

# Simultaneous Screening and Target Analytical Approach by Gas Chromatography-Quadrupole-Mass Spectrometry for Pesticide Residues in Fruits and Vegetables

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**A full-scan GC/quadrupole/MS method has been developed to perform large-scale screenings of pesticides and simultaneous quantification of 95 target compounds in a single run of 21 min. The screening method was performed by using a deconvolution of the spectrum of the full-scan data files acquired under a retention time locked method. The identification performance of the screening method was evaluated in eight different food matrixes at three different concentrations. The system was equipped with a programmable temperature vaporizing inlet, allowing 10 L injections. The LOQ in the full-scan mode and linearity were studied for four different matrixes. Correlation coefficients >0.99 were achieved in all cases, and the LOD was <20 g/kg for 80% of the studied pesticides. Maintenance of the system was reduced by the use of a QuickSwap device that provided backflush capabilities by reversing column flow immediately after elution of the last compound of interest. The combined screening and target method was used in the analysis of more than 100 food samples, including a carrot sample from the European Proficiency Test FV 10, with good results.**

Target analysis methods applied in many laboratories for routine pesticide residue control basically consist of a list of around 100–150 GC- and LC-amenable compounds. The analyte list is selected by using the established priority lists combined with any other relevant information related to agricultural uses in local regions (1, 2). This means that the majority of the low-frequency or misused

(nonpriority) compounds typically fall outside of any extensive control. Thus, they are detected purely by chance, based on extra information or analytical work. An example of this is the case of the European Union safety alert generated in 2006 because of the presence of the nonauthorized insecticide isofenphos-methyl found in pepper samples (3, 4). This is becoming more important, given that the pesticides currently authorized in Europe (Annex I, Directive 91/414/EEC; 5) and other developed countries have been reduced to around 50% of the total amount of compounds manufactured. Consequently, in the field of food safety, there is an obvious need for methods offering the rapid and reliable screening of a large number of compounds.

From an analytical point of view, this task is difficult to accomplish since it involves extending the scope of the multiresidue methods to cover several hundred chemicals. It is difficult to carry out these approaches cost-effectively due to the time and money required for upgrading methods to incorporate new compounds, and management of the standards and solutions. Extra analytical effort and an overall decrease in laboratory throughput result.

Thus, other alternatives should be explored and evaluated. A good alternative is the application of combined analyses based on the target/screening approach. This is done by targeting a group of priority compounds based on their toxicity and/or frequency of detection and, at the same time, carrying out a rapid screening of a much larger number of compounds for identification purposes only (6–9).

GC/MS has been used for many years to identify pesticides in food samples. Generally, to efficiently remove interference from coeluting peaks and to ensure sensitivity, selective ion monitoring (SIM) or MS/MS by selection of a precursor ion, as opposed to full scanning (monitoring the whole spectrum), has been used to detect trace levels of pesticides in complex samples (10, 11). However, these methods rely on only a few ions and are not designed to find compounds unless they are on the target list.

Table 1. Match obtained by AMDIS in eight selected matrixes at the three different concentrations<sup>a</sup>

Spiked pesticides	AMDIS match																							
	Aubergine, g/kg		Potato, g/kg		Cucumber, g/kg		Banana, g/kg		Tangerine, g/kg		Orange, g/kg		Melon, g/kg		Olive oil, g/kg									
	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100						
Dichlorvos	45	69	82	<LOI <sup>b</sup>	66	67	<LOI	55	51	71	74	81	NS <sup>c</sup>	NS	NS	NS	49	77	85	51	80	86		
Mevinphos	77	92	92	71	93	93	90	93	90	92	94	98	<LOI	78	75	48	60	81	81	64	83	90		
Diphenylamine	79	74	75	83	88	87	NS	NS	NS	NS	NS	NS	NS	NS	83	88	83	NS	NS	<LOI	93	97		
Etoprophos	79	90	96	76	88	92	75	85	93	75	84	93	<LOI	56	83	<LOI	53	81	75	87	93	94		
Chlorpropham	88	91	92	88	93	94	90	93	94	49	79	94	<LOI	49	67	56	80	83	91	92	92	94		
Monocrotophos	<LOI	66	80	56	62	83	<LOI	70	69	<LOI	82	84	NS	NS	NS	NS	50	54	79	NS	NS	NS		
DiDoran	52	81	89	<LOI	72	77	76	81	87	76	88	93	56	74	80	NS	69	81	86	47	84	91		
Dimethoate	64	67	66	54	69	77	65	68	69	68	70	77	<LOI	48	63	NS	61	67	75	68	70	72		
Ethoxyquin	97	99	100	97	99	100	96	98	99	93	98	99	88	95	96	66	81	89	99	76	93	97		
Lindane	70	85	94	70	80	93	80	85	92	85	90	94	70	74	75	60	65	65	NS	NS	NS	NS		
Fonophos	88	93	95	88	94	94	90	90	91	83	91	93	73	84	90	79	85	90	90	88	92	95		
Propyzamide	88	92	93	90	92	93	90	91	92	86	91	93	81	88	91	75	85	92	88	92	93	90		
Pyrimethanil	93	96	97	92	96	97	89	92	95	95	98	98	87	93	93	80	86	90	90	95	96	99		
Diazinon	93	98	99	93	96	99	93	96	98	92	96	98	74	86	89	73	82	87	93	98	94	99		
Pirimicarb	94	97	98	93	97	99	91	97	98	87	96	98	82	92	95	72	78	93	93	97	98	99		
Chlorpyrifos-methyl	90	95	94	92	93	95	73	80	85	91	94	95	85	92	94	86	93	93	88	93	94	95		
Vinclozolin	87	92	93	89	91	93	83	87	89	84	90	92	69	83	87	81	83	91	87	90	92	93		
Tolclophos-methyl	93	96	98	94	94	98	95	97	98	95	95	98	82	91	93	88	94	96	89	96	97	99		
Alachlor	83	93	95	85	93	96	86	94	95	83	92	95	66	89	93	72	84	94	83	94	96	95		
Metalaxyl	75	90	89	80	84	91	NS	NS	NS	NS	NS	NS	NS	NS	NS	45	59	85	NS	NS	61	79		
Prometryn	66	77	84	60	68	80	89	91	94	78	90	92	<LOI	64	72	<LOI	63	70	86	90	92	82		
Fenitrothion	70	71	87	58	76	81	69	79	85	51	66	86	<LOI	65	73	52	76	89	60	70	88	89		
Pirimiphos-methyl	80	94	96	89	93	95	91	94	96	88	93	95	84	92	93	85	88	94	87	94	95	96		
Dichlorfluandid	NS	NS	NS	NS	NS	NS	NS	NS	NS	55	68	80	<LOI	62	75	NS	NS	NS	69	78	52	68		
Malathion	70	84	88	79	80	88	47	66	67	57	80	93	53	74	73	NS	NS	NS	77	86	90	91		
Fenthion	59	83	92	76	80	86	NS	NS	NS	NS	NS	NS	NS	NS	NS	69	80	87	NS	NS	71	88		
Dimethylvinphos		74	74	59	53	76	83	88	86	88	88	88	69	86	77	NS	NS	NS	56	76	77	NS		
Chlorpyrifos	76	84	85	79	83	88	82	91	92	97	97	97	92	94	92	65	73	70	83	90	90	88		
Parathion	<LOI	51	49	NS	NS	NS	<LOI	51	60	51	73	81	<LOI	57	74	NS	NS	NS	54	68	72	83		
Triadimefon	84	91	96	87	94	97	87	92	94	81	94	94	61	89	89	57	75	93	76	89	94	96		

Table 1. (continued)

