Residues of Highly Polar Pesticides in Samples from the Market

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CRL for Pesticide Residues using Single Residue Methods hosted at the

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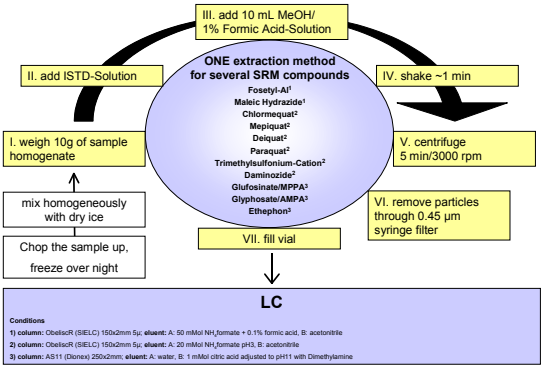
Introduction

The increasing use of LC-MS/MS and the introduction of new multiresidue methods covering a broader range of pesticides, especially towards the polar end of the spectrum (e.g. QuEChERS), have significantly contributed to the remarkable increase in the number of pesticides regularly targeted by the laboratories in recent years. Pesticides not covered by multiresidue methods (MRMs) require the use of single residue methods (SRMs) or group-specific methods. However, due to the lack of resources, and attractive methods, laboratories, if at all, only cover very few of these pesticides on a routine basis. There is obviously a need to develop and validate attractive and economic analytical methods for such pesticides and this task is among the core activities of the Community Reference Laboratory for Single Residue Methods (CRL-SRM).

As a first step in this direction, the focus was set on the development of methods for a group of highly polar and widely employed pesticides such as ethephone, maleic hydrazide, glyphosate (and AMPA), glyfosinate (and MPPA) as well as fosetyl aluminum. The goal was to develop a simple fast, attractive and readily transferable methodology for these compounds employing a common extraction step followed by as few as possible LC-MS/MS runs. Currently, very few laboratories check for these compounds on a regular basis and if so, only a small fraction of the samples entering the lab is typically targeted. The need to intensify the controls for these compounds in food, not only to check for the MRL-compliance but also in order to gain the ability to assess the consumer intake, is obvious.

Methodology



Results

The methodology developed by the CRL-SRM was employed for the analysis of many samples from the market and the following findings were recorded up to March 2008.

Glyphosate: 202 samples (28 commodities, no cereals) from 16 countries were tested for this compound. 3 samples of those, originating from 3 countries and concerning 2 commodities (asparagus and shallots), were found to contain glyphosate residues. No MRL-violations were noticed The concentrations in the positive samples ranged between 0.012 and 0.04 mg/kg (median 0.02 mg/kg).

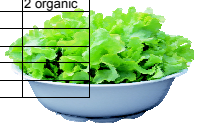
Glufosinate, AMPA and MPPA were not detected in any of the samples.

Ethephon: 472 samples (40 different commodities) from 28 countries were tested for this compound. 41 samples (9 commodities) from 12 countries were found to contain ethephon residues with 4 samples (kaki and durian) exhibiting MRL-violations. The concentrations in the positive samples ranged between <0.01 and 10.1 mg/kg (median 0.13 mg/kg).

Commodity	Country of Origin	No. of findings	Minimum Value (mg/kg)	Maximum Value (mg/kg)	Remarks
Pineapple	Africa	6	0.1	0.73	1 organic
	South / Central America	3	0.03	0.4	
	unknown	1	0.17		
Pineapple Juice	unknown	6	<0.01	0.22	3 organic
Apples	Germany	3	<0.01	0.1	
Pears	Italy	1	0.01		
Durian	Thailand	2	0.31	10.1	2 > MRL
Sweet Pepper	Spain	4	0.049	1.2	
Kaki/Sharon	Italy	1	0.12		1 > MRL
	Spain	4	0.024	0.61	1 > MRL
Tomatoes	Belgium	1	0.12		
Grapes	Italy	7	0.28	0.78	
	South Africa	2	>0.01	0.13	1 organic

Fosetyl Aluminium: 499 samples (58 commodities) from 28 countries were tested for this compound. 24 samples (7 commodities) from 6 countries were found to contain fosetyl residues. No MRL-violations were detected but 5 organic cucumbers were found to contain residues ranging between 0.03 and 0.3 mg/kg. The concentrations in the positive samples ranged between <0.01 and 1.1 mg/kg (median 0.04 mg/kg).

Commodity	Country of Origin	No. of findings	Minimum Value (mg/kg)	Maximum Value (mg/kg)	Remarks
Strawberries	Germany	13	0.019	0.067	
	Spain	1	1.1		
Cucumber	Spain	2	0.032	0.043	2 organic
	Morocco	1	0.045		1 organic
	Italy	2	0.14	0.3	2 organic
Lettuce	Germany	1	0.009		
	Spain	1	0.027		
Lollo rosso	France	1	<0.01		
Tomatoes	Spain	1	0.014		
Grapes	The Netherlands	1	0.040		



Maleic Hydrazide: 123 samples (8 commodities) from 9 countries were tested for this compound. 15 samples (3 commodities garlic, onion and shallots) from 4 countries, were found to contain maleic hydrazide residues. One MRL-violation was noticed in shallots from France with 17.2 mg/kg. One organic onion sample from Italy was found to contain 1.7 mg/kg. The concentrations in the positive samples ranged between 0.2 and 17.2 mg/kg (median 6.9 mg/kg).

Commodity	Country of Origin	No. of findings	Minimum Value (mg/kg)	Maximum Value (mg/kg)	Remarks
Garlic	France	1	14,3		
Onions	France	4	0.27	15	
	Germany	1	1.4		Illegal use
	Italy	1	1.7		1 organic
	The Netherlands	2	4.1	8.4	
	Unknown	1	0,2		
Shallots	France	5	6.6	17.2	1 > MRL

ETU, PTU: 33 samples of processed fruits and vegetables were tested for these compounds using a modified QuEChERS method. ETU and PTU are metabolites of dithiocarbamates which are mainly built during heating processes. Only one sample of apple sauce from Poland contained residues of ETU in a very low concentration.

Commodity	No. of Samples	No. of Findings	ETU (mg/kg)	PTU (mg/kg)	Remarks
Vegetable Juices	6	0			
Fruity Baby Food	14	0			
Tomatoe Products	6	0			
Apple Sauce	7	1	0.01		From Poland

Conclusion

With the help of a newly developed method for the simultaneous analysis of polar pesticides, classically requiring single residue methods, we were able to efficiently test a wide range of food commodities.

As several of these pesticides are frequently found as residues, they should be considered in routine pesticide testing schemes.