EURL-FV

Multiresidue Method using QuEChERS followed by GC-QqQ/MS/MS and LC-QqQ/MS/MS for Fruits and Vegetables

CONTENTS

1. Aim and Scope

This report describes a validation data of 138 pesticides included in the Coordinated Multiannual Community Control Programme for 2010, 2011 and 2012 (Commission Regulation (EC) No 901/2009) using a multiresidue method by LC-MS/MS and GC-MS/MS in four representative matrices.

2. Short Description

The analysis of pesticide residues was performed by using QuEChERS Method.

The homogeneous sample is extracted with acetonitrile. After salts addition the mixture is shaken intensively and centrifuged for phase separation. An aliquot of the organic phase is taken for the clean up with bulk sorbents (PSA) and $MgSO_4$ anhydrous to remove the residual water. Extracts are shaken by vortex and a small aliquot is diluted with acetonitrile.

3. Apparatus and Consumables

- Sample processing equipment, e.g. Dito Sama-K55 Food Processor.
- Automatic pipettes, suitable for handling volumes of 10 to 20 μL, 100 to 1000 μL, 0.5 to 5 mL and 1 to 10 mL.
- 50 ml centrifuge tubes with screw caps, for example 50 mL centrifuge tubes with screw cabs (e.g Sharlab S. L, Spain, article-no 027 – 409926).
- 10 mL centrifuge tubes with screw caps.
- 10 mL solvent-dispenser for acetonitrile.
- Test tubes, e.g. 10 mL.
- Centrifuge, suitable for the centrifuge tubes employed in the procedure and capable of achieving at least 4000 rpm.
- Syringes, e.g. 2 mL disposable syringes.
- Syringes filters, 0.45 μm pore size.
- Injection vials, 1.5 ml, suitable for LC auto-sampler.
- Concentration Workstation, e.g. TurboVap LV, Zymark

4. Chemicals

- Acetonitrile, HPLC quality
- NaCl pa.
- Magnesium sulphate, anhydrous, grit, for example MERCK 1.06067. *Phthalates can be removed in a muffle furnace by heating to 550ºC.*
- Disodium hydrogencitratesesquihydrate (e.g. Fluka 71635)
- Trisodium citrate dehydrate (e.g. Sigma S4641)
- Magnesium sulphate anhydrous coarsely grained.
- PSA, for example UCT CUMPS2CT
- Pesticides Standards, e.g. Dr. Ehrenstorfer, Scharlab.
- Cyclohexane, for GC residue analysis
- Acetone, for GC residue analysis

5. Procedure

5.1 Sample preparation

Samples were prepared according to the Quality Control procedure established in the "Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed" (Document No. SANCO/10684/2009).

Following this document, the sample was perfectly homogenised by grinding finely at its arrival to the laboratory.

Sample was frozen for its storage immediately after grinding it.

5.2 Recovery Experiments for Method Validation

Commodities used for fortification were:

- Avocado
- Carrot
- Orange
- Pepper

Commodities employed should not contain any of the pesticides analyzed.

Organically grown samples are recommended for the analysis.

The validation method has to be performed at two spiking levels (0.10 mg/Kg and 0.01 mg/Kg). For each commodity five spiked samples and a blank have to be analyzed at each level. In total eleven samples per commodity.

The working solutions were prepared adding the 138 pesticides used for the validation method at two concentrations as follows:

- FORT LOW: Pesticides at 1 µg/ml acetonitrile
- FORT HIGH: Pesticides at 10 µg/ml acetonitrile