Spiked pesticides	AMDIS match																										
	Aubergine, g/kg			Potato, g/kg			Cucumber, g/kg			Banana, g/kg			Tangerine, g/kg			Orange, g/kg			Melon, g/kg			Olive oil, g/kg					
	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100			
Tetraconazole	95	97	98	95	97	99	95	98	98	93	96	98	88	94	96	88	92	96	94	98	98	94	98	98	93	97	98
Isocarbofos	69	87	90	71	72	88	65	82	78	81	88	94	68	84	87	55	69	86	76	88	92	76	88	92	NS	NS	NS
Cyprodinil	96	97	98	95	98	98	96	98	98	93	95	98	93	96	96	89	92	97	95	97	98	95	97	98	95	98	99
Isofenphos-methyl	87	93	95	85	94	96	88	92	94	81	91	94	76	88	93	76	89	92	84	90	96	84	90	96	89	95	97
Penconazole	94	98	98	92	97	98	92	92	93	87	96	97	48	86	89	67	79	74	94	97	98	94	97	98	89	97	98
Thiabendazole	69	89	94	82	85	92	<LOI	52	58	73	88	87	73	79	86	75	82	91	<LOI	89	90	<LOI	89	90	53	48	45
Tolyfluanide	NS	NS	NS	<LOI	71	72	56	72	71	63	78	86	<LOI	68	71	<LOI	69	73	53	81	81	53	81	81	73	83	87
Isofenphos	85	91	93	87	90	94	86	91	93	82	90	94	79	90	92	73	86	91	83	91	93	83	91	93	90	95	96
Quinalphos	<LOI	60	75	45	62	76	70	81	84	87	91	94	69	89	92	64	76	89	52	66	78	52	66	78	84	94	94
Mecarban	63	77	79	71	75	71	NS	NS	NS	77	72	70	45	72	80	53	65	77	65	76	77	65	76	77	59	75	72
Triadimenol	49	76	79	61	75	78	53	62	68	75	60	69	<LOI	78	82	47	65	78	<LOI	76	80	<LOI	76	80	54	70	76
Procymidone	65	83	83	72	81	85	83	90	91	81	90	91	67	83	85	60	68	75	82	87	91	82	87	91	89	93	94
Fipronil	78	83	90	81	89	91	89	93	93	92	96	96	86	87	89	79	90	84	84	91	92	84	91	92	87	91	93
Methidathion	50	70	77	<LOI	61	74	<LOI	67	85	79	87	86	50	70	72	60	60	61	67	80	91	67	80	91	66	85	87
Endosulfan ( )	83	93	96	84	92	96	84	91	91	76	90	95	55	83	91	65	76	88	83	94	96	83	94	96	89	96	98
Mepanipyrim	88	91	98	88	94	97	93	96	99	73	95	97	70	83	91	69	80	92	87	95	84	87	95	84	84	91	90
Hexaconazole	77	85	90	81	88	91	85	91	94	64	90	94	<LOI	69	67	<LOI	54	76	83	89	92	83	89	92	83	92	92
Phenamiphos	64	73	84	72	83	89	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	77	85	90
Imazalil	<LOI	48	76	<LOI	58	73	<LOI	78	88	69	82	85	86	90	95	95	95	96	<LOI	56	71	<LOI	56	71	NS	NS	NS
Flutolanil	91	93	98	92	95	97	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	94	92	95
Fludioxonil	82	90	95	89	96	98	92	97	98	90	96	99	75	88	93	64	64	79	89	96	97	89	96	97	72	84	96
Myclobutanil	83	90	93	86	91	94	87	91	94	80	89	93	71	86	87	51	70	84	81	89	92	81	89	92	79	92	94
Buprofezin	82	81	83	76	87	89	<LOI	86	89	NS	NS	NS	58	80	78	48	60	82	82	83	85	82	83	85	84	87	91
Flusilazole	94	97	98	94	97	98	95	97	97	93	97	97	87	96	97	89	93	95	NS	NS	NS	NS	NS	NS	92	95	97
Bupirimate	93	96	98	94	97	98	93	96	97	87	96	97	87	93	95	81	90	96	94	96	97	94	96	97	96	98	98
Kresoxim-methyl	87	92	95	84	97	94	86	91	89	86	90	94	67	86	91	69	86	90	<LOI	94	93	<LOI	94	93	89	95	95
Iprobalicarb	<LOI	48	65	<LOI	57	57	63	66	72	NS	NS	NS	<LOI	60	61	<LOI	50	56	NS	NS	NS	NS	NS	NS	50	68	68
Endosulfan ( )	75	88	92	74	85	86	82	89	90	76	90	91	50	77	82	52	69	77	79	89	91	79	89	91	78	92	93
Chlorfenapyr	77	89	92	77	88	91	84	90	92	76	86	90	65	85	86	65	81	88	75	86	90	75	86	90	80	88	92
Oxadixyl	62	84	90	71	82	88	74	88	92	65	89	93	52	81	84	53	58	75	68	86	84	68	86	84	49	71	82

**Table 1. (continued)**

Spiked pesticides	AMDIS match																							
	Aubergine, g/kg		Potato, g/kg		Cucumber, g/kg		Banana, g/kg		Tangerine, g/kg		Orange, g/kg		Melon, g/kg		Olive oil, g/kg									
	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100	20	50	100
Triazophos	82	88	93	82	87	91	69	84	92	84	88	93	66	91	93	77	84	90	72	84	90	74	87	90
Benalaxyl	92	94	95	91	94	95	91	95	95	89	95	94	84	92	92	82	90	93	93	95	96	95	96	96
Endosulfan sulfate	48	58	58	57	67	69	61	68	70	75	77	80	<LOI	50	51	<LOI	45	63	62	77	81	65	64	71
Quinoxifen	91	92	93	89	92	92	92	89	93	90	92	93	90	92	95	87	91	94	86	89	89	87	90	93
Propiconazole	97	98	99	97	98	98	95	98	98	<LOI	98	98	89	95	96	83	94	96	96	98	98	96	98	99
Trifloxystrobin	52	64	74	56	72	82	81	85	87	71	86	92	57	78	81	53	75	80	59	74	80	64	81	88
Nuarimol	58	72	74	65	74	81	82	88	89	79	88	82	66	82	87	60	68	83	78	84	89	73	80	82
Tebuconazole	<LOI	67	81	56	73	82	58	75	85	71	76	80	53	73	73	50	70	80	63	78	84	70	68	69
Iprodione	NS	NS	NS	NS	NS	NS	NS	NS	NS	72	78	77	NS	NS	NS	NS	NS	NS	49	71	76	NS	NS	NS
Phosmet	NS	NS	NS	NS	NS	NS	<LOI	60	81	76	84	91	NS	NS	NS	NS	NS	NS	47	74	81	NS	NS	NS
Bromopropylate	92	95	97	94	97	98	94	97	97	91	95	97	86	93	95	83	88	95	88	92	94	90	96	97
Bifenthrin	93	98	99	94	99	98	96	97	98	95	96	97	87	94	97	90	94	96	92	93	95	92	97	97
Fenpropathrin	72	85	85	75	80	87	NS	NS	NS	NS	NS	NS	NS	NS	NS	59	74	86	NS	NS	NS	74	83	89
Tebufenpyrad	96	98	98	96	98	99	95	98	98	92	92	95	89	95	97	91	96	98	94	97	98	94	98	98
Tetradifon	84	92	95	84	93	95	87	93	96	76	91	95	<LOI	69	79	<LOI	70	83	83	91	95	72	92	95
Bifenox	NS	NS	NS	NS	NS	NS	NS	NS	NS	46	51	71	<LOI	60	76	NS	NS	NS	NS	NS	NS	NS	NS	NS
Phosalone	<LOI	70	81	63	77	83	56	79	75	74	88	92	49	73	78	48	61	76	71	86	92	75	77	88
Pyriproxyfen	84	92	94	83	88	95	93	94	94	83	93	94	83	89	91	62	79	85	81	90	94	91	92	96
Cyhalothrin	67	84	81	84	84	57	50	73	76	77	85	88	<LOI	59	52	57	61	82	71	78	80	80	90	93
Fenarimol	83	90	94	89	92	95	85	91	93	60	63	74	65	70	86	45	75	85	75	84	83	76	89	92
Pyrazophos	73	87	91	79	84	89	NS	NS	NS	NS	NS	NS	NS	NS	NS	49	67	81	NS	NS	NS	69	86	88
Acrinathrin	<LOI	67	63	49	64	73	NS	NS	NS	80	81	85	NS	NS	NS	NS	NS	NS	58	79	83	60	61	72
Permethrin	81	94	96	85	94	94	86	93	95	75	85	91	60	69	83	68	80	87	80	86	91	84	93	94
Prochloraz	<LOI	73	95	45	63	82	<LOI	63	69	62	78	89	<LOI	55	57	<LOI	60	62	69	84	90	<LOI	71	79
Pyridaben	87	93	90	84	94	95	NS	NS	NS	NS	NS	NS	NS	NS	NS	82	89	93	NS	NS	NS	73	91	89
Fenbuconazole	63	74	75	60	75	82	NS	NS	NS	NS	NS	NS	NS	NS	NS	48	66	75	NS	NS	NS	54	75	74
Azoxystrobin	59	81	87	54	84	86	62	74	80	83	85	90	<LOI	62	64	<LOI	80	83	78	85	85	<LOI	80	82
Dimetomorphe	NS	NS	NS	80	83	89	NS	NS	NS	<LOI	81	88	70	85	88	73	86	88	84	90	90	71	82	80
Toffenyprad	68	84	90	<LOI	72	83	60	78	91	76	85	89	<LOI	83	86	66	80	87	66	89	89	<LOI	76	84

<sup>a</sup> In all of the cases included in this table, the DRS results were confirmed by NIST, and retention time differences (compared to the pesticide database) were <5 s.

<sup>b</sup> LOI = Limit of identification.

<sup>c</sup> NS = Not spiked.

Table 2. Locked retention time, selected ion, and limits of identification (LOI) for cucumber, olive oil, potato, and tangerine for selected target compounds

