Analysis of 168 Pesticides in Fruits and Vegetables using Modified QuEChERS Method and Gas Chromatography and Tandem Mass Spectrometry

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Outline of the Study

Target analytes: 168 pesticides

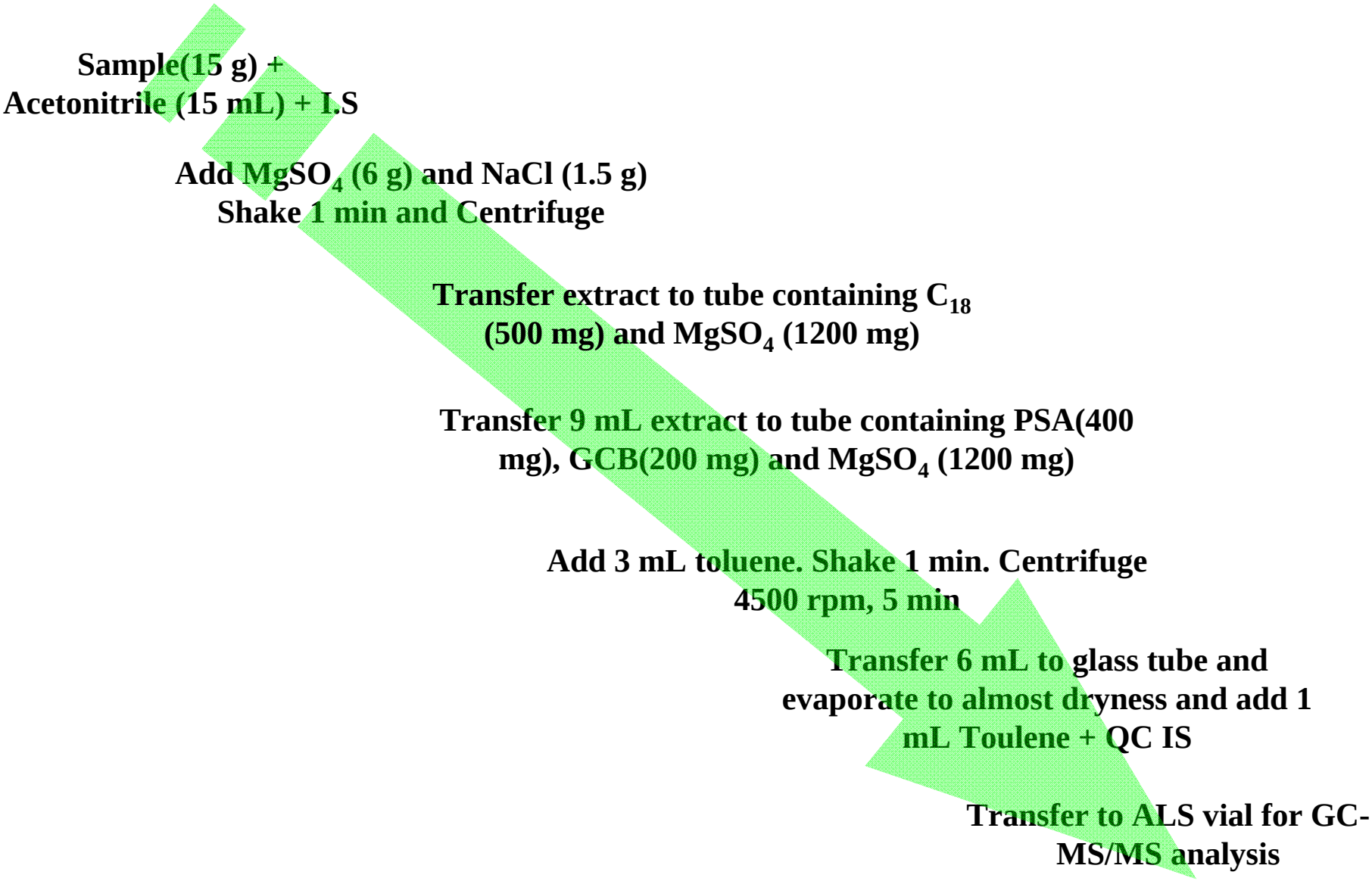
Food matrices: fresh fruits and vegetables (spinach, carrot, orange, peach, pepper, tomato, potato, onion, cantaloupe, and broccoli)

