Analytical study of an Official Monitoring of fruit and vegetables for residue pesticides in Andalusia (Spain)

EPRW 2022 BOLOGNA

M.M. Gómez-Ramos, L. Manzano-Sánchez, M. Murcia-Morales, F.J.Díaz-Galiano, P. Blanco-Muñoz, G. García-Gallego, A. Martínez, C. Ferrer, A. R.Fernández-Alba

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: **mgr337@ual.es***

UNIVERSIDAD DE ALMERÍA

Co-funded by the European Union

Introduction

During 2021-2022 the European Reference Laboratory of Fruits and Vegetables (EURL-FV) has performed official monitoring studies for pesticide residues in fruit and vegetables samples in Andalusia, Spain. The analysis were done in accordance with ISO 17025 and have enabled to obtain useful analytical information that allows identifying and solving some difficulties that can arise in multi-residue pesticide analysis. Throughout the analysis of these samples, some analytical issues associated with the extraction, identification and/or quantitation were evaluated.

Methods

Extraction methods for LC/GC-QqQ-MS/MS

QuEChERS and modified QuEChERS

Multiresidue method 178 pesticides

10 g sample or
5 g starch samples+ 10 mL water
2 g tea and infusions + 10 mL water
2 g spices+ 7 ml mL water

→ 10 ml AcN+ IS

→ Shake 6 min

→ Add 4 g MgSO4 anhidrous + 1 g NaCl + 1 g CitNa3·2H2O + 0.5 g CitNa2H·3/2·H2O

→ Shake 6 min

→ Centrifuge 5 min. 3500 r.p.m.

→ Clean-up step

Modifications

Tea and infusions	Spices	High starch/protein and seeds
5 mL extract 750 mg MgSO4 +250 mg CaCl2 + 150 mg PSA	5 mL extract dSPE (EMR-lipid and EMR-Lipid polish)	Freezing Out 5 mL extract 750 mg MgSO4 + 125 mg PSA

5 mL extract 750 mg MgSO4 anh. + 125 mg PSA

→ Centrifuge 5 min. 3500 r.p.m.

→ LC-MS/MS Analysis (0.2/0.1/0.04 g sample/mL extract)

→ GC-MS/MS Analysis (1/0.5/0.2 g sample/mL extract)

Samples were analyzed in accordance with ISO17025

Agilent Intuvo 9000 system

2 planar columns
(15 m × 0.25 mm × 0.25 µm)
Splitless injection
Total runtime 12.4 min
Injection volume 1 µL

Agilent 7010B Triple Quad

Ionization mode: EI
Acquisition mode: dMRM

Agilent 1290 UPLC system

Column: C_{18} 2.1 x 100 mm, particle size 1.8 µm
Flow rate: 0.3 ml/min)
Injection volume: 5 µL
Total runtime 18 min

Triple Quadrupole Agilent 6490

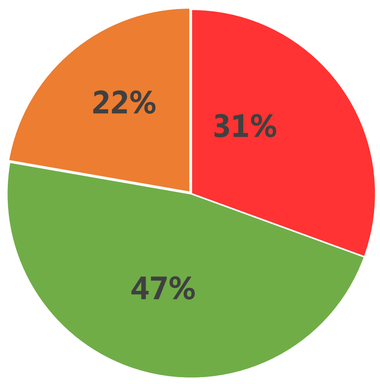
ESI (+/-) mode
Nebulizer: 45 psi
Gas Temp : 120 °C
Sheath Gas Temp: 375°C
Cap. Voltage: 3000 V
Acquisition mode: dMRM

Analyzed samples:337

High water content		Watermelon	2
Apple	5	Zucchini	5
Aubergine	9	**High acid and water content**	
Banana	11	Grape	9
Broccoli	7	Grapefruit	9
Carrot	17	Kiwi	9
Cauliflower	14	Mandarin	1
Cherimoya	4	Orange	44
Cucumber	7	Pineapple	4
Fungi	9	Raspberry	2
Garlic	1	Strawberry	13
Lettuce	6	**High starch/protein content**	
Melon	17	Bean	20
Onion	29	Rice	14
Peach	9	**Tea and Infusions**	
Pear	40	Tea	5
Pepper	15	**Spices**	
Potato	27	Cinnamon	1
Spinach	1	Paprika	1
Tomato	14		