Compound	R <sub>t</sub> , min <sup>a</sup>	Target ion <sup>b</sup>	Q1 <sup>b</sup>	Q2 <sup>b</sup>	Q3 <sup>b</sup>	LOI, g/kg			
						Cucumber	Olive oil	Potato	Tangerine
Dichlorvos	2.915	108.9 (100)	184.9 (25.50)	186.9 (7.90)	144.9 (7.20)	20 < LOI > 50	10 < LOI > 20	20 < LOI > 50	50 < LOI > 100
Mevinphos	3.797	127.0 (100)	192.0 (26.10)	109.0 (25.40)	67.0 (12.60)	5 < LOI > 10	10 < LOI > 20	5 < LOI > 10	5 < LOI > 10
Methomil	4.763	105.0 (100)	88.0 (37.10)	77.0 (22.60)	<sup>c</sup>	100 < LOI > 500	100 < LOI > 500	100 < LOI > 500	100 < LOI > 500
Omethoate	5.003	156.0 (100)	110.0 (94.20)	109.0 (43.70)	79.0 (45.70)	100 < LOI > 500	100 < LOI > 500	100 < LOI > 500	100 < LOI > 500
Diphenylamine	5.258	169.1 (100)	168.1 (62.40)	167.1 (33.40)	83.5 (9.90)	NS <sup>d</sup>	LOI 5	LOI 5	NS
Etoprophos	5.371	157.9 (100)	126.0 (46.10)	139.0 (45.60)	200.0 (32.00)	10 < LOI > 20	10 < LOI > 20	5 < LOI > 10	20 < LOI > 50
Chlorpropham	5.522	127.0 (100)	213.0 (39.60)	153.0 (49.60)	171.0 (30.30)	LOI 5	5 < LOI > 10	LOI 5	LOI 5
Monocrotophos	5.868	127.0 (100)	192.0 (15.60)	109.0 (11.20)	193.0 (8.90)	20 < LOI > 50	100 < LOI > 500	10 < LOI > 20	NS
Dicloran	6.279	206.0 (100)	176.0 (93.60)	124.0 (50.50)	160.0 (47.60)	5 < LOI > 10	20 < LOI > 50	20 < LOI > 50	10 < LOI > 20
Dimethoate	6.340	87.0 (100)	125.0 (59.50)	93.0 (60.00)	143.0 (12.60)	10 < LOI > 20	20 < LOI > 50	10 < LOI > 20	20 < LOI > 50
Ethoxyquin	6.415	202.1 (100)	174.1 (45.80)	145.0 (21.30)	203.1 (14.80)	LOI 5	LOI 5	LOI 5	LOI 5
Lindane	6.730	180.9 (100)	182.9 (94.80)	218.9 (77.00)	111.0 (67.70)	10 < LOI > 20	5 < LOI > 10	10 < LOI > 20	5 < LOI > 10
Fonophos	6.944	109.0 (100)	137.0 (42.50)	246.0 (36.90)	110.0 (22.20)	LOI 5	LOI 5	LOI 5	LOI 5
Propyzamide	6.974	172.9 (100)	174.9 (63.40)	144.9 (32.00)	255.0 (22.70)	LOI 5	LOI 5	LOI 5	LOI 5
Pyrimethanil	7.064	198.1 (100)	199.1 (46.50)	200.0 (5.60)	100.0 (3.20)	LOI 5	LOI 5	LOI 5	5 < LOI > 10
Diazinon	7.233	179.0 (100)	137.0 (95.60)	152.0 (64.50)	199.0 (58.10)	LOI 5	LOI 5	LOI 5	LOI 5
Pirimicarb	7.838	166.1 (100)	72.0 (70.80)	238.1 (22.40)	167.1 (10.10)	LOI 5	LOI 5	LOI 5	LOI 5
Chlorpyrifos-methyl	8.296	285.9 (100)	287.9 (72.20)	125.0 (57.70)	290.0 (15.90)	5 < LOI > 10	LOI 5	LOI 5	LOI 5
Vinclozolin	8.315	212.0 (100)	285.0 (67.80)	198.0 (96.50)	186.9 (80.60)	LOI 5	LOI 5	LOI 5	LOI 5
Tolclophos-methyl	8.404	265.0 (100)	267.0 (37.60)	125.0 (21.70)	266.0 (10.80)	LOI 5	LOI 5	LOI 5	LOI 5
Alachlor	8.515	160.0 (100)	188.0 (91.40)	146.0 (36.20)	237.0 (26.40)	LOI 5	5 < LOI > 10	LOI 5	10 < LOI > 20
Metolaxyl	8.668	206.1 (100)	160.1 (57.90)	249.2 (38.90)	220.2 (39.80)	NS	10 < LOI > 20	LOI 5	NS
Prometryn	8.670	241.0 (100)	184.0 (71.20)	226.0 (55.00)	106.0 (28.80)	LOI 5	LOI 5	5 < LOI > 10	20 < LOI > 50
Methiocarb	9.024	168.0 (100)	153.0 (60.70)	109.0 (46.10)	91.0 (23.70)	100 < LOI > 500	NS	10 < LOI > 20	100 < LOI > 500
Fenitrothion	9.036	277.0 (100)	125.0 (96.50)	109.0 (77.20)	260.0 (52.80)	10 < LOI > 20	10 < LOI > 20	5 < LOI > 10	20 < LOI > 50
Primiphos-methyl	9.153	290.0 (100)	276.0 (80.50)	305.0 (36.20)	233.0 (31.70)	LOI 5	LOI 5	LOI 5	LOI 5
Dichlofluanid	9.207	123.0 (100)	167.0 (36.60)	224.0 (31.10)	225.9 (21.70)	100 < LOI > 500	20 < LOI > 50	50 < LOI > 100	20 < LOI > 50
Malathion	9.400	173.0 (100)	127.0 (84.90)	125.0 (82.60)	158.0 (43.40)	10 < LOI > 20	10 < LOI > 20	10 < LOI > 20	10 < LOI > 20
Fenithion	9.560	278.0 (100)	125.0 (23.30)	109.0 (18.10)	169.0 (17.30)	5 < LOI > 10	5 < LOI > 10	LOI 5	10 < LOI > 20
Dimethylvinphos	9.575	295.0 (100)	297.0 (66.00)	109.0 (84.10)	204.0 (10.40)	10 < LOI > 20	10 < LOI > 20	10 < LOI > 20	10 < LOI > 20

Table 2. (continued)

Compound	R <sub>t</sub> , min <sup>a</sup>	Target ion <sup>b</sup>	Q1 <sup>b</sup>	Q2 <sup>b</sup>	Q3 <sup>b</sup>	LOI, g/kg			
						Cucumber	Olive oil	Potato	Tangerine
Chlorpyrifos	9.617	197.0 (100)	199.0 (95.90)	314.0 (78.80)	316.0 (51.10)	5 < LOI > 10	5 < LOI > 10	5 < LOI > 10	LOI 5
Parathion	9.637	291.0 (100)	109.0 (77.90)	97.0 (65.90)	139.0 (43.60)	20 < LOI > 50	10 < LOI > 20	100 < LOI > 500	20 < LOI > 50
Triadimefon	9.693	57.1 (100)	208.0 (44.20)	128.0 (25.10)	181.0 (23.50)	5 < LOI > 10	LOI 5	LOI 5	5 < LOI > 10
Isocarbofophos	9.802	136.0 (100)	121.0 (67.50)	120.0 (45.10)	110.0 (36.60)	10 < LOI > 20	50 < LOI > 100	10 < LOI > 20	10 < LOI > 20
Tetraconazole	9.932	336.1 (100)	338.1 (33.10)	337.0 (15.20)	100.9 (13.90)	LOI 5	LOI 5	LOI 5	LOI 5
Cyprodinil	10.282	224.1 (100)	225.1 (62.40)	210.0 (9.90)	70.0 (6.90)	LOI 5	LOI 5	LOI 5	LOI 5
Isofenphos methyl	10.418	199.0 (100)	121.0 (80.00)	241.0 (40.00)	231.0 (30.00)	5 < LOI > 10	LOI 5	LOI 5	5 < LOI > 10
Thiabendazole	10.469	201.0 (100)	174.0 (75.60)	129.0 (6.20)	c	50 < LOI > 100	10 < LOI > 20	5 < LOI > 10	5 < LOI > 10
Perconazole	10.514	248.0 (100)	159.0 (94.60)	161.0 (61.00)	250.0 (33.10)	LOI 5	LOI 5	LOI 5	10 < LOI > 20
Tolyfluanid	10.623	137.0 (100)	106.0 (39.40)	240.0 (27.80)	181.0 (25.90)	10 < LOI > 20	10 < LOI > 20	20 < LOI > 50	20 < LOI > 50
Isofenphos	10.808	213.0 (100)	121.0 (53.90)	255.0 (44.30)	185.0 (40.40)	LOI 5	LOI 5	LOI 5	LOI 5
Quinalphos	10.826	146.0 (100)	157.1 (61.00)	156.1 (35.50)	118.0 (44.40)	10 < LOI > 20	5 < LOI > 10	10 < LOI > 20	5 < LOI > 10
Triadimenol	10.834	112.0 (100)	168.1 (80.00)	128.0 (67.70)	131.0 (49.80)	10 < LOI > 20	10 < LOI > 20	10 < LOI > 20	20 < LOI > 50
Mecarban	10.870	131.0 (100)	159.0 (54.30)	160.0 (42.50)	96.9 (103.50)	10 < LOI > 20	10 < LOI > 20	5 < LOI > 10	10 < LOI > 20
Fipronil	10.905	367.0 (100)	369.0 (69.19)	213.0 (30.20)	351.0 (6.60)	LOI 5	10 < LOI > 20	10 < LOI > 20	5 < LOI > 10
Procymidone	10.981	96.0 (100)	283.0 (70.50)	285.0 (45.60)	67.0 (41.40)	LOI 5	5 < LOI > 10	LOI 5	LOI 5
Methidathion	11.150	145.0 (100)	85.0 (58.80)	93.0 (16.00)	125.0 (15.20)	20 < LOI > 50	10 < LOI > 20	20 < LOI > 50	10 < LOI > 20
-Endosulfan	11.318	240.9 (100)	236.9 (98.30)	238.9 (93.50)	194.9 (89.10)	5 < LOI > 10	LOI 5	5 < LOI > 10	10 < LOI > 20
Mepanipyrim	11.532	222.1 (100)	223.0 (51.80)	77.0 (11.80)	67.0 (11.10)	LOI 5	LOI 5	LOI 5	LOI 5
Hexaconazole	11.761	83.0 (100)	214.0 (63.60)	216.0 (42.30)	175.0 (28.70)	LOI 5	5 < LOI > 10	LOI 5	5 < LOI > 10
Imazalil	11.894	215.0 (100)	172.9 (93.70)	217.0 (64.20)	174.9 (62.50)	20 < LOI > 50	10 < LOI > 20	20 < LOI > 50	LOI 5
Flutolanil	11.920	172.9 (100)	145.0 (28.90)	281.1 (20.40)	323.1 (13.80)	NS	LOI 5	LOI 5	NS
Fludioxonil	12.045	248.0 (100)	127.0 (36.30)	154.0 (28.40)	153.0 (18.50)	LOI 5	10 < LOI > 20	LOI 5	LOI 5
Myclobutanil	12.220	179.0 (100)	150.0 (47.90)	181.0 (33.00)	152.0 (26.90)	LOI 5	5 < LOI > 10	LOI 5	5 < LOI > 10
Iprobalicarb	12.255	119.0 (100)	134.0 (58.00)	116.0 (51.90)	158.0 (27.30)	5 < LOI > 10	20 < LOI > 50	20 < LOI > 50	20 < LOI > 50
Buprofezin	12.289	105.0 (100)	106.0 (48.00)	104.0 (46.80)	172.0 (40.20)	LOI 5	LOI 5	LOI 5	5 < LOI > 10
Flusilazole	12.297	233.1 (100)	206.0 (31.70)	234.0 (19.30)	220.1 (8.00)	LOI 5	LOI 5	LOI 5	LOI 5
Bupirimate	12.403	273.1 (100)	208.1 (77.80)	316.2 (37.70)	166.1 (50.20)	LOI 5	LOI 5	LOI 5	LOI 5
Kresoxim-methyl	12.454	116.0 (100)	206.0 (59.40)	131.0 (55.20)	132.0 (23.90)	LOI 5	LOI 5	LOI 5	LOI 5
-Endosulfan	12.579	194.9 (100)	236.9 (85.10)	207.0 (81.10)	159.0 (66.80)	5 < LOI > 10	5 < LOI > 10	5 < LOI > 10	10 < LOI > 20