Sample preparation: Fillion et al. + QuEChERS

Instrumentation: Varian 1200 L GC-QQQ-MS

Comparison to GC-MS/SIM

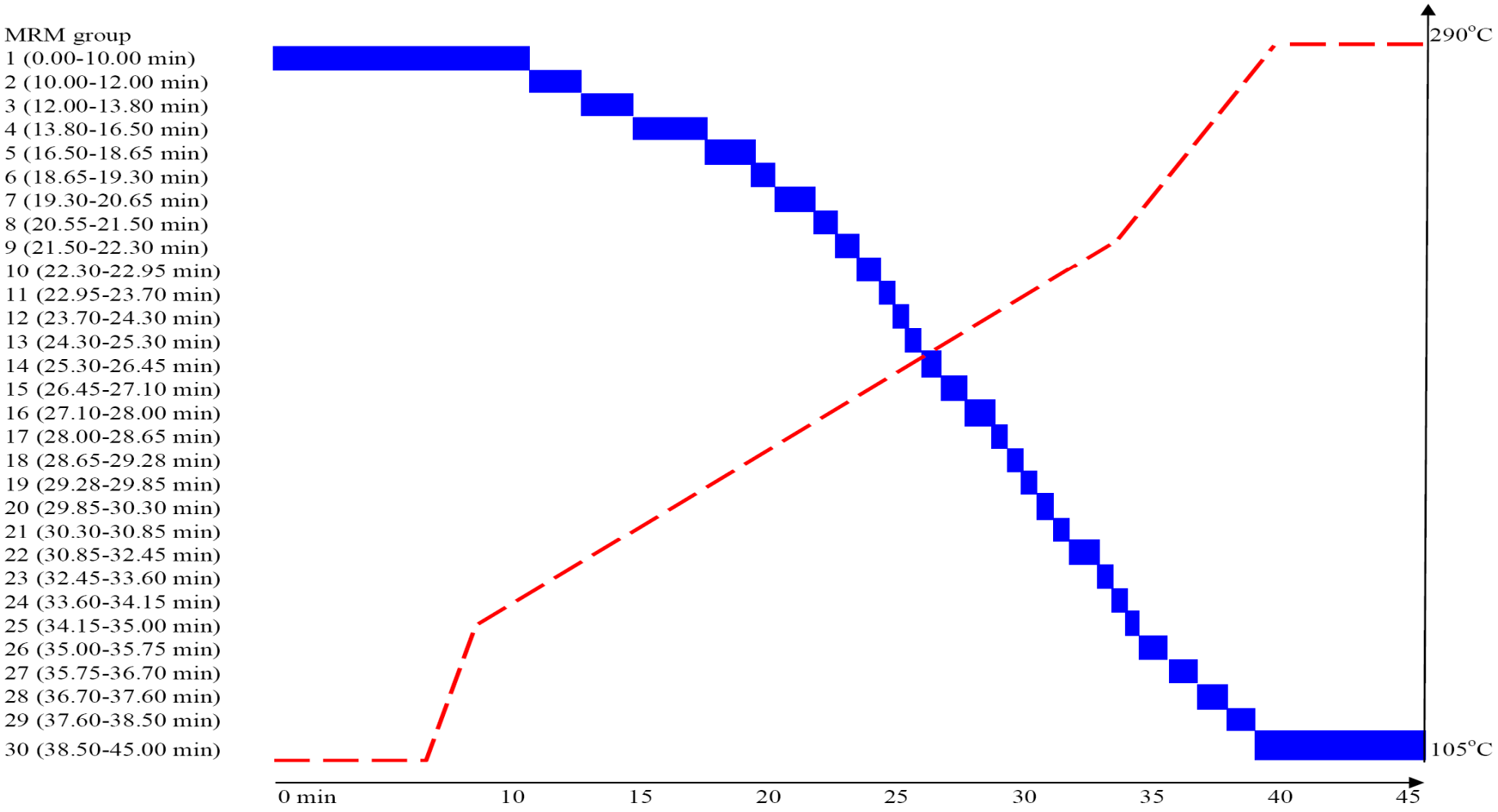
Sample Preparation Procedures



Overview of GC-MS/MS Method

MRM Group No. Target Pesticides

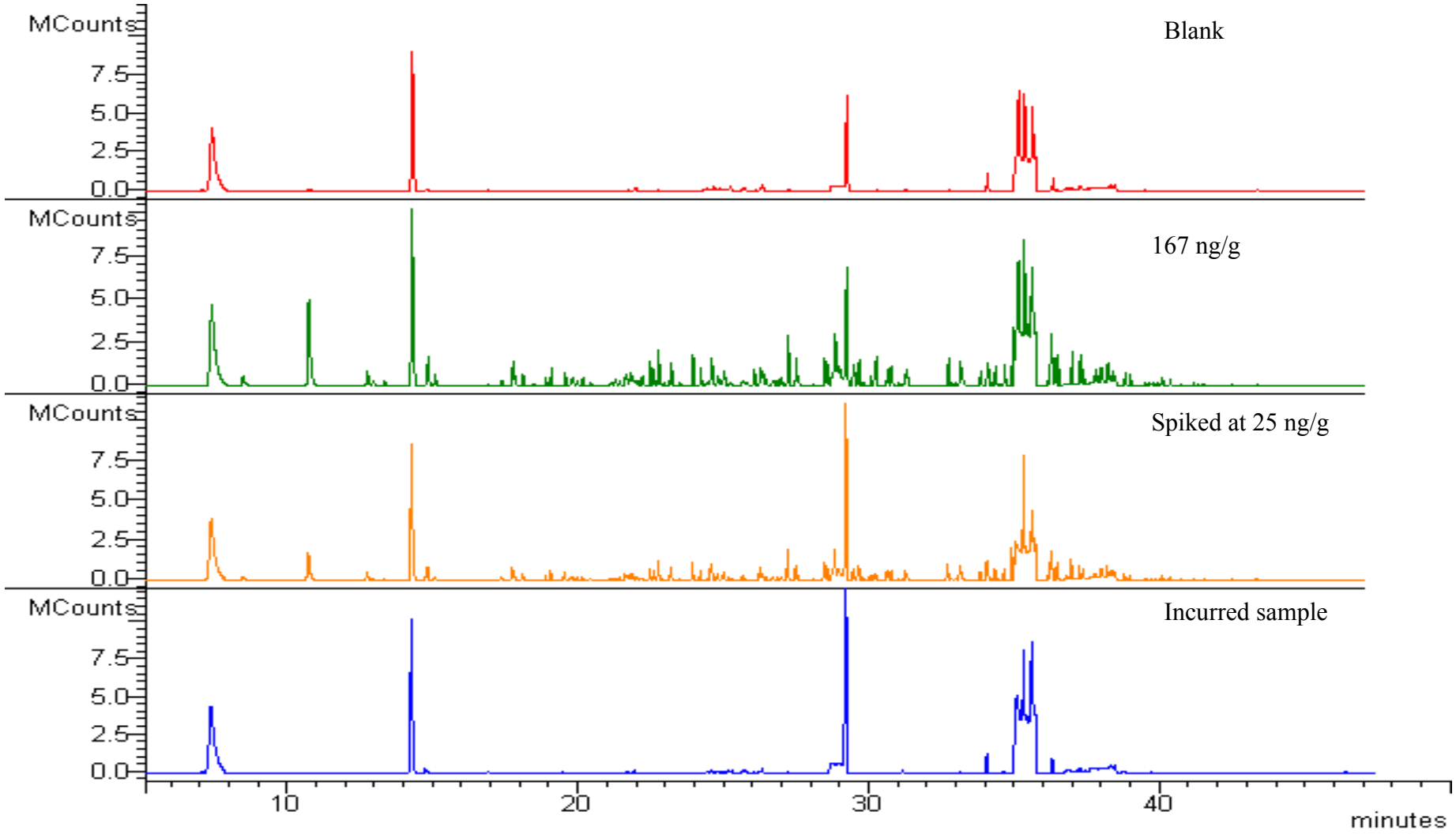
1 (0.00-10.00 min) Naphthalene-d_8, Dichlorvos
2 (10.00-12.00 min) Dichlobenil
3 (12.00-13.80 min) Mevinphos, Dicloran, Etridazole
4 (13.80-16.50 min) Acenaphthene-d_{10}, Chloroneb, Pentachlorobenzene
5 (16.50-18.65 min) TCNB, Propachlor, Demeton-S-methyl, Tetrachloraniline, Ethoprop, Ethalfluralin
6 (18.65-19.30 min) Trifluralin, Dioxabenzofos, Sulfotep-ethyl
7 (19.30-20.55 min) Phorate, Diallate, α-BHC, Hexachlorobenzene, Diamidafos, Pentachloroanisole, 3,4'-Dichloroaniline
8 (20.55-21.50 min) Simazine, PCNB, Atrazine, Propazine, Pentachlorobenzonitrile, β-BHC, Dioxathion
9 (21.50-22.30 min) Ethion, Cyanophos, Terbuthylazine, Propetamphos, Fonophos, Propyzamide, Diazinon, Chlorothalonil, Fluchloralin