Results

Pesticide occurrence



- Maximum number of pesticides detected in a sample: 10 (pear)
- 61 different residues of pesticides were detected
- More frequent detected pesticides :
  - Insecticide: Acetamiprid (35 samples)
  - Fungicide Imazalil (34 samples)

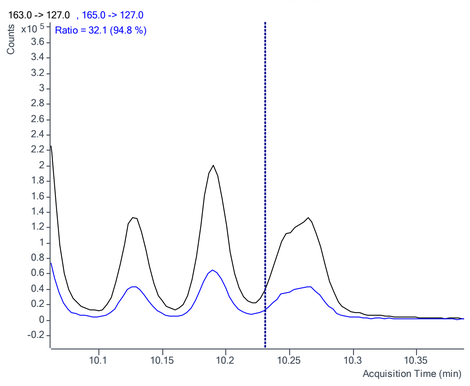
10 samples with pesticide concentrations above LMRS

■ ≥ 2detections ■ Samples with no detections ■ 1 pesticide detection

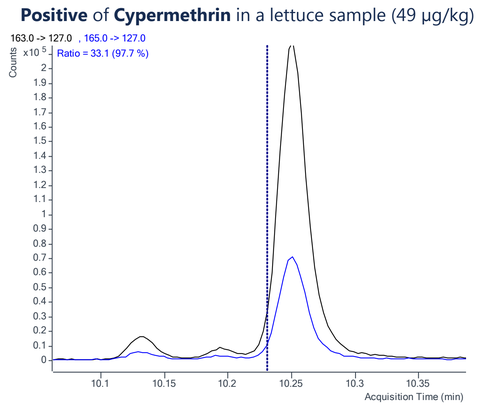
Identification Issues

In the case of pesticide residues of multiple isomers as Cypermethrin or Deltamethrin, changes in relative abundances of the isomers in the sample could interfere with the identification.

Cypermethrin Standard (100 µg/kg) Tomato matrix



Positive of **Cypermethrin** in a lettuce sample (49 µg/kg)



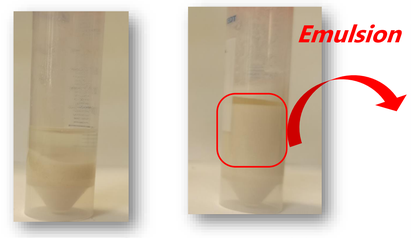
Extraction Issues

In some cases, matrix components can retain or promote pesticide degradation processes during the extraction

- **Low recoveries of Dichlorvos in some legume matrices**

Water addition, typically added in dry matrices during the extraction, generate a protein emulsion that can reduce recoveries of the pesticide Dichlorvos

Bean Sample Extractions



Due to the high content of proteins, filtration of this type of matrices after the extraction is essential to avoid clogging the instrument

Recoveries of Dichlorvos (0.01 mg/kg) Bean Matrix		
Extractions	**Recovery (%)**	**RSD (%) (n=5)**
Water addition	**62**	**28**
No water addition	103	10
SDS* addition	90	5
30 min of additional agitation	71	2

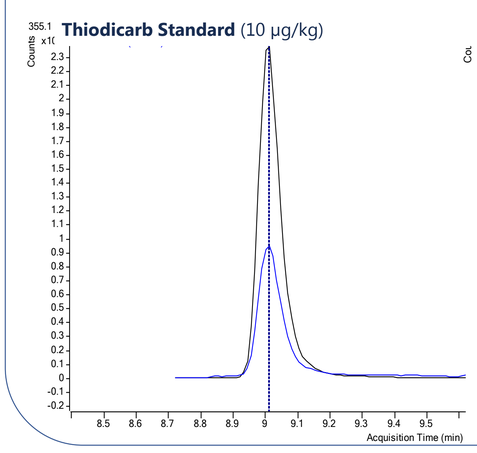
***Sodium Dodecyl Sulfate**

- **Low recoveries of Thiodicarb**

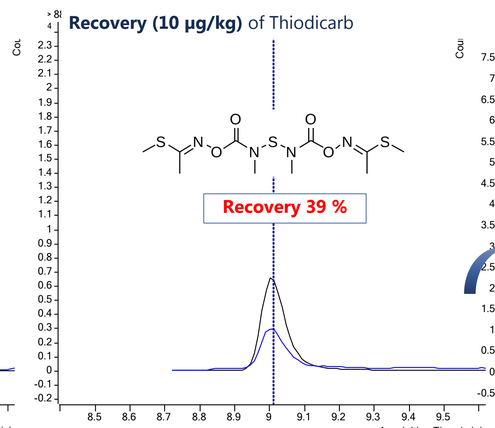
Low recoveries of Thiodicarb in some matrices can be due to its degradation into methomyl