Table 2. (continued)

Compound	R <sub>t</sub> , min <sup>a</sup>	Target ion <sup>b</sup>	Q1 <sup>b</sup>	Q2 <sup>b</sup>	Q3 <sup>b</sup>	LOI, g/kg			
						Cucumber	Olive oil	Potato	Tangerine
Chlorfenapyr	12.613	59.0 (100)	247.0 (7.80)	249.0 (5.90)	408.0 (4.90)	5 < LOI > 10	5 < LOI > 10	5 < LOI > 10	10 < LOI > 20
Oxadixyl	12.949	105.0 (100)	163.0 (97.80)	132.0 (76.30)	120.0 (45.30)	5 < LOI > 10	10 < LOI > 20	5 < LOI > 10	10 < LOI > 20
Triazophos	13.228	161.0 (100)	162.0 (67.00)	172.0 (40.90)	257.0 (29.40)	5 < LOI > 10	10 < LOI > 20	5 < LOI > 10	10 < LOI > 20
Oflurace	13.283	132.0 (100)	160.0 (77.80)	232.1 (54.80)	281.1 (39.40)	5 < LOI > 10	10 < LOI > 20	20 < LOI > 50	NS
Benalaxil	13.373	148.0 (100)	91.0 (41.80)	206.0 (26.90)	204.0 (20.10)	LOI 5	LOI 5	LOI 5	LOI 5
Endosulfan sulfate	13.380	272.0 (100)	274.0 (83.50)	229.0 (61.00)	387.0 (45.60)	10 < LOI > 20	20 < LOI > 50	10 < LOI > 20	20 < LOI > 50
Quinoxifen	13.385	237.0 (100)	272.0 (39.10)	307.0 (32.60)	309.0 (19.60)	LOI 5	LOI 5	LOI 5	LOI 5
Propiconazole	13.470	173.0 (100)	259.0 (72.60)	175.0 (63.20)	261.0 (54.70)	LOI 5	5 < LOI > 10	LOI 5	LOI 5
Trifloxystrobin	13.657	116.0 (100)	131.0 (61.70)	222.0 (34.10)	186.0 (24.20)	5 < LOI > 10	10 < LOI > 20	10 < LOI > 20	10 < LOI > 20
Tebuconazole	13.716	125.0 (100)	250.0 (98.80)	127.0 (35.60)	252.0 (32.40)	10 < LOI > 20	20 < LOI > 50	5 < LOI > 10	10 < LOI > 20
Nuarimol	13.724	235.0 (100)	107.0 (88.20)	203.0 (80.20)	139.0 (75.20)	5 < LOI > 10	LOI 5	5 < LOI > 10	LOI 5
Triphenyl phosphate	13.862	326.0 (100)	325.0 (80.70)	215.0 (19.10)	170.0 (17.80)	LOI 5	LOI 5	LOI 5	LOI 5
Iprodione	14.195	187.0 (100)	314.0 (69.70)	189.0 (65.80)	244.0 (65.30)	5 < LOI > 10	100 < LOI > 500	20 < LOI > 50	50 < LOI > 100
Phosmet	14.252	160.0 (100)	317.0 (4.10)	192.0 (1.50)	c	20 < LOI > 50	20 < LOI > 50	50 < LOI > 100	50 < LOI > 100
Bromopropylate	14.308	340.9 (100)	338.9 (51.30)	342.9 (49.20)	182.9 (48.70)	5 < LOI > 10	LOI 5	LOI 5	LOI 5
Bifenthrin	14.419	181.1 (100)	165.0 (31.40)	166.0 (29.60)	182.1 (15.10)	LOI 5	LOI 5	LOI 5	5 < LOI > 10
Tebufenpyrad	14.547	318.0 (100)	171.0 (52.70)	333.0 (78.20)	276.0 (38.50)	LOI 5	LOI 5	LOI 5	LOI 5
Bifenox	14.592	341.0 (100)	343.0 (65.90)	311.0 (35.60)	189.0 (34.20)	10 < LOI > 20	10 < LOI > 20	100 < LOI > 500	20 < LOI > 50
Tetradifon	14.690	159.0 (100)	111.0 (72.00)	299.0 (59.70)	227.0 (58.90)	LOI 5	5 < LOI > 10	LOI 5	20 < LOI > 50
Phosalone	14.838	182.0 (100)	121.0 (40.50)	184.0 (33.40)	367.0 (25.40)	10 < LOI > 20	20 < LOI > 50	10 < LOI > 20	10 < LOI > 20
Pyriproxyfen	14.928	136.0 (100)	78.0 (14.10)	96.0 (13.00)	226.0 (8.30)	LOI 5	LOI 5	LOI 5	LOI 5
Cyhalothrin	15.185	181.0 (100)	197.0 (84.20)	208.1 (50.50)	141.1 (30.30)	10 < LOI > 20	10 < LOI > 20	5 < LOI > 10	20 < LOI > 50
Fenarimol	15.201	139.0 (100)	219.0 (69.70)	107.0 (68.60)	251.0 (60.00)	LOI 5	5 < LOI > 10	LOI 5	LOI 5
Pyrazophos	15.359	221.1 (100)	232.1 (34.60)	373.1 (25.50)	237.1 (18.70)	100 < LOI > 500	10 < LOI > 20	5 < LOI > 10	NS
Acinatrif	15.362	208.0 (100)	181.0 (80.00)	289.0 (59.90)	209.0 (52.20)	10 < LOI > 20	10 < LOI > 20	10 < LOI > 20	100 < LOI > 500
Permethrin	15.684	183.1 (100)	163.0 (19.40)	165.0 (16.70)	184.0 (15.80)	20 < LOI > 50	5 < LOI > 10	5 < LOI > 10	5 < LOI > 10
Pyridaben	15.762	147.0 (100)	117.0 (15.00)	148.1 (12.00)	309.1 (8.00)	100 < LOI > 500	10 < LOI > 20	5 < LOI > 10	100 < LOI > 500
Prochloraz	15.865	180.1 (100)	308.0 (53.20)	310.0 (52.40)	198.0 (18.00)	50 < LOI > 100	20 < LOI > 50	5 < LOI > 10	20 < LOI > 50
Cyfluthrin	16.109	163.0 (100)	206.0 (70.70)	165.0 (67.50)	227.0 (52.60)	100 < LOI > 500	100 < LOI > 500	100 < LOI > 500	100 < LOI > 500
Fenbuconazole	16.116	129.0 (100)	198.1 (46.10)	125.0 (39.30)	211.1 (6.00)	100 < LOI > 500	10 < LOI > 20	10 < LOI > 20	100 < LOI > 500

Table 2. (continued)

Compound	R <sub>t</sub> , min <sup>a</sup>	Target ion <sup>b</sup>	Q1 <sup>b</sup>	Q2 <sup>b</sup>	Q3 <sup>b</sup>	LOI, g/kg			
						Cucumber	Olive oil	Potato	Tangerine
Cypermethrin	16.484	163.0 (100)	181.0 (71.60)	165.0 (65.60)	209.0 (45.10)	100 < LOI > 500	100 < LOI > 500	100 < LOI > 500	100 < LOI > 500
Fluvalinate tau	17.359	250.0 (100)	252.0 (34.30)	209.0 (28.80)	181.0 (24.30)	100 < LOI > 500	100 < LOI > 500	100 < LOI > 500	100 < LOI > 500
Deltamethrin	18.000	181.0 (100)	253.0 (66.90)	251.0 (42.90)	255.0 (32.60)	100 < LOI > 500	100 < LOI > 500	100 < LOI > 500	100 < LOI > 500
Azoxystrobin	18.315	344.0 (100)	388.0 (30.00)	345.0 (28.40)	372.0 (16.10)	10 < LOI > 20	20 < LOI > 50	LOI 5	20 < LOI > 50
Dimethomorph	18.342	301.0 (100)	303.0 (34.20)	387.0 (30.30)	165.0 (26.00)	50 < LOI > 100	20 < LOI > 50	10 < LOI > 20	20 < LOI > 50
Tofenpyrad	18.423	383.0 (100)	197.0 (73.60)	171.0 (65.40)	211.0 (40.10)	10 < LOI > 20	20 < LOI > 50	5 < LOI > 10	20 < LOI > 50

<sup>a</sup> R<sub>t</sub> = Retention time.<sup>b</sup> Percent relative abundance shown in parentheses.<sup>c</sup> Only two qualifier ions selected.<sup>d</sup> NS = Not spiked.