10 (22.3-22.95 min) Disulfoton, Isazophos, Tefluthrin, Triallate, Lindane, Pheneanthrene-d_{10}
11 (22.95-23.70 min) δ-BHC, Tebupirimfos, IBP, Pentachloroaniline, Endosulfan ether
12 (23.70-24.30 min) Dichlorfenthion, Dimethachlor, Chlorpyrifos-methyl
13 (24.30-25.30 min) Vinclozolin, Tolclofos-methyl, Alachlor, Parathion methyl, Heptachlor, α-Chlordene, Ronnel
14 (25.30-26.45 min) Pirimiphos methyl, Fenitrothion, Pentachlorothioanisole, Dichlofluanid, Malathion, γ-Chlordene, Metalochlor, β-Chlordene, Aldrin
15 (26.45-27.10 min) Chlorpyrifos, DCPA, Fenthion, Parathion, Cyanazine, Dicapthon
16 (27.10-28.00 min) 4,4'-Dichlorobenzophenone, Bromophos methyl, Pirimiphos ethyl
17 (28.00-28.65 min) Isofenfos, Tolylfluanid, Chlorfenvinfos, Heptachlor expoxide A
18(28.65-29.28 min) Quinalphos, Allethrin, Captan, Procymidone, Folpet
19 (29.28-29.85 min) Bromophos ethyl, cis-Chlordane, Methidathion, Akton, o,p'-DDE, Stirofos
20 (29.85-30.30 min) trans-Chlordane, Endosulfan I, trans-Nonchlor, Ditalimfos
21 (30.30-30.85 min) Iodofenphos, Prothiophos, Fenamiphos
