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## INTRODUCTION

Countries in the European Union have increased imports of foodstuff in the last years. Nowadays European population enjoy a great variety of nourishing goods in their shopping basket, coming from different origins. This fact obligates public health laboratories to develop strategies in order to control these foodstuffs.

Laboratories must give results with the maximum confidence, due to the legal consequences for consumers as well as for food producers. In order to assure food safety, the latest instrumental novelties, like the use of high resolution mass spectrometers (HRMS) has become a basic tool.

A method based on GC-HRMS to confirm the presence of pesticides in food commodities was developed two years ago. During this time, all suspicious results from GC-LRMS (low resolution mass spectrometry) have been confirmed by GC-HRMS, to avoid false compliant or false-non-compliant results. Combining the instrumental method based on full scan and SIM acquisition modes and the GC-HRMS Compound Data Base that we have validated, the confirmation procedure has become extremely agile and effective.

In addition, due to European alerts on potential contaminated products, new pesticides have been necessarily included in the scope of the Laboratory. Following European legislation, results of the analysis of foodstuff must be released under ISO/IEC 17025 accreditation. As the accreditation process in the Spanish market is usually not flexible, ENAC (Spanish Accreditation Body) developed procedures enabling laboratories to release analytical results of new matrices or pesticides under ISO/IEC 17025 accreditation.

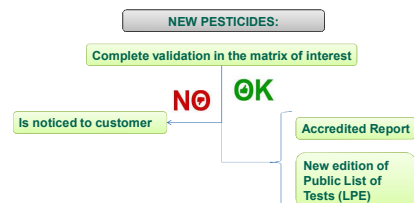
The Laboratory of Public Health Agency of Barcelona has established a system for the management of its flexible scope of analysis based on:

- LPE: list of pesticides under accreditation
- Split of the matrices in 4 different groups:
  - Vegetal matrices and honey: 7 categories
  - Animal foodstuff: 4 categories
  - Infant food
  - Single Residue Methods: dithiocarbamates and Quats

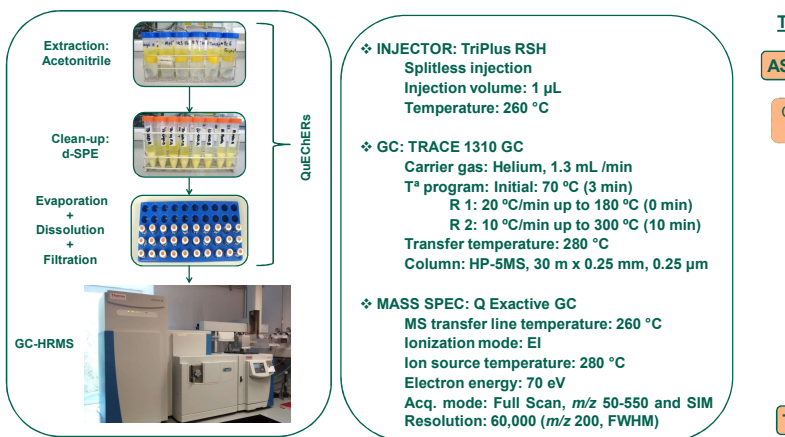
**Public list of tests (LPE)**

- Public document, improved, revised and controlled by the laboratory.
- Lists the techniques which they can use as accredited.
- Helps the clients who request an analysis.

In the present work, some results of these new pesticides, as well as the confirmed suspicious results will be shown, to explain the internal standard procedure established in the Laboratory of Public Health Agency of Barcelona



## ANALYSIS



### Theoretical approach

#### ASPB Pesticides Scope

Create a Compound Data Base (CDB)



Updated from NIST

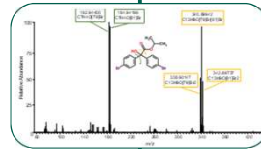


Theoretical HR-CDB

### Experimental approach

#### Full Scan analysis of 150 standards in solvent

Spectral characterization



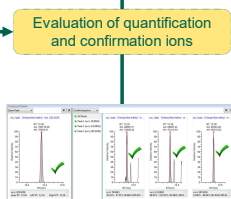
Selection of the five most abundant and specific m/z for each compound