The full-scan mode is a standard feature in all MS detectors. However, most methods employ it for qualitative analysis only. A major advantage of the full-scan mode over the SIM mode is the simultaneous identification of other eluted compounds that could be of interest. A major disadvantage is that, generally, the full-scan method is less sensitive than the SIM method, although new generation equipment yields sufficient sensitivity to meet current regulations (12). Recently, the use of library searching methods for GC/MS has made it possible to search the large National Institute of Standards and Technology (NIST) pesticide libraries in minutes (13).

With retention time locked (RTL)-GC/MS, the detection selectivity is greatly improved by linking the locked retention time to the mass spectral data. This reduces the risk of false positives. Nowadays, these methods have been widely developed to analyze multiresidues in fresh vegetables, fruit, and honey (14–16). The automated mass spectral deconvolution and identification system (AMDIS; 13) is post-processing software for extracting “purified” mass spectra from a one-dimensional gas chromatogram. The AMDIS offers the possibility of identifying compounds by both mass spectra and retention index (or retention time) together.

This paper reports the development and evaluation of a rapid, automated screening method for the detection of pesticide residues in food using GC/MS. It is based on the use of deconvolution reporting software (DRS) together with a database containing mass spectra and locked retention times for 927 pesticides and endocrine disruptors (13). Simultaneously with the screening, the method performs an automatic quantification of 95 target pesticides. The method is RTL, and the analytical column is backflushed by reversing the column flow at the end of the run in order to minimize maintenance of the system.

## Experimental

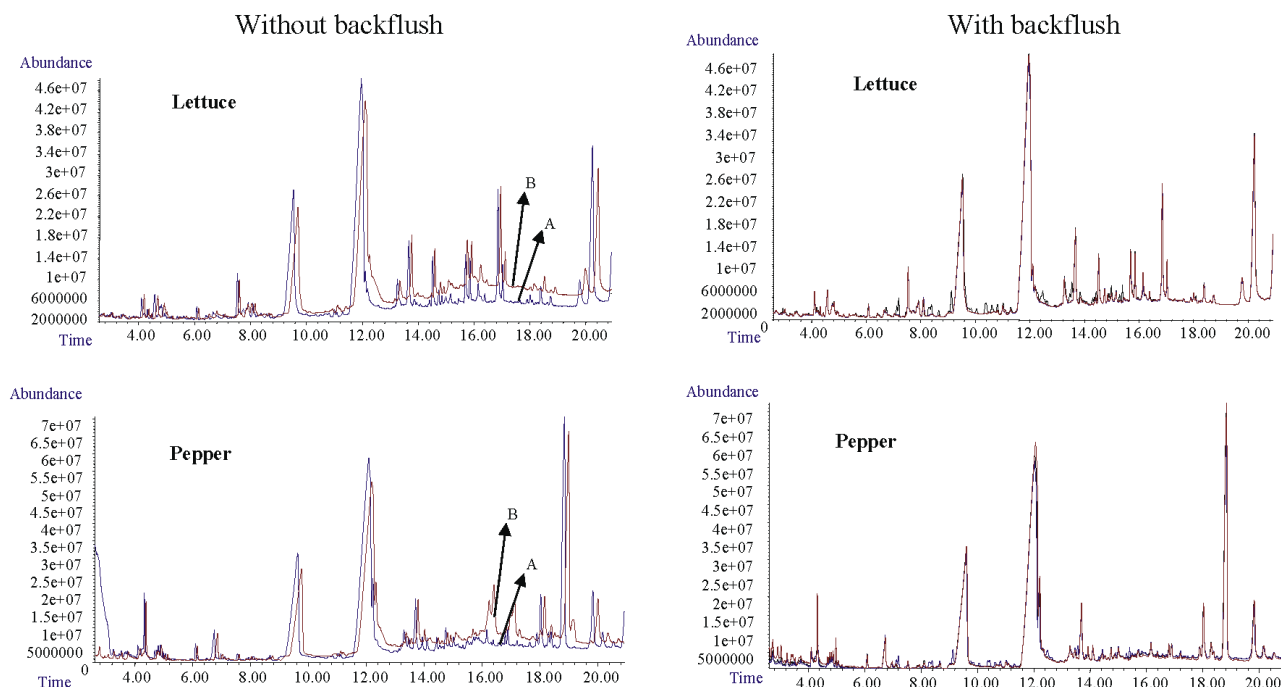
### Chemicals and Reagents

Pesticide analytical standards were purchased from Dr. Ehrenstorfer (Ausborg, Germany) or Riedel de-Haën (Seelze, Germany). Individual pesticide stock solutions (approximately 500 g/mL) were prepared in methanol or ethyl acetate and were stored at –18 C. HPLC grade acetonitrile (ACN) and methanol were obtained from Merck (Darmstadt, Germany). Primary-secondary amine (PSA) sorbent material was obtained from Supelco (Bellefonte, PA).

### Sample Treatment

Fruit, vegetable, and olive oil samples were purchased from different local markets. The extraction procedure used for fruit and vegetable samples [the so-called quick, easy, cheap, effective, rugged, and safe (QuEChERS) method, described elsewhere; 17, 18], comprised the following steps: A representative 15 g portion of previously homogenized sample was weighed in a 200 mL PTFE centrifuge tube. Then 15 mL ACN was added, and the tube was shaken vigorously for 1 min. After this, 1.5 g NaCl and 4 g MgSO<sub>4</sub> were added,





**Figure 1.** Extracts of lettuce and pepper injected 3 times with a 2 min backflush and 3 times without backflush. The first and third injections are shown in each case. Without backflushing, the third injection (B) shows carryover, and retention time shifts compared to the first injection (A).

and the shaking process was repeated for 1 min. The extract was then centrifuged (3700 rpm) for 1 min. A 5 mL amount of the supernatant (acetonitrile phase) was then transferred to a 15 mL graduated centrifuge tube containing 250 mg PSA and 750 mg  $MgSO_4$ , which was then shaken energetically for 20 s. Following this, the extract was centrifuged again (3700 rpm) for 1 min. Finally, an extract containing the equivalent of 1 g of sample/mL of nearly 100% ACN was obtained.

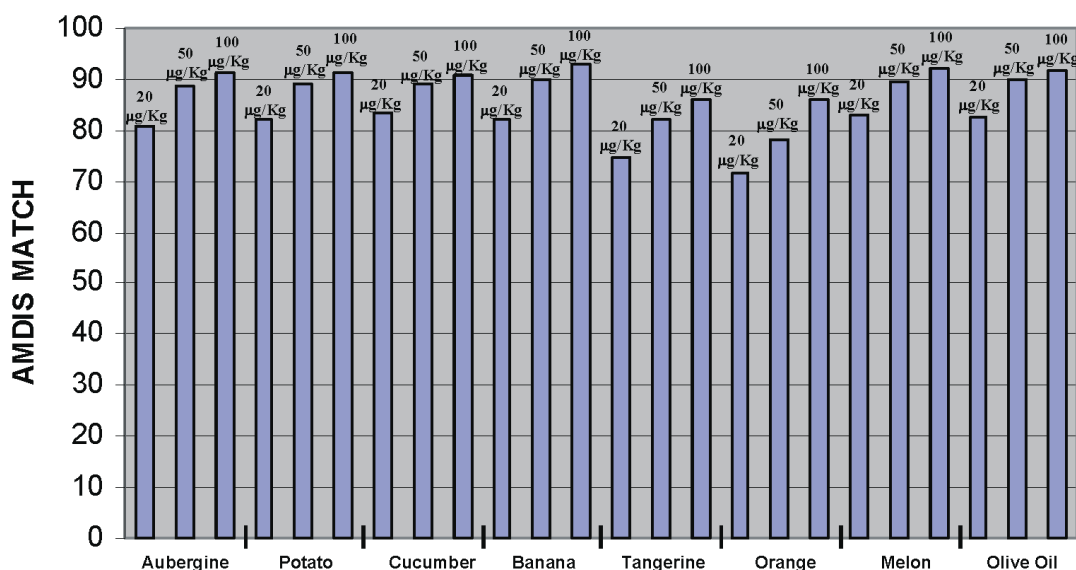
Olive oil samples were extracted by matrix solid-phase dispersion, with a preliminary liquid-liquid extraction using aminopropyl as the sorbent material, with a cleanup performed in the elution step with Florisil. The complete procedure was described previously (19).

### GC/MS System

GC/MS analyses were run on an Agilent 7890 series gas chromatograph (Agilent Technologies, Santa Clara, CA) interfaced to an Agilent 5975 mass selective detector (MSD). Retention time locking, data acquisition, processing, and instrumental control were performed by the Agilent MSD ChemStation software (E.0200.493 version). A programmable temperature vaporizing (PTV) inlet was used in the solvent vent mode; an empty 1.8 mm id liner was placed in the PTV injector. Analytes were separated in an Agilent HP-5MSi capillary column (5% biphenyl/95% dimethylsiloxane), 15 m  $\times$  0.25 mm id, 0.25  $\mu$ m film thickness. A deactivated fused-silica restrictor (0.171 m  $\times$  0.120 mm id, 0.1  $\mu$ m film thickness) was placed in the transfer

line, which was connected to the capillary column through a QuickSwap device. The QuickSwap device is a purged T-connection placed between the end of the GC column and the entrance to the MSD transfer line. The inlet operating conditions were injection volume, 10  $\mu$ L, and injection speed, 30 000  $\mu$ L/min; the temperature program was set at 79 C for 0.25 min, programmed to 300 C at 710 C/min, and kept at this temperature for 2 min. The helium carrier gas flow was maintained at a constant pressure of 17.296 psi. As RTL method was used, using the locked retention time of chlorpyrifos methyl divided by 2 (8.297 min) as the reference; this retention time was taken from the Agilent Pesticide and Endocrine Disruptor database. The retention time database was created with a chromatographic method in which the run time was double the run time proposed in this paper. All of the conditions in the methods were the same except for the column length; the reference method used a column length of 30 m length, and the proposed method 15 m. To compare experimental retention times with those registered in the database, division by 2 was required.