22 (30.85-32.45 min) Profenofos, p,p'-DDE, Dieldrin, Oxadiazon, DEF, Endrin
23 (32.45-33.60 min) Chlorobenzilate, Endosulfan II, Fensulfothion, cis-Nonachlor, o,p'-DDD, p.p'-DDD, Chlorthiophos, Endrin aldehyde, o,p'-DDT
24 (33.60-34.15 min) Sulprofos, Triazophos, Azamethiophos, Famphur, Tris-(1,3-dichlorisopropyl)-phosphate
25 (34.15-35.00 min) Carbophenothion, Edifenfos, Endosulfan sulfate, p,p'-DDT, p,p'-Methoxychlor
26 (35.00-35.75 min) Triphenylphosphate, Captafol, Resmethrin
27 (35.75-36.70 min) Pyridaphenthion, Endrin ketone, Phosmet, Bifenthrin, Chrysene-d_{12}, Iprodione, Bromopropylate, EPN, Tetramethrin, Cyhalothrin, o,p'-Methoxychlor
28 (36.70-37.60 min) Phenothrin, Dibutyl chlorendate, Leptophos, Phosalone, Azinphos methyl, Cyhalothrin-λ
29 (37.60-38.50 min) Mirex, Acrinathrin, Pyrazophos, Fenarimol, Azinphos ethyl, Dialifor, Pyraclofos
30 (38.50-45.00 min) Permethrin, Couphos, Cyfluthrin, Cypermethrin, Flucythrinate, Fluridone, Deltamethrin, Fluvalinate, Fenvalerate



