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INTRODUCTION

Fruits and juices are often consumed by children, a group of population very sensitive to the presence of pesticide residues in foodstuffs. So, methods of control with high sensitivity are demanded. The improvement in sensitivity together with its enhanced resolution power, high selectivity and the possibility of use for retrospective analysis of HRMS convert it in worthy rivals of the traditional triple quadrupoles. A new methodology based on a QuEChERS extraction followed by GC-Q-Exactive Orbitrap HRMS determination has been validated for determining 262 pesticide residues at ppt levels in fruits and juices. NIST spectral database, TraceFinder and Xcalibur software have been used. It was applied to the analysis of 83 fruit samples and 15 juices finding pesticide residues at different concentrations.

METHODOLOGY

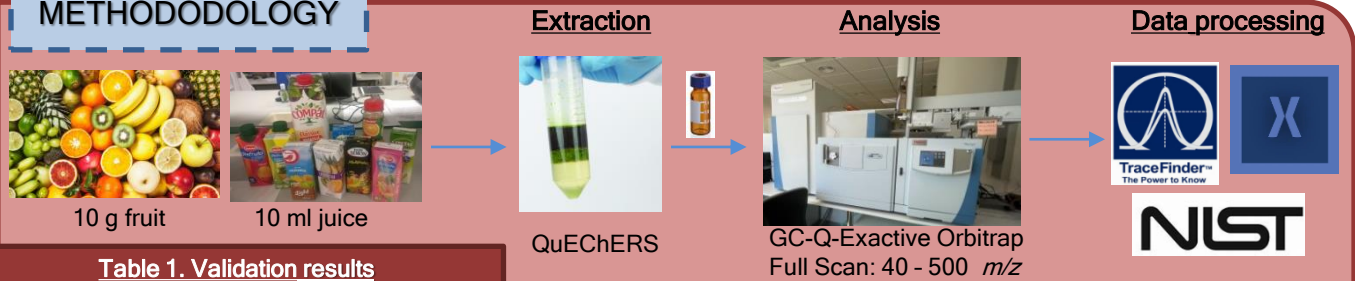
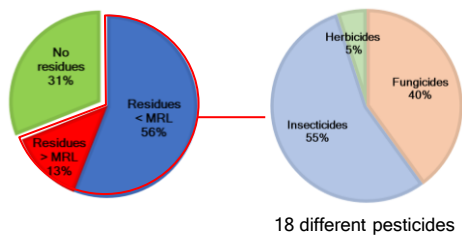


Table 1. Validation results

	Fruit (µg/kg)	Juice (µg/l)
Recovery %	1 µg/kg	70 - 112
	10 µg/kg	70 - 110
RSD %	1 µg/kg	1 - 16
	10 µg/kg	1 - 12
Lineal Range	5 - 100	0.5 - 20
LOD	0.1 - 3	0.1 - 1
LOQ	0.1 - 7	0.1 - 4

Fruits (n = 83 samples)



Juices (n = 15 samples)*

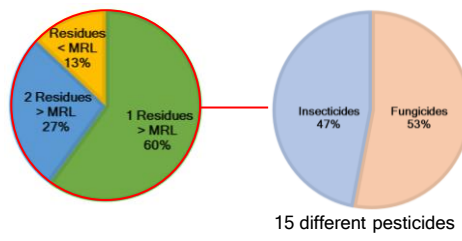
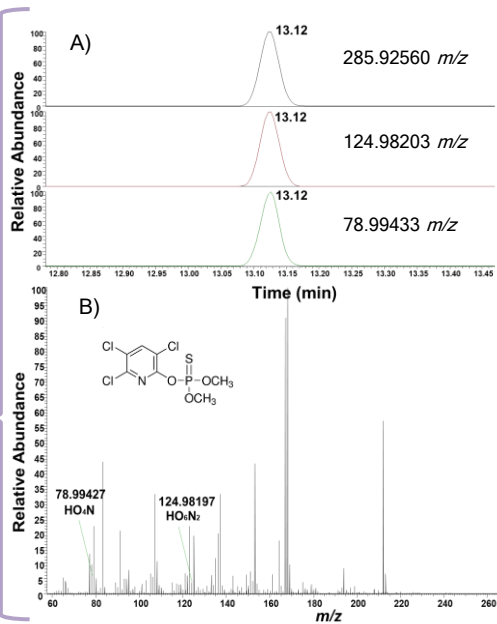


Figure 1. Interpretation of the results obtained in pie charts.* 100% of juice samples analyzed presented pesticide residues at different levels.



RESULTS

Figure 2. (A and B) Extracted-ion chromatograms and mass spectrum of chlorpyrifos methyl, pesticide residue > MRL in orange sample. (C) Mass spectrum of this compound in NIST mass spectra library.

Table 2. Pesticides residues > MRL detected in fruits and juice samples

Matrix	Pesticide	Classification	Concentration range (µg/kg)	MRL EU (µg/kg)	No. of samples > MRL
Fruits	Metalaxyl	Fungicide	12.4	10	1
	Chlorpyrifos methyl	Insecticide	10.5-57.5	10	8
	Chlorpyrifos ethyl	Insecticide	17.6	10	1
	Ethoxyquin	Insecticide	50.6	50	1
Juices	cis 1,2,3,6-Tetrahydrophthalimide	Insecticide	10.4-12.1	10	2
	Dieldrin	Insecticide	255.3-370.3	10	13
	Phthalimide	Fungicide	9.9-58.1	10	2

CONCLUSIONS

The use of GC-HRMS has demonstrated its capacity for determining pesticide residues in fruits and juices at ppt levels. The elevated percentage of positives found, some of them higher than the stated MRL, evidences the need of increasing controls and efficiency of the techniques of analysis for ensuring food safety, especially taking into account the significant consume of such food commodities by children.