As an example, the retention time of chlorpyrifos methyl (used as the reference) in the original method with a column of 30 m length was 16.594 min, and in the proposed method using a column of 15 m was 8.297 min. The oven temperature program was 70 C for 1 min, programmed to 150 C at 50 C/min, then to 200 C at 6 C/min, and finally to 280 C at 16 C/min; it was kept at this temperature for 5 min. After that, a post-run of 5 min was carried out with a temperature of



**Figure 2.** Mean AMDIS match values obtained after DRS analysis of full-scan chromatograms obtained by RTL GC of aubergine, potato, cucumber, banana, tangerine, orange, melon, and olive oil extracts at three concentration levels of 20, 50, and 100 g/kg.

290 C. During the post-run, the column head pressure was lowered to 1 psi and the pressure in the Quick Swap increased to 60 psi. During this post-run time, the column flow was reversed in order to backflush high-boiling components from the head of the column and out through the split vent of the PTV inlet.

Electron impact mass spectra in the full-scan mode were obtained at 70 eV; the monitoring was from  $m/z$  50 to 400. The ion source and quadrupole analyzer temperatures were fixed at 230 and 150 C, respectively.

Trace ion detection (20) was turned on. This is a filtering algorithm to smooth peaks. This filtering is an advanced form of averaging used to remove the noise riding on the signal. Trace ion detection provides better S/N values and helps deconvolution to confirm target compounds.

#### Automatic Screening

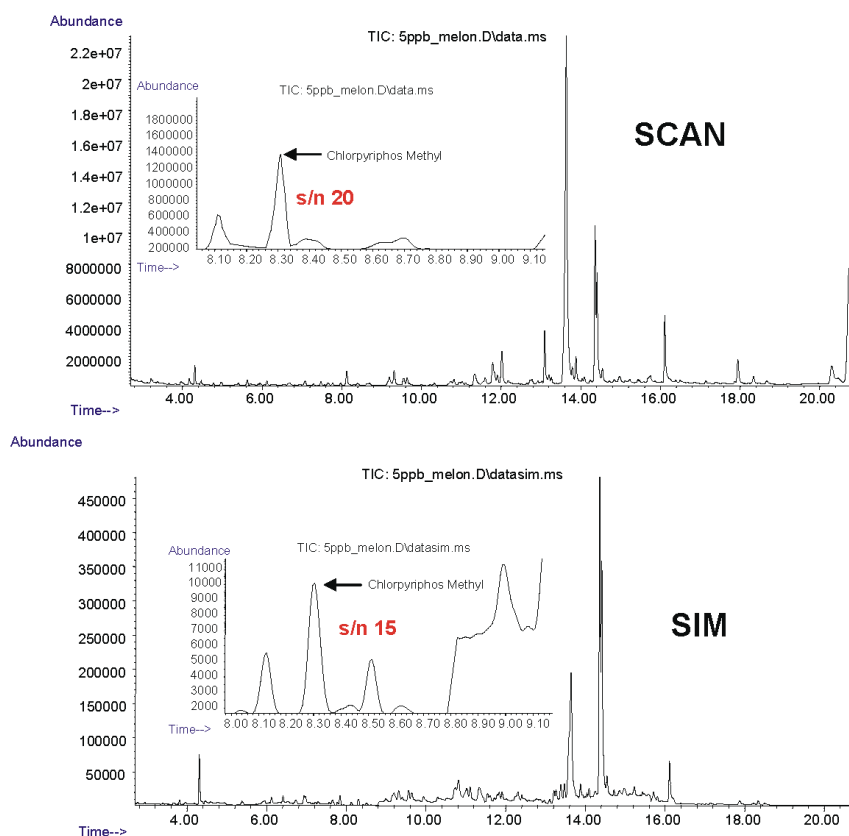
A pesticide mixture containing the compounds listed in Table 1 was spiked into eight different matrix extracts: aubergine, potato, cucumber, banana, tangerine, orange, melon, and olive oil. All compounds were added at three spiking levels: 20, 50, and 100 g/kg. The spiked extracts were analyzed by GC/MS in the full-scan mode using the RTL method detailed above. DRS (Version A.03.00) was used to identify the compounds in chromatograms obtained in the full-scan mode in these matrixes. This software results from a marriage of three different software packages: the Agilent GC/MS ChemStation, the NIST Mass Spectral Search Program with the NIST'05 MS Library, and the Automated Mass Spectral Deconvolution and AMDIS software (Version 2.64), also from NIST. The deconvolution parameters in AMDIS were fixed as follows: adjacent peak subtraction, 2; resolution, high; sensitivity, very high; and shape requirements, medium.

The used database has the possibility of increasing the number of compounds. This feature is very interesting for the user. The way to include new compounds in the database is by analyzing a pure standard of the new substance using the proposed RTL method and storing the mass spectrum in the database, along with its locked retention time. This retention time must be expressed in seconds because absolute retention times in seconds instead of retention index values are employed for this method. The AMDIS software allows the substitution of retention times expressed in seconds for retention index values. Therefore, retention times obtained must be multiplied by 60. The retention times must also be multiplied by 2, because the original database retention times were obtained by analysis in an analytical column of 30 m length using a method that took exactly twice as long; the retention times obtained for this method are exactly half of those stored in the Pesticide and Endocrine Disruptor database. The AMDIS retention index calibration file automatically converts real retention times obtained in the chromatogram, so they are comparable to those stored in the database.

#### Quantification of Target Compounds

Table 2 lists the locked retention time (min), the target ion, and the qualifier ions for the 95 pesticides selected for full-scan quantification. Matrix-matched solutions were prepared by spiking the selected matrixes (after the extraction) with all of the pesticides at 5, 10, 20, 50, 200, and 500 g/kg.

The quantification of target compounds was performed in the full-scan mode. An automatic method was used to identify and quantify the samples. For this automatic method, three ions and the retention time were selected for each compound (Table 1).



**Figure 3. Total ion chromatograms in full-scan and SIM modes of a melon extract spiked at 5 g/kg. The areas of the chromatograms where chlorpyrifos-methyl elutes are magnified. The S/N of chlorpyrifos-methyl is shown in the chromatograms.**

Limit of identification (LOI) values were determined for each compound; this limit was considered to be the minimum concentration identified by the DRS software with the selected library.

The LOI of each compound in each matrix was investigated to ensure the S/N was equal to or higher than 10, and they were used as LOQs. Linearity of the analytical response was evaluated by the injection of a matrix-matched solution at six concentrations levels, ranging from the LOI of each compound up to 500 g/kg.

## Results and Discussion

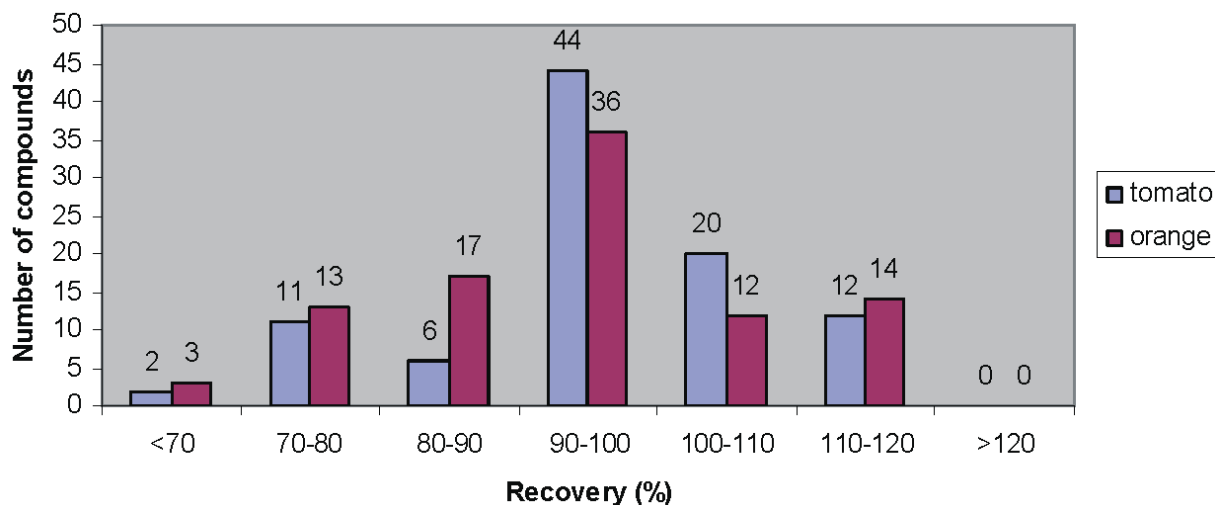
### GC/MS System

The GC system employed had a QuickSwap device placed between the end of the column and the entrance to the MSD transfer line. A small purge gas flow mixed with the column effluent and passed through the deactivated fused silica restrictor inside the transfer line and into the MSD source. This device provided a means of removing or changing the column without needing to cool and vent the mass spectrometer; gave protection against unwanted air entry when doing routine maintenance on columns and inlets; and offered a means for backflushing columns to remove high-boiling components, thus reducing both run times and

cool-down times, as well as minimizing ghosting from run to run.

Backflush is a means of discarding high-boiling compounds from a column after the peaks of interest have eluted. It saves analysis time and has the following additional benefits: longer column life (due to less high-temperature exposure), protection from air and water at high temperatures, and less chemical background and contamination of the MSD source.