Multi reaction monitoring groups

GC temperature program

Spinach Blank, matrix-matched standard, spiked and incurred samples



Method Development: Effect of scan time

(spiked cantaloupe sample at 45 µg/kg)

Endrin keton

Pyridaphenthion

Iprodone

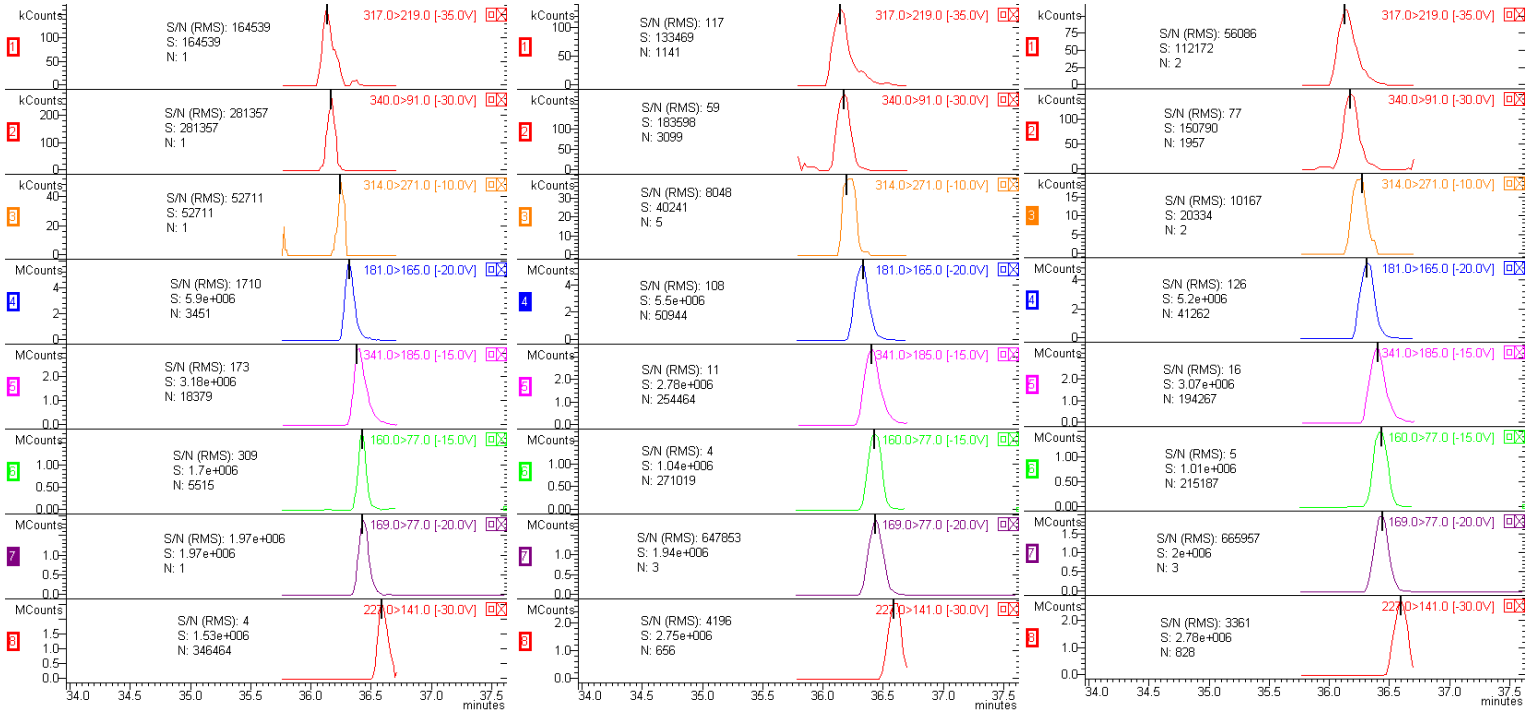
