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Benefits and pitfalls of the application of screening methods for the analysis of pesticide residues in fruits and vegetables

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ABSTRACT

The goal of this study was to expand knowledge on the performance of screening methods based on accurate mass measurements using a liquid chromatography electrospray quadrupole time-of-flight mass spectrometry (LC-ESI-QTOF-MS) system operating in full scan mode and with automatic identification based on the use accurate-mass databases. The study involved the analysis of 97 pesticides, in five matrices (tomato, pepper, zucchini, orange and leek) and at three concentration levels (20, 50 and 100 μg kg^{-1}). Aspects concerning optimization of the search parameters, sensitivity, matrix effects, efficiency of the algorithm search, usefulness of fragment ions, etc., are evaluated in deep. Sensitivity requirements have been identified as the main obstacle affecting the automatic identification of pesticides, especially in complex matrices, where the ionization suppression reduces the detectability of analytes. In addition, we have detected some failures in the software used for automatic data processing in terms of analysis of isobaric compounds, use of isotopic clusters, spectral deconvolution and data processing speed that hamper the correct identification in some pesticide/matrix combinations. These drawbacks should be improved in the future for its effective implementation in routine residue analysis.

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1. Introduction

Pesticide control in foodstuffs is an extensively regulated issue in the European Union (EU). Member State authorities are responsible for control and enforcement of the maximum residue levels (MRLs) and the co-ordinated EU multi-annual control programme sets out for each Member State the main pesticide–crop combinations to monitor and the minimum numbers of samples to take. Thus, most of the analytical methods currently applied in food control laboratories, both administration and private, are aimed at the identification of target compounds [1]. These multiresidue methods are typically carried out using high-performance liquid chromatography (HPLC) coupled to triple quadrupole mass spectrometry (QqQ-MS) [2–8]. This technique provides high sensitivity and selectivity operating in selective reaction monitoring mode (SRM), but in return requires extensive and time-consuming method set-up and the number of compounds that can be simultaneously analyzed in a single run is limited. However, the main drawback of this technique is the inability to detect non-target compounds or to perform retrospective data analysis.

Given the current need to detect illegal or misused compounds, whose presence is not expected in the samples [9] it is necessary to extend the scope of the methods to include a larger number of potential compounds. This possibility is not always straightforward, because the capability of analytical instrumentation is limited, especially if you want to maintain the same level of demand in the results, both qualitatively and quantitatively. In addition, development of wide scope methods is expensive and time consuming and requires extensive work for their development, validation and quality control. Thus, an alternative that is attracting great interest is the use of quick and simple screening methods to allow positive identification, within a wide range of compounds, along with subsequent confirmation and quantification of them. The goal of this work has been gaining insight in the performance of current screening methods based on the use of full scan LC-ESI-TOF-MS and automated library-based detection using accurate mass databases.

The advantage of TOF-MS analysers is their ability to determine a theoretically unlimited number of compounds with high sensitivity within one run, thus expanding the capacity for screening several hundreds of compounds. Furthermore, full scan data can be reprocessed without any a priori knowledge about the presence of certain compounds; that is, no analyte-specific information is required before injecting a sample and the presence of newly identified compounds can be confirmed in previously analyzed samples simply by reprocessing the data. These capabilities were initially explored for identifying unexpected pesticide residues or their metabolites based on concept of diagnostic fragment ions [10–12]. Further approaches proposed identification of possible unknown pesticides by using accurate mass data for generating empirical

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Table 1
Pesticides identified automatically (in white) and manually (M) in solvent solution and in the five matrices tested at three concentration levels (20, 50 and 100 μg kg^{-1}). Pesticides analyzed in negative ionization mode are showed as (−). Compounds that are not detected in certain conditions are shown with lines and those that are not detected in any case appear in gray. NR: non resolved.

	Solvent			Tomato			Pepper			Zucchini			Orange			Leek		
Compound	**20**	**50**	**100**	**20**	**50**	**100**	**20**	**50**	**100**	**20**	**50**	**100**	**20**	**50**	**100**	**20**	**50**	**100**
Aclonifen																		
Alachlor																		
Atrazine																		
Azocyclotin																		
Benalaxyl																		
Bromacil																		
Bromoxynil	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)
Carbophenothion																		
Chinomethionat																		
Chlorfluazuron	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)
Chlortoluron																		
Chlozolinate																		
Chromafenozide																		
Cinosulfuron													M					
Clethodim																		
Clopyralid			M															
Cyanazine																		
Cycloate																		
Cymoxanil																		
Cyromazine								M	M							M	M	M
Demeton-S-methyl																		
Diafenthiuron																		
Diethofencarb																		
Diflubenzuron																		
Diflufenican									M									
Diniconazole																		
Diuron																		
Ethiofencarb																		
Ethoxiquin			M															
Etrimfos																		
Famoxadone	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)
Fenamidone																		
Fenpropidin																		
Fenpyroxymate																		
Fenuron									M			M						
Flazasulfuron																		
Flonicamid																		
Fluazifop-butyl	M	M	M	M	M	M							M	M				
Flubendiamide																		
Flucythrinate																		
Flufenacet																		
Fluometuron																		
Fluroxypyr																		
Fonofos																		
Forchlorfenuron																		
Fuberidazole																		
Furathiocarb																		
Halfenprox																		
Haloxyfop-methyl																		

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