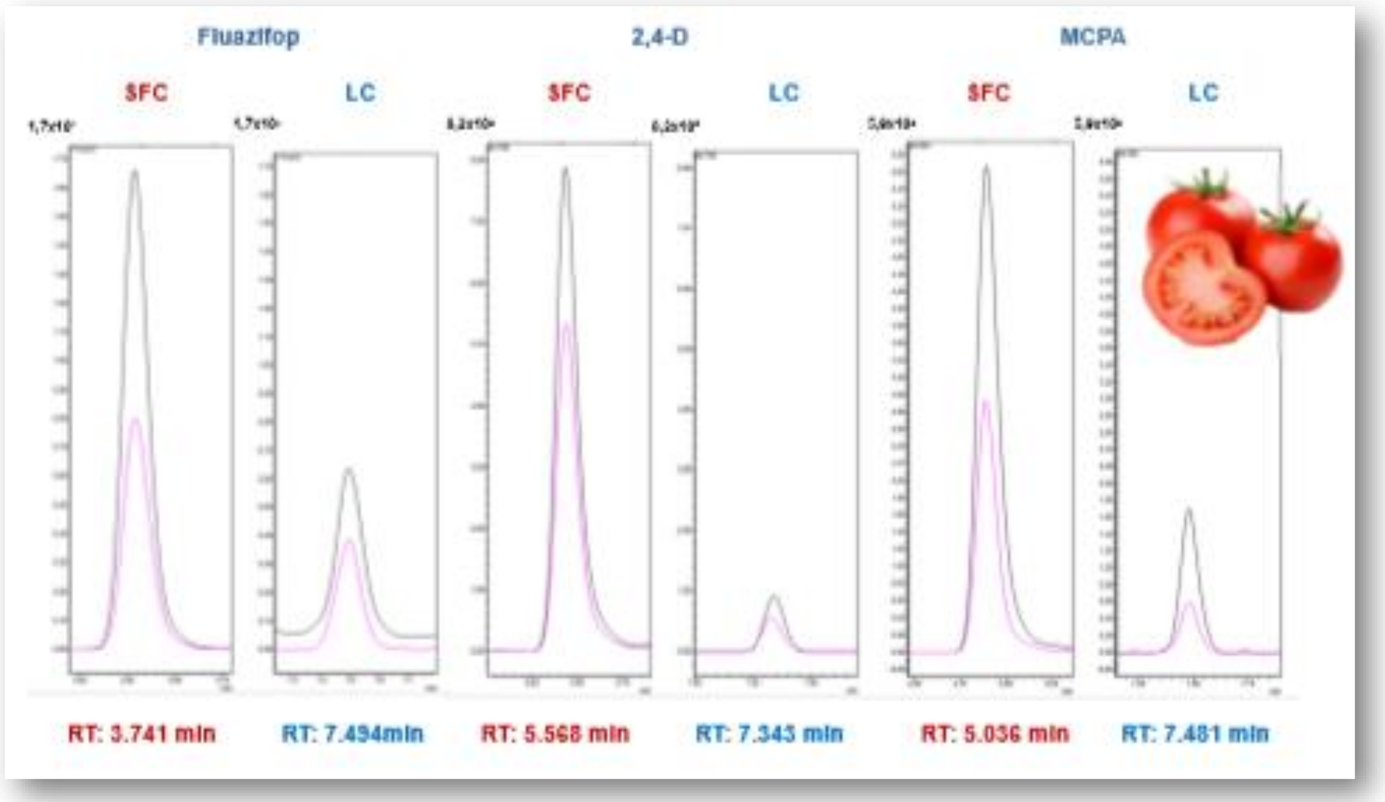

Figure 3: Examples of some compounds that increase their sensitivity using SFC-MS/MS.100 µg/kg tomato

All 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. 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

Conclusion

SFC-MS/MS using 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 and is an ideal addition to the analytical toolbox for determination of pesticides in fruit and vegetables.

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