Bifenthrin

Bromopropolate

Tetramethrin

EPN

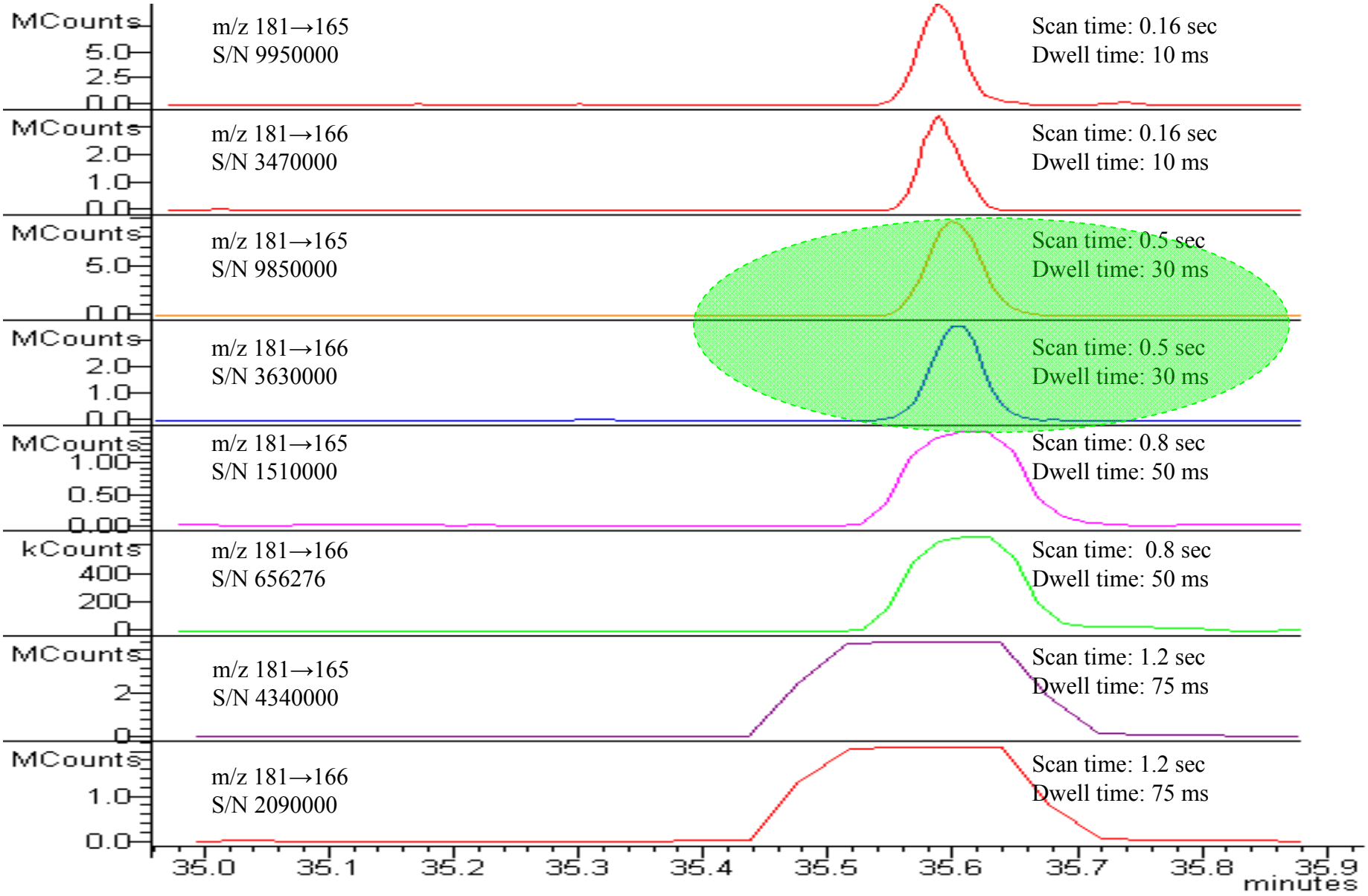
Methoxychlor, o,p-



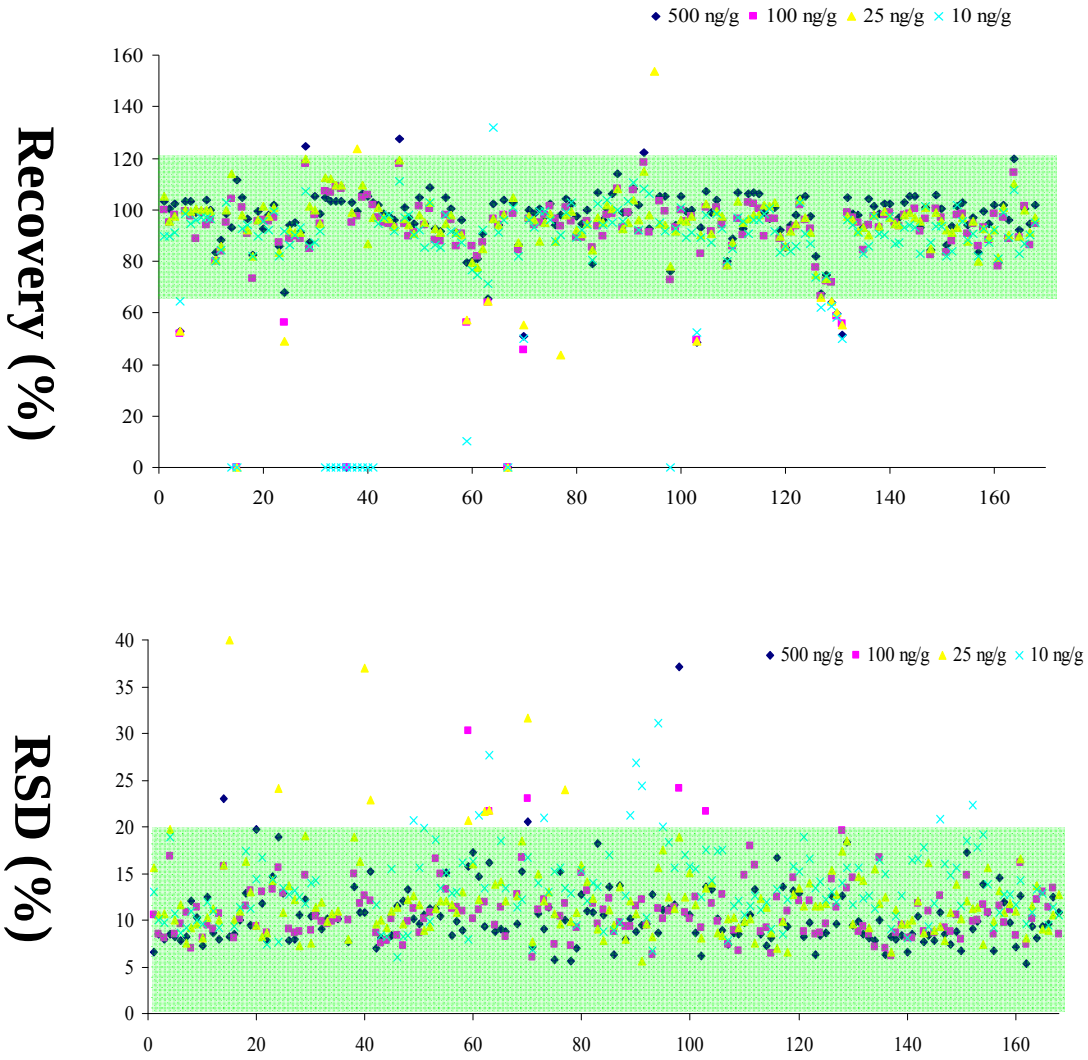
0.5 s **0.8 s** **1.2 s**

Method Development: Effect of scan time

(spiked cantaloupe sample at 45 µg/kg)