The advantage of using backflush in the column was demonstrated for two different matrixes: lettuce and pepper. Six 10 L injections were made of each extract—three with and three without backflushing; the chromatograms obtained are shown in Figure 1. Both lettuce and pepper samples showed the same results. When analyses were run without backflush, the baseline increased, and retention times shifted a mean of 5 s after three injections. In Figure 1, the third injection (labeled B) shows considerable chromatographic deterioration compared to the first injection (labeled A). However, when injections were performed with 2 min of backflushing at the end of each run, the baseline and retention times were stable. As shown by the overlapped chromatograms in Figure 1, backflushing eliminated carryover and retention time shifts.



**Figure 4.** Distribution of recoveries studied in two matrixes for 95 pesticides using QuEChERS as the extraction procedure.

### Automatic Screening

Matrixes from different categories were chosen to perform this study. Spiked samples of aubergine, potato, cucumber, banana, tangerine, orange, melon, and olive oil at 20, 50, and 100 g/kg were analyzed by the RTL GC/MS method; full-scan spectra were analyzed with DRS. Analysis with DRS provides a report with the following information: the retention time of the identified compound, CAS number, compound name, match quality, and the retention time difference (in seconds) between the observed peak and the database value, and the match and hit number—all by searching the deconvoluted spectrum against the entire NIST Mass Spectral Library.

In Table 1, the match values obtained by AMDIS for all of the compounds in the selected matrixes at the three concentrations are given. In all cases included in Table 1, DRS showed confirmation by NIST and retention time differences (compared to the pesticide database) of less than 5 s.

This study has been performed to find out about the influence of concentration and matrix in the identification capabilities of the proposed method. Means of the AMDIS match values are shown in Figure 2 for all of the selected pesticides in aubergine, potato, cucumber, banana, tangerine, orange, melon, and olive oil extracts at 20, 50, and 100 g/kg. A clear relationship is observed between the mean match values for all of the studied matrixes and the pesticide concentration level. Match values increased when the concentration was higher. Lower concentrations imply lower S/Ns, and deconvoluted spectra are affected with ions from the matrix.

The influence of the matrix was also observed (Figure 2); matrixes with high acid content, such as tangerine and orange, usually showed lower match values compared to the rest of the studied matrixes. The extracts of matrixes with high acid content probably also contained the largest number of volatile natural products. They could interfere with the pesticide

analysis, and the deconvolution process was less effective than in other types of matrixes.

The AMDIS match values were, in general, better than 90. A small group of pesticides (dichlorvos, monocrotophos, dimethoate, metalaxyl, prometryn, fenitrothion, malathion, fenthion, parathion, isocarbophos, thiabendazole, tolylfluanide, methidathion, phenamiphos, buprofecin, iprovalicarb, ofurace, endosulfan sulphate, trifloxystrobin, nuarimol, tebuconazole, iprodione, phosmet, fenpropathrin, phosalone, -cyhalothrin, pyrazophos, acrinathrin, prochloraz; fenbuconazole, azoxystrobin, and imazalil) showed lower match values (70–90). Taking into account these results, the target match value was fixed at 70. Furthermore, a reduced group of pesticides with specific commodities at low concentration (20 g/kg) showed match values lower than 70 (Table 1). Those cases represented 3% of the total determinations performed. In such cases, the NIST match value obtained and the retention time difference in AMDIS were 60 and 5 s, respectively. Therefore, they were considered as possible positive findings, but some additional parameters should be necessary for confirmation.

With regard to automatic screening, isofenphos methyl is a special case. Although this compound was not included in the commercial library due to its particular interest (3, 4), it was introduced additionally into the commercial database. Its determination was performed following the procedures described in the *Experimental* section.

### Analysis of Target Compounds

Our first option for performing analysis of target compounds was to develop an acquisition method in the SIM mode, since the system provides the possibility of acquiring data in full-scan and SIM modes within the same analysis. Two alternatives were considered: to make a unique method that includes the acquisition of 100 compounds in SIM; or to develop two different SIM methods, each including

**Table 3. Carrot sample from European Proficiency Test (EUPT) FV 10 analyzed by the RTL method for simultaneous screening and target compound quantification**

Pesticide	Concn, mg/kg, EUPT FV 10	Positives found with the proposed screening method	Quantification with the proposed method, concn, mg/kg
Acetamiprid	0.419	Yes	<sup>a</sup>
Boscalid	0.238	Yes	<sup>a</sup>
Chlorpyrifos-methyl	0.078	Yes	0.076
Diazinon	0.603	Yes	0.609
Endosulfan sulfate	0.107	Yes	0.119
Hexythiazox	0.509	No <sup>b</sup>	<sup>a</sup>
Isofenphos-methyl	0.499	Yes	0.521
Kresoxim-methyl	0.050	Yes	0.049
Malathion	0.771	Yes	0.769
Metamidophos	0.342	Yes	0.342
Methiocarb	0.043	Yes	0.050
Methiocarb sulfone	0.065	No <sup>b</sup>	<sup>a</sup>
Methiocarb sulfoxide	0.051	No <sup>b</sup>	<sup>a</sup>
Methomyl	0.739	Yes	0.790
Oxamyl	0.322	Yes	<sup>a</sup>
Pendimethalin	0.074	Yes	<sup>a</sup>
Phosmet	0.236	Yes	0.235
Quinoxifen	0.298	Yes	0.298
Triadimenol	0.331	Yes	0.325
Vinclozolin	1.040	Yes	1.038

<sup>a</sup> Not included in the quantification method.

<sup>b</sup> Not included in the database used.

50 compounds. When the SIM LOD values of the target compound, calculated as the minimal concentration with  $S/N = 3$ , were evaluated and compared with the LOI in the full-scan mode, our expectation was to improve the sensitivity by 10 times when working in SIM compared with full scan. However, the LOD achieved for most of the compounds in both SIM alternatives (the SIM method with 100 compounds, and the two different methods with 50 compounds each) were similar to those in the full-scan mode.

The proposed method had an analysis time of 22 min. In order to perform a SIM method for 50 selected pesticides, it was necessary to create 13 retention time windows with 166 selected ions. Due to the properties of the pesticides, 76% of them eluted between 6 and 15 min.

Figure 3 shows chromatograms in full-scan and SIM models of a melon extract spiked at 5 g/kg. The areas of the chromatograms where chlorpyrifos-methyl elutes are magnified.  $S/N$  ratio values are very close in SIM ( $S/N = 11$ ) and full-scan ( $S/N = 14$ ) chromatograms for chlorpyrifos-methyl, and the same trend was observed for the other compounds (data not shown). The difference in the  $S/N$  values in SIM and full-scan chromatograms were in the range of  $\pm 5$ . The developed quantification method was performed in full-scan mode.

LOI was evaluated for all compounds in the eight different matrixes. In Table 2, values for four different matrixes are shown, corresponding to the four commodity categories: cucumber (high water content), olive oil (high oil content), potato (high protein or high starch content), and tangerine (high acid content). LOIs lower than 20 g/kg were achieved for 70% of the studied pesticides.

The linearity of the pesticides listed in Table 2 was studied in aubergine, potato, cucumber, banana, tangerine, orange, melon, and olive oil matrixes from the LOI to 500 g/kg. A linear response was obtained for all pesticides in all of the selected matrixes within the studied range, and  $r^2$  values  $> 0.99$  were obtained in all cases.

For the recovery study, spiked samples were prepared for each of the two matrixes selected (tomato and orange) at the 100 g/kg level. The QuEChERS method was carried out 5 times on each matrix. The data evaluation was carried out by comparing the peak intensities of the spiked samples to those obtained by matrix-matched standard calibration. Extracted "blank" matrixes may have contained some of the investigated pesticides. Therefore, blank correction from the calibration samples and also from the spiked samples was necessary during the analysis. The distribution of the recoveries is shown in Figure 4. More than 95% of the pesticides under

**Table 4. Analysis of 117 market-purchased fruit, vegetable, and olive oil samples using the proposed automatic simultaneous screening and quantification method**

Sample	Identified pesticides	Concn, g/kg
Red_apple_s1	Chloropyrifos	30
	Thiabendazole	<sup>a</sup>
	Imazalil	23
	Diclorvos	<sup>a</sup>
Green_pepper_s2	—	
Red_pepper_s3	—	
Carrot_s4	—	
Kiwi_s5	Fenhexamid	<sup>a</sup>
Lettuce_s6	—	
Apple_s7	Thiabendazole	<sup>a</sup>
	Imazalil	<sup>a</sup>
Apple_s8	Thiabendazole	<sup>a</sup>
	Imazalil	<sup>a</sup>
Pear_s9	Imazalil	<sup>a</sup>
Pear_s10	Ethoxyquin	<sup>a</sup>
	Imazalil	<sup>a</sup>
Pear_s11	Dichlorvos	15
	Ethoxyquin	<sup>a</sup>
	Thiabendazole	<sup>a</sup>
	Imazalil	<sup>a</sup>
Pepper_s12	—	
Pepper_s13	Cyprodinil	40
Tomato_s14	—	
Carrot_s15	—	
Kiwi_s35	—	
Strawberry_s36	—	
Carrot_s16	—	
Watermelon_s17	Bifenthrin	28
Melon_s18	Pirimiphos-methyl	15
Nectarine_s19	Fenthion	<sup>a</sup>
Red_pepper_s20	—	
Leek_s21	—	
Tomato_s22	Bifenthrin	12
Banana_s23	—	
Melon_s24	—	
Apple_s25	—	
Apple_s26	—	
Tomato_s27	Procymidone	83
Peach_s28	—	
Tangerine_s29	Isoproc carb	<sup>a</sup>
Peach_s30	—	
Lettuce_s31	—	
Onion_s32	—	