Rice matrix

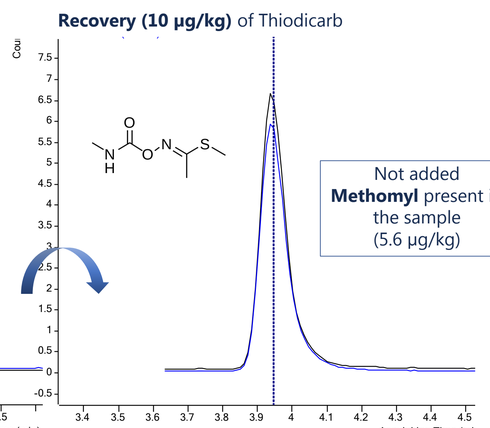
Thiodicarb Standard (10 µg/kg)



Recovery (10 µg/kg) of Thiodicarb

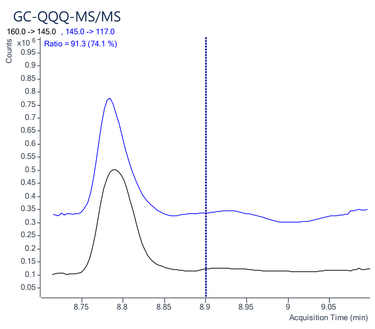


Recovery (10 µg/kg) of Thiodicarb

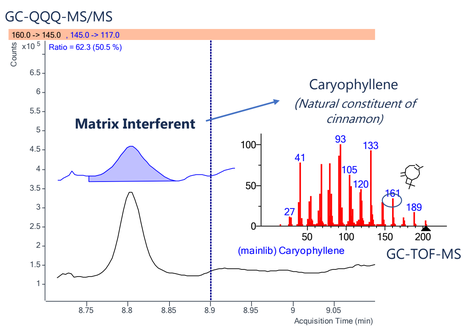


The high number of interfering compounds, especially in more complex matrices, increase possible false positives detections

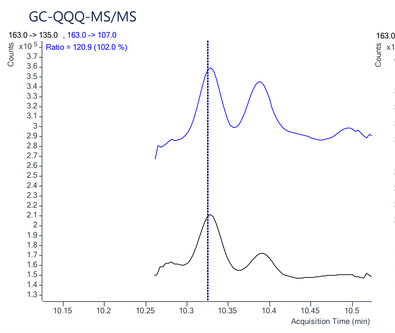
Fenazaquin Standard (200 µg/kg)
Cinnamon matrix



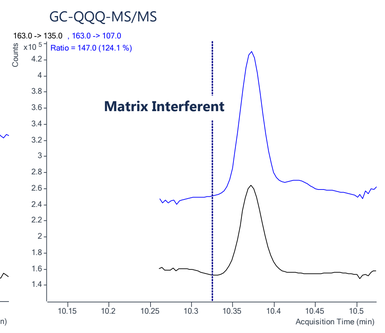
Cinnamon sample
False positive of Fenazaquin



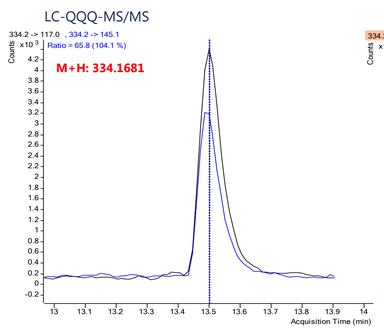
Etofenprox Standard (10 µg/kg)
Tea matrix



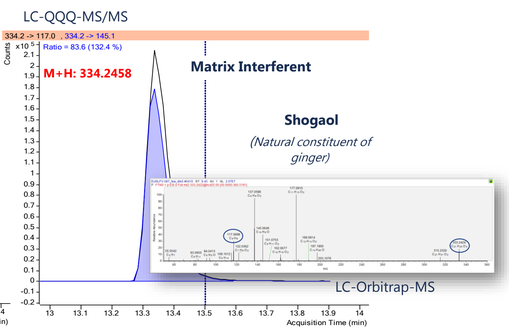
Tea sample
False positive of Etofenprox



Tebufenpyrad Standard (10 µg/kg)
Tea matrix



Tea (with ginger) sample
False positive of Tebufenpyrad



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.