Recovery Study

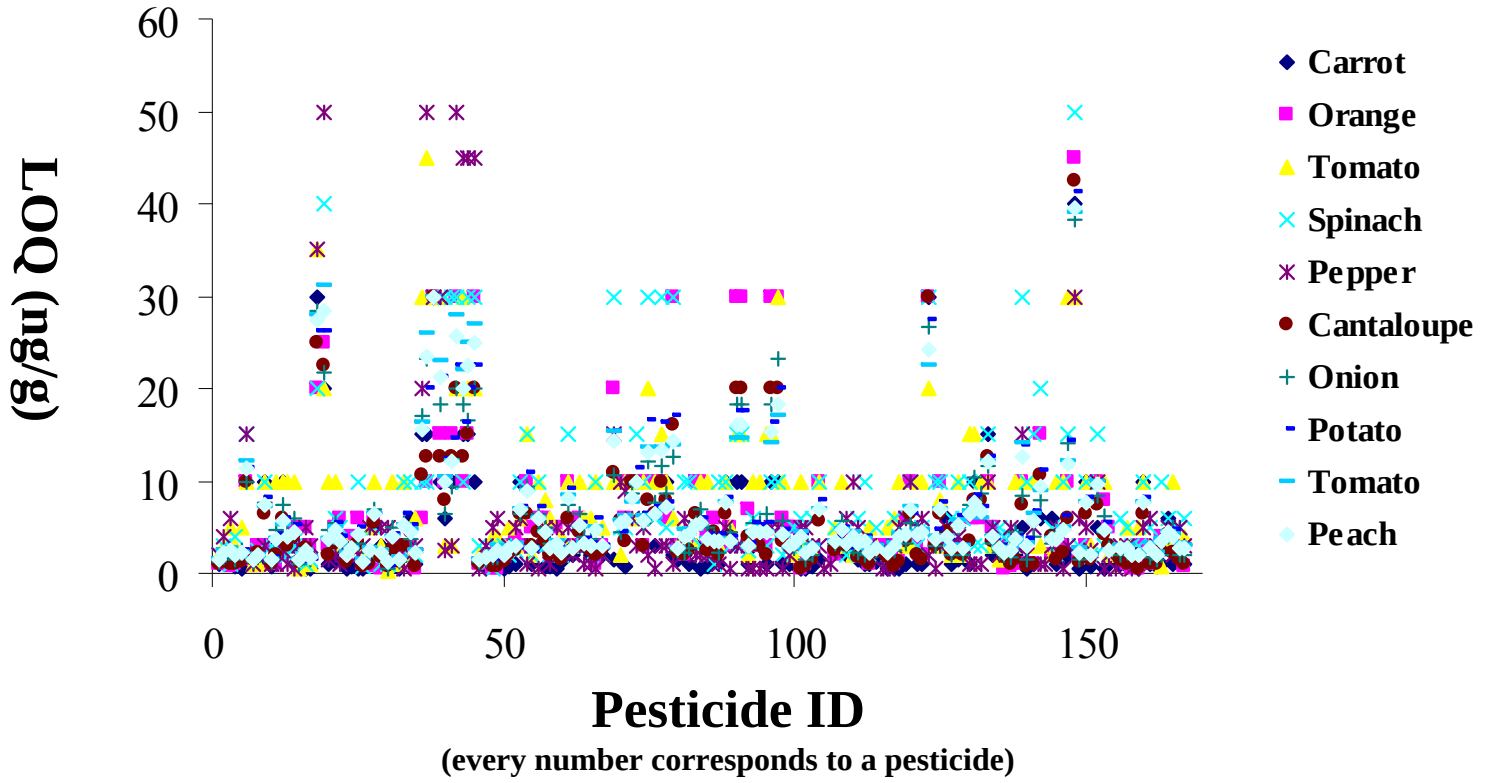


70-120%

80% of the pesticides at 10 and 25 µg/kg and 90% of the pesticides at 100 and 500 µg/kg with RSDs ≤ 20%.

20% ≥

Estimated LOQs



Problematic Pesticides

	Spiking levels (µg/kg)							
	500		100		25		10	
Pesticide	Recovery	RSD (%)	Recovery	RSD (%)	Recovery	RSD (%)	Recovery	RSD (%)
Aldrin	53	8	52	17	53	20	65	19
Captan					ND		ND	

Thermal lability: Captan, Captafol and Chlorothalonil

Cyfluthrin I							ND	
Cyfluthrin II							ND	
Cyfluthrin III							ND	
Cyfluthrin IV							ND	
Cyhalothrin	ND		ND		ND		ND	
Cyhalothrin isomer							ND	

MS fragile fragmentation: Cypermethrin, Cyfluthrin

Cypermethrin IV					124	19	ND	
Dichlofluanid			56	30	57	21	10	8
Dichloro-4-nitroaniline					85	22		
Dichlorobenzenamine	65	16	64	22	65	22	71	28
Dichlorobenzophenone							132	28
Dioxabenzofos	ND		ND		ND		ND	
Ditalimfos	51	21	45	23	55	32	50	17

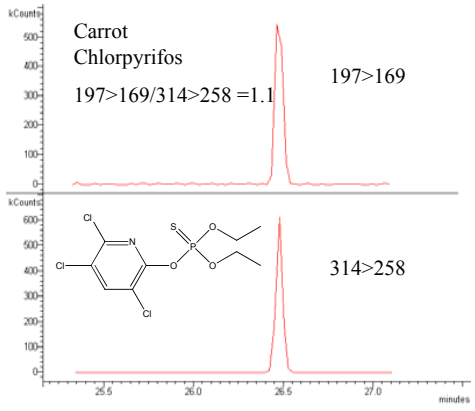
Strong adsorption: Hexachlorbenzene, Pentachlorobenzene, Pentachloroaniline

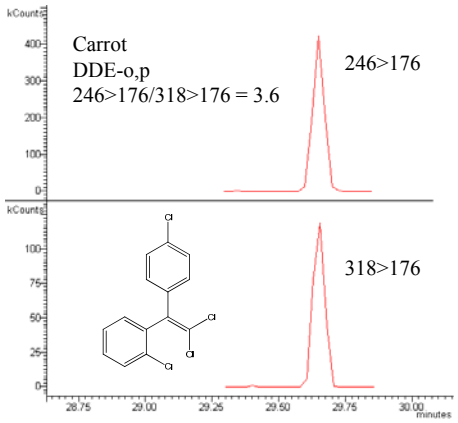
Fluridone	180	11	169	10	154	18	170	20
Folpet	76	37	73	24			ND	
Hexachlorbenzene	48	14	49	22	49	13	52	18
Pentachloroaniline	67	10	67	11	66	13	62	12
Pentachlorobenzene	64	18			65	18	63	16
Pentachlorobenzonitrile	60	9	59	15	60	10	58	12
Pentachlorothioanisole	52	10	56	9	55	15	50	16

