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Comprehensive screening, quantitation and confirmation of pesticide residues by GC-MS and LC-MS

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Background

The food safety outlook keeps expanding with an ever-increasing regulation and the need of a reliable but also efficient alternative to check compliance has become a hard task. A number of techniques can be of great help for particular analytical duties, however none of them can stand independently since their best features might represent a comprise for some other relevant aspects.

Objective

For the determination of very low levels of forbidden and regulated pesticides in use (including both GC and LC-amenable analytes) a joint effort between several techniques was adressed to build up a comprehensive approach to check compliance of tropical fruits.

Methodology

Modern methods have to cope with the most stringent requirements in terms of sensitivity without limiting the number of target compounds. Screening of large numbers of pesticides, quantitation of positive findings and confirmation of identity was reasoned as a targeted analytical strategy able to reach low sensitivity levels by using state-of-the-art technologies.

Comprehensive analytical strategy		MS performance capabilities	
		HRMS	QqQ
Analyte amenability	GC	Full-spectra GCxGC-TOF	MS/MS spectra
	LC	Exact mass LC-Orbitrap	
Specificity		Full-scan MS False (-) Targeted	MRM False (+) Targeted
Selectivity		hrMS|amMS	Ratio (T1/T2)
Sensitivity		Same (large or small set)	Higher (smaller set) Lower (larger set)

Table 1. Outline of the used analytical strategy showing the capabilities of each technique and differences between their performance criteria.

Screening

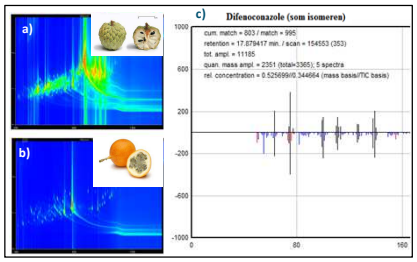

Figure 1. 2D GCxGC-TOF chromatogram for screening purposes a) complex chirimoya and b) simpler sweet granadilla extract. c) Difenoconazole in lulo using MetAlign™ a powerful programme written by Arjen Lommen for the pre-processing and comparison of full scan MS data.

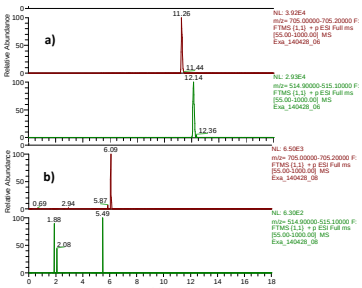

Figure 2. LC-HRMS search for flubendiamide and novaluron showing extracted ion chromatograms of [M-Na]+ clusters (705,01254; 515,00153) respectively . Check by exact mass comparison. a) Standard 100ng/mL b) treetomato extract.

- Full-spectra matching of GCxGC-TOF aimed to look for 550 GC-amenable contaminants in a complex background was used for screening by using an automated analysis of datasets keeping a low rate of false negatives.
- LC-single stage Orbitrap technology enabled sub-ppm mass accuracy to assess the absence of LC-amenable pesticides by exact mass comparison. Chromatographic separation was essencial to avoid false possitives.

Quantitation

- The high sensitivity of GC and LC-MS/MS instruments made possible the quantitation of low concentration levels with ease.
- All the other fruits in the study were found free of the pesticides within the scope being below the reporting limit (0.010 mg/kg).

Tree tomatoes
Carbendazim* 0,430 mg/kg

Lulo

Carbendazim*	0,183 mg/kg
Difenoconazol *	0,028 mg/kg
Methomyl *	0,064 mg/kg
Oxamyl *	0,041 mg/kg
Propamocarb *	0,238 mg/kg
Procymidone *	0,296 mg/kg
Chlorpyrifos*	0,018 mg/kg

Feijoa
Carbendazim 0,036 mg/kg

Sweet granadilla

Difenoconazole*	0,376 mg/kg
Dimetoate *	0,270 mg/kg
Omethoate *	0,047 mg/kg

Tamarillo
Carbendazim 0,028 mg/kg

Guava

Carbendazim*	0,124 mg/kg
Dimetoate*	0,038 mg/kg
Omethoate *	0,036 mg/kg

Figure 3. Results showing positive findings out of 10 fruits involved in the study (below heading). No available regulatory data was found for all the fruits except tree tomatoes and tamarillo. *Exceedance of LMR default.

Confirmation

The use of a second qualifying transition in the MRM events was especially aimed to avoid false positives. Ratios (T1/T2) were matched against the SANCO/12571/2013 criteria as confirmative method.

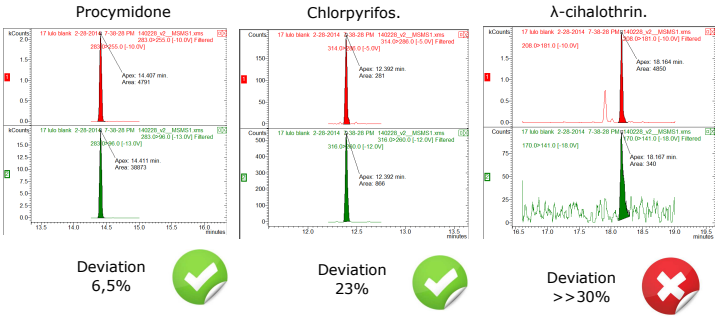

Figure 4. Confirmatory GC-MS/MS transitions in lulo extract. Identity of procymidone and chlorpyrifos were confirmed with ion ratios below 30%. However, λ-cihalothrin notably exceeded tolerances, pointing out a screening false positive probably due to a low concentration.

Conclusions

- This comprehensive analytical strategy enabled a survey of hundreds of pesticides under regulation by using screening, quantitative and confirmatory methods in a complementary approach.

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