Updated CDB

### Matrix approach

#### Surrogate matrix-matched standards in 9 different matrices

Injection in Full Scan



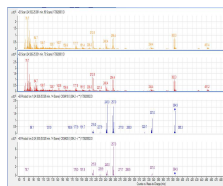
GC-HRMS Compound Data Base

## EXAMPLE OF CONFIRMATION OF NEW PESTICIDES: FIPRONIL SULFONE

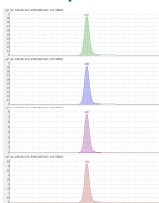
When the **Fipronil scandal** was notified to the EU members (summer 2017) the LASPB was only analyzing Fipronil, but not any metabolite. The necessity to inform of the Fipronil (sum fipronil + sulfone metabolite expressed as fipronil) forced the LASPB to analyze a new pesticide : **Fipronil Sulfone**.

### 1) INSTRUMENTAL OPTIMIZATION USING GC-MS/MS

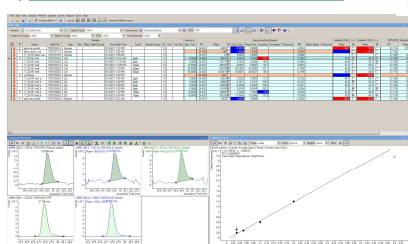
#### Full Scan



#### MRM Optimization

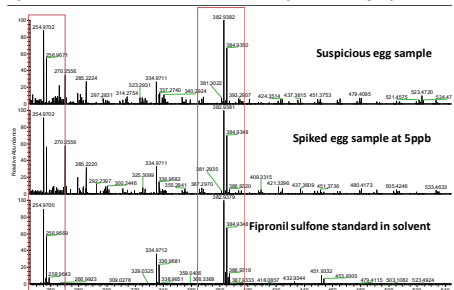


### 2) VALIDATION IN MATRIX OF INTEREST



The new pesticide was also analyzed using GC-HRMS. The high resolution (R=60,000 m/z 200 FWHM) full scan spectra of a suspicious egg sample, of a spiked egg sample at 5ppb and of the fipronil sulfone standard in solvent can be seen in the Figure below. The main quantification and confirmation ions are highlighted in red.

### 3) CONFIRMATION BY GC-HRMS (Q-Orbitrap®)



## EXAMPLE OF CONFIRMATION OF DOUBTFUL RESULT: PROPARGITE

A batch of suspicious **orange samples** containing the pesticide residue PROPARGITE arrived into the LASPB.

The usual procedure using QuEChERS and GC-MS/MS analysis was applied, finding that all the samples have some signal for both transitions and only in some cases the ion ratio criteria for confirmation was fulfilled (orange sample 2).

The Maximum Residue Limit is 0.010 mg/kg (10 ppb) for oranges and some of the suspicious samples were above this limit.

To confirm the results, the method was rapidly set up into the GC-Orbitrap and all the samples were reinjected; in order to distinguish between the signal coming from the pesticide and signals coming from matrix interferences.

### Propargite

**MRL = 10 ppb**

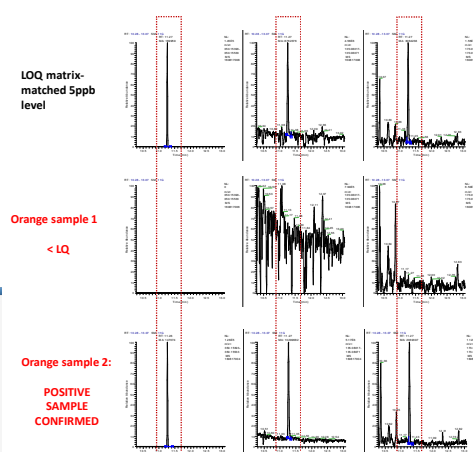
Suspicious of exceeding the MRL!

Name	Type	Level	RT	Resp.	Final Conc.	Accuracy	Qualifier (135.1 → 77.3) Results
Orange 5ppb	Cal	5ppb	27.79	1134781	4.9	98.0	26.89
Orange 10ppb	Cal	10ppb	27.77	3762552	10.1	101.1	32.05
Orange 50ppb	Cal	50ppb	27.71	20254551	50.0	100.0	35.35
Orange sample 1	Sample		27.85	1006233	3.4		142.49
Orange sample 2	Sample		27.78	6207842	17.3		34.61

Target Ion  
m/z 350.15463

Confirming Ion 1  
m/z 135.08044

Confirming Ion 2  
m/z 173.09609



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