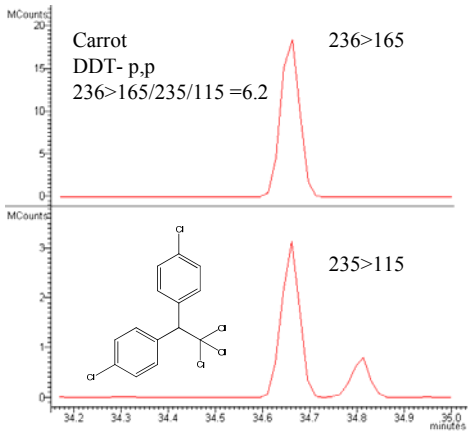
Identified Pesticides

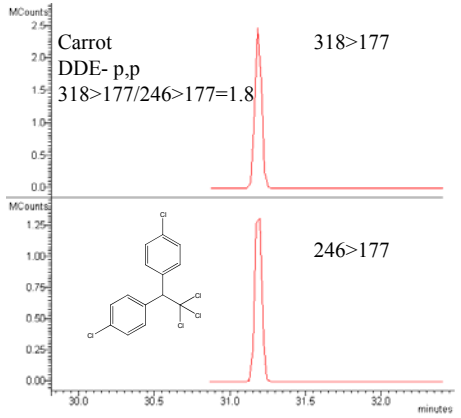
Pesticide (µg/kg)	Carrot	Pepper	Spinach	Tomato
Bifenthrin		50±2.4		
Chlorothalonil				180±4.5
Chlorpyrifos	6.7±0.8			
DDE p,p-	54±3.2		24±0.2	
DDD p,p-	13±1.1		6.9±1.4	
DDT p,p-	37±1.5		4.9±0.7	
Endo Sulfan I		5.6±2.2		24±2.1
Endo Sulfan II				63±12
Endo Sulfate		13±2.7		15±1.8

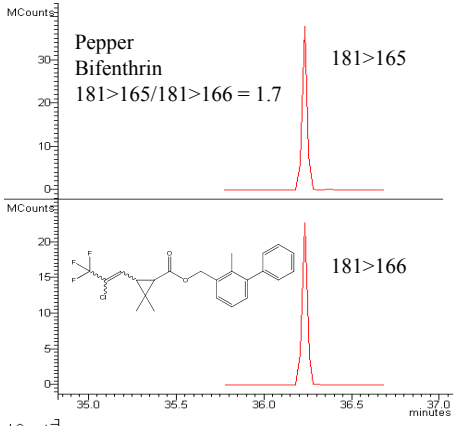
Identified Pesticides

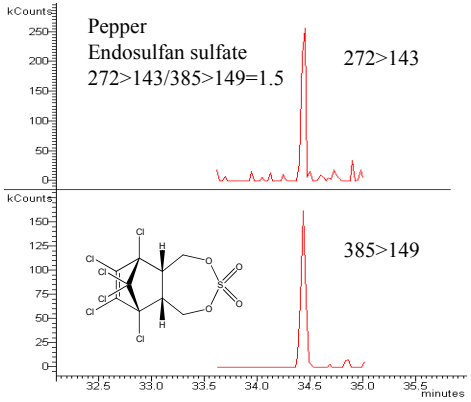


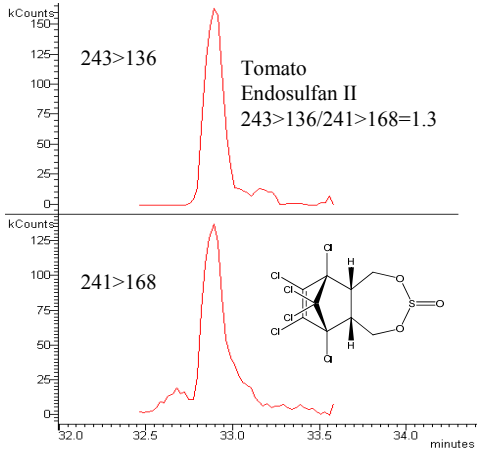


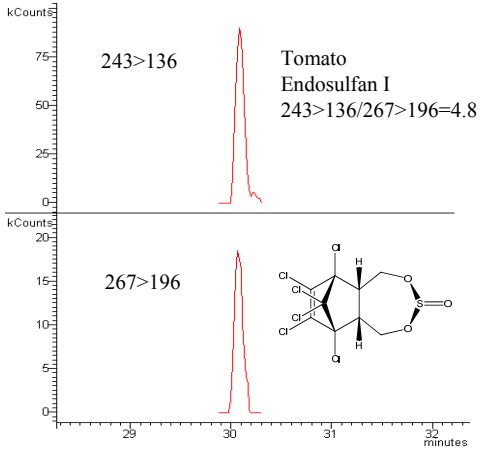


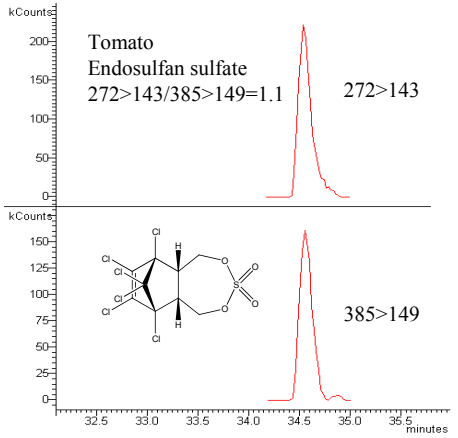












Conclusions

The sample preparation procedures can be applied to fruits and vegetables for multi residue pesticide analysis

The GC-MS/MS method can be used for quantification and confirmation with satisfactory sensitivity

Compared to a GC-MS/SIM method, the GC-MS/MS method provides better sensitivity and confirmation

Acknowledgements

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