**Table 4. (continued)**

Sample	Identified pesticides	Concn, g/kg
Banana_s33	—	
Apple_s34	Pirimicarb	<sup>a</sup>
	Fenhexamid	<sup>a</sup>
Apple_s37	Dichlorvos	15
	Ethoxyquin	<sup>a</sup>
	Chlorpyrifos	20
	Thiabendazole	<sup>a</sup>
	Imidazole	<sup>a</sup>
Strawberry_s38	Fludioxonil	35.22
	Cyprodinil	20
	Kresosim-methyl	24.85
Strawberry_s39	Bupirimate	25.15
	Cyprodinil	2.66
Strawberry_s40	Benzophenone	<sup>a</sup>
Strawberry_s41	Benzophenone	<sup>a</sup>
Strawberry_s42	Benzophenone	<sup>a</sup>
Strawberry_s43	Benzophenone	<sup>a</sup>
Strawberry_s44	Benzophenone	<sup>a</sup>
	Cyprodinil	83
	Fludioxonil	51.39
	Myclobutanil	3.66
	Bupirimate	57
Strawberry_s45	Benzophenone	<sup>a</sup>
	Ciprodinil	106.38
	Fludioxonil	27.55
	Miclobutanil	14.08
	Kresosim-methyl	8.68
Strawberry_s46	Benzophenone	<sup>a</sup>
	Ciprodinil	6.48
	Miclobutanil	28.63
	Ciproconazole	<sup>a</sup>
Strawberry_s47	Benzophenone	<sup>a</sup>
	Cyprodinil	7.21
	Fludioxonil	10.84
	Bupirimate	1.89
Strawberry_s48	Benzophenone	<sup>a</sup>
	Cyprodinil	5.76
	Azoxystrobin	7.15
Strawberry_s49	Benzophenone	<sup>a</sup>
	Metalaxyl	<sup>a</sup>
	Cyprodinil	830.84
	Penconazole	6.74
	Fludioxonil	589.84
	Bupirimate	64.02

Table 4. (continued)

Sample	Identified pesticides	Concn, g/kg
Strawberry_s50	Benzophenone	<i>a</i>
	Mepaipyrim	<i>a</i>
Strawberry_s51	Benzophenone	<i>a</i>
Strawberry_s52	Diphenylamine	<i>a</i>
	Benzophenone	<i>a</i>
	Azoxystrobin	<i>a</i>
	Nuarimol	2.07
Courgette_s53	Benzophenone	<i>a</i>
Courgette_s54	Benzophenone	<i>a</i>
Courgette_s55	Benzophenone	<i>a</i>
	Tetraconazole	<i>a</i>
	Mehomil	11.66
	Pyrimethanil	1.21
Tomato_s56	Benzophenone	<i>a</i>
	Metribuzin	<i>a</i>
	Terbucarb	<i>a</i>
	Rabendazole	<i>a</i>
	Mepanipyrim	<i>a</i>
	Chloropropylate	<i>a</i>
Tomato_s57	Benzophenone	<i>a</i>
	Pyrimethanil	3.98
	Tebuconazole	33.03
	Bromopropylate	305.91
Tomato_s58	Benzophenone	<i>a</i>
	Triadimenol	<i>a</i>
Tomato_s59	Benzophenone	<i>a</i>
	Bromopropylate	7.82
	Pyriproxyfen	6.28
Green beans_s60	Benzophenone	<i>a</i>
	Metalaxyl	<i>a</i>
Cucumber_s61	Benzophenone	<i>a</i>
Tangerine_s62	Imazalil	1.61
	Chlorpyrifos	22.01
Lemon_s63	Thiabendazole	144.26
	Imazalil	1754.92
Lemon_s64	Imazalil	2.79
Orange_s65	Imazalil	111.15
	Malathion	67.93
	Thiabendazole	17
Orange_s66	Imazalil	93.63
	Thiabendazole	3.35
	Prochloraz	39.70
Banana_s67	Benzophenone	<i>a</i>
	Chlorpyrifos	2.4
Banana_s68	Benzophenone	<i>a</i>
	Chlorpyrifos	5.7

Table 4. (continued)

Sample	Identified pesticides	Concn, g/kg
Banana_s69	Chlorpyrifos	232.5
	Imazalil	307.8
Pear_s70	Diphenylamine	973.59
	Imazalil	609.16
	Iprodione	1116.79
	Phosalone	113.46
Endive_s71	Cyhalothrin	25.99
Pepper_s72	—	
Pepper_s73	—	
Carrot_s74	—	
Carrot_s75	—	
Carrot_s76	—	
Cucumber_s77	—	
Tomato_s78	Pyriproxyfen	43.47
Tomato_s79	Pyriproxyfen	27.16
Apple_s80	Diphenylamine	20
	Ethoxyquin	33.48
	Pirimicarb	22.34
	Chorpyrifos	3.91
	Thiabendazole	1931.06
	Diphenylamine	32
Apple_s81	Chorpyrifos	4.91
	Thiabendazole	38.58
	Diphenylamine	35.00
Apple_s82	Fuberidazole	<i>a</i>
	Chlorpyrifos	3.09
	Imazalil	14.42
	Quinoxifen	2.28
	Boscalide	<i>a</i>
Melon_s83	—	
Melon_s84	Cyprodinil	8.39
	Procymidone	59.95
Melon_s85	—	
Melon_s86	—	
Melon_s87	—	
Melon_88	Cyproconazole	<i>a</i>
	Azoxystrobin	101.52
Pear_s89	Boscalide	<i>a</i>
	Diphenylamine	15
Pear_s90	Imazalil	722.01
	Ethoxyquin	19
Apple_s91	—	
	Thiabendazole	1686.21
Watermelon_s92	—	
Watermelon_s93	—	

**Table 4. (continued)**

Sample	Identified pesticides	Concn, g/kg
Watermelon_s94	—	
Watermelon_s95	Tebufenpyrad	50.46
Watermelon_s96	Tebufenpyrad	38.12
Kiwi_s97	Chlorpyrifos	11.15
Nectarine_s98	Myclobutanil	13.47
Peach_s98	Tetraconazole	26.72
Potato_s99	Flutolanil	<sup>a</sup>
Potato_s100	Flutolanil	<sup>a</sup>
	Chlorpropham	1.43
Potato_s101	Chlorpropham	2.16
Potato_s102	Chlorpropham	4.9
Potato_s103	—	
Olive oil_s106	—	
Olive oil_s107	—	
Olive oil_s108	—	
Olive oil_s109	—	
Olive oil_s110	—	
Olive oil_s111	—	
Olive oil_s112	—	
Olive oil_s113	—	
Olive oil_s114	Terbutylazine	<sup>a</sup>
Olive oil_s115	Terbutylazine	<sup>a</sup>
Olive oil_s116	—	
Olive oil_s117	—	

<sup>a</sup> Not included in the quantification method.

study presented recoveries between 80 and 110%. These recoveries were in the 70–120% acceptance range of the DG SANCO/2007/3131 of the European Quality Control Guidelines in all cases. The generally good recoveries obtained indicate the adequacy of the method for application over a wide multiresidue range.

#### Screening of Real Samples

To evaluate the performance of the automated screening, it was first tested with a carrot sample from the European Proficiency Test (EUPT) FV 10 (21) extracted by the QuEChERS method. The obtained results, shown in Table 3, were satisfactory. Acetamiprid, boscalid, chlorpyrifos-methyl, diazinon, endosulfan sulfate, isofenphos-methyl, kresoxim-methyl, malathion, metamidophos, methiocarb, methomyl, pendimethalin, phosmet, quinoxifen, triadimenol, and vinclozolin were identified by the screening method in the carrot EUPT sample. Hexythiazox, methiocarb sulfone, and methiocarb sulfoxide were not identified by the screening method since these compounds were not included in the AMDIS database.

Quantification of the sample was performed with the automatic quantification method. Concentrations of chlorpyrifos-methyl, diazinon, kresoxim-methyl, malathion, metamidophos, methomyl, pendimethalin, phosmet, quinoxifen, triadimenol, and vinclozolin were typically within 7% of the concentrations given by the EUPT. Acetamiprid, boscalid, oxamyl, and pendimethalin were not included in the quantification method, and their concentrations are not given.

After that, the proposed approach was applied to different market-purchased samples. Results obtained are shown in Table 4. Eighty percent of the samples contained at least one pesticide. A total of 131 positives was found by the screening method, and the concentrations of 93 positives were determined. Quantification of each sample was made with the corresponding matrix-matched calibration plot, depending on the specific commodity category. All samples shown in this table were analyzed by DRS; the match values obtained were higher than 60%, and retention time differences between the pesticide database and observed values were <5 s. In addition, all positive results given by AMDIS were confirmed as being positive by the NIST library.

#### Conclusions

A rapid method for the simultaneous screening and quantification of pesticide residues in food has been developed and evaluated. It uses GC-quadrupole-MS together with DRS and a commercial pesticide database. The results obtained in the analysis of a EUPT sample, as well as 118 market-purchased samples, yielded satisfactory results. For quantification purposes, 95 pesticides were included in the method, but the scope is clearly extendable to a greater number of pesticides. Furthermore, the commercial database used for the automatic screening can be easily enlarged to include new compounds. Eighty percent of the analyzed samples gave positive findings for a total of 113 pesticide hits. This represents a higher number of hits than reported by the enforcement laboratories, which is a consequence of the greater screening capability of the proposed method. A smaller number, 71% of the positive samples detected, were quantified with the quantification method proposed.

We consider the LOI values achieved to be adequate, lower than 20 g/kg in 80% of the studied pesticides, and lower than 5 g/kg in 40% of the pesticides studied. It is important to note that, in acidic commodities, such as oranges, the AMDIS matches obtained were lower than in the other studied matrixes.

The use of backflushing represents a very important advantage in the robustness of the method. Another important advantage of the method is the capability to perform retrospective analysis in food samples.

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