5.3 Extraction

Pesticides analysed by HPLC-MS/MS

1. Weigh 10 g ± 0.1g sample in 50 mL centrifuge tube
2. Sample spiking:
   - Low level concentration (0.01 mg/Kg): add 100 µL FORT LOW
   - High level concentration (0.10 mg/Kg): add 100 µL FORT HIGH
3. Shake vigorously for 1 min to allow pesticides distribution
4. Add 10 ml of acetonitrile
5. Salt-mixtures addition for the Partitioning Step:
   - 4 g ± 0.2 g Magnesium sulphate anhydrous
   - 1 g ± 0.05 g Sodium chloride
   - 1 g ± 0.05 g Trisodium citrate dihydrate
   - 0.5 g ± 0.03 g Disodium hydrogencitrate sesquihydrate
6. Shake vigorously by hand or vortex for 1 min
7. Centrifuge for 5 min at 4000 rpm (Extract I)
8. Clean-up: 6 mL Extract I is transferred into a Polipropilene – single centrifuge tube which contains 150 mg PSA and 900 mg magnesium sulphate anhydrous (25 mg PSA and 150 mg magnesium sulphate per mL extract). Shake vigorously by hand or vortex for 1 min
9. Centrifuge for 2 min at 6000 rpm (Extract II)
10. Transfer 1mL Extract II into a test tube. Add 220 µL of acetonitrile
11. Vortex sample to mix it properly (Extract III)
12. Filter Extract III into a injection vial suitable for LC

Pesticides analysed by GC-MS/MS

The extraction method is the same until step 10:

10. Transfer 1 mL Extract II into a test tube. Evaporate to dryness
11. Add 1mL cyclohexane: acetone (9:1)
12. Vortex sample to mix it properly (Extract III)
13. Filter Extract III into a injection vial suitable for GC.

5.4 Measurement

Run the system in MRM-mode using the mass transitions presented in Appendix II.

Pesticides expressed according to the residue definition appear on the table with the index (RD).

5.5 Instrumentation and Analytical Conditions for the LC/QqQ (MS/MS) System

LC-MS/MS System 3200 Q TRAP, Applied Biosystem:

- Column: Atlantis T3 2.1x100 mm, 3 µm
- Column temperature: 40 ºC
- Mobile phase A: H_2O, 2 mM ammonia formiate, 0.1 1% formic acid.
- Mobile phase B: methanol
- Injection volume: 10µL
- Autosampler temperature: 10 ºC
- Analysis time: 18 min.

TABLE III: FLOW RATE AND ELUTION GRADIENT

Time (min)	A (%)	B (%)	Flow (µL/min)
0,0	95	5	300
1,0	95	5	300
1,1	70	30	300
10,0	0	100	300
13,0	0	100	300
13,1	95	5	300

5.6 Instrumentation and Analytical Conditions for the GC/QqQ (MS/MS)

- GC: Agilent 7890 Series
- Autosampler: Agilent 7683 Injector and sample tray
- Inlet: Splitless
- Carrier gas: Helium
- Inlet pressure: 22.73 psi
- Inlet temperature: 250ºC
- Injection volume: 1 µL

- Oven temperature program:

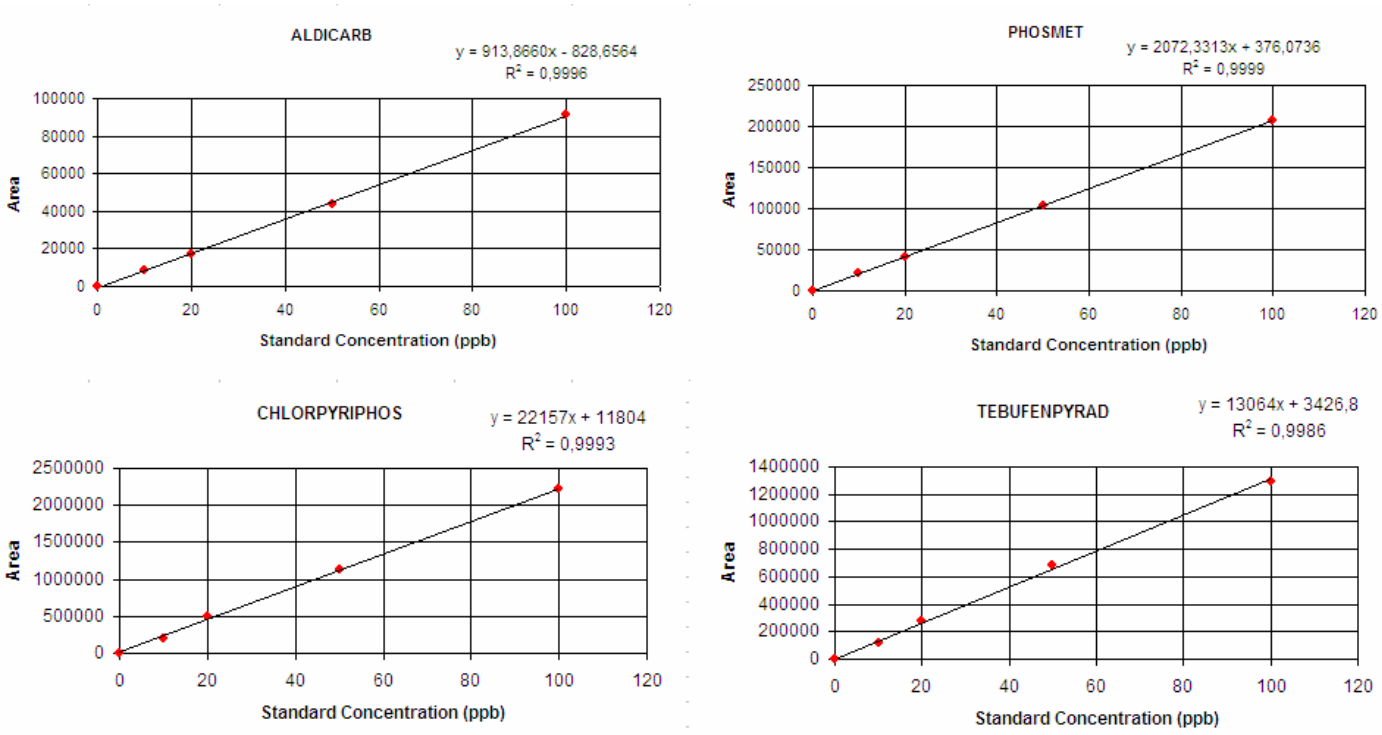
	Rate (ºC/min)	Value (ºC)	Hold Time (min)	Run Time (min)
Initial		70	2	2
Ramp 1	25	150	0	5.2
Ramp 2	3	200	0	21.9
Ramp 3	8	280	10	41.9

- Analytical column: Agilent J&W HP-5ms 30 m x 250 µm x 0.25 µm
- Retention time locking: Chlorpyrifos methyl locked to 16.596 min
- Spectrometer: Agilent 7000B Series
- Source temperature: 280ºC
- Quadrupole temperature: Q1 and Q2 = 150ºC
- Collision gas flows: Nitrogen at 1.5 mL/min, Helium at 25 ml/min

6 Calibration Curves

A calibration curve was calculated for each pesticide at four calibration levels; 0.01 µg/mL, 0.02 µg/mL, 0.05 µg/mL and 0.1 µg/mL. The calibration curves were best fitted to a linear curve.

Figure 1: Examples of calibration curves



7. Evaluation of results

In the Appendix I are shown the results for the mean recovery and RSD (Relative Standard Deviation) for the quantified pesticides at both levels.

The majority of validation results are acceptable for the recovery and RSD values for the representative matrices.

It is worth mentioning that there are some mean and RSD values slightly higher than the values recommended by the Document No. SANCO/10684/2009. Nevertheless, these values can be considered as acceptable, in certain justified cases, as multiresidue methods working at the limit of quantification (0.01 mg/Kg).

8. Conclusion

This survey provides validation data for the pesticides included in the Community Control Programme for 2010, 2011 and 2012 for four representative matrixes.

The results obtained are considered acceptable within the studied range. As this multiresidue method is used at the present time by a large number of laboratories within the European Pesticides Residues Monitoring Programme for fruit and vegetables, this survey can help to improve the analysis of pesticides mentioned above.

9. References

- Multiannual Community Control Programme for 2010, 2011 and 2012 (Commission Regulation (EC) No 901/2009)
- Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed (Document No. SANCO/10684/2009)
- http://www.quechers.com
- http://www.crl-pesticides.eu

APPENDIX I: VALIDATION RESULTS

RD= Average or all compounds included in the residue definition

PESTICIDE	MEAN% (0,01 mg/Kg)	RSD% (0,01 mg/Kg)	MEAN% (0,1 mg/Kg)	RSD% (0,1 mg/Kg)	TECHNIQUE
ACEPHATE	88	7	89	3	HPLC/QqQ (MS/MS)
ACETAMIPRID	84	10	102	4	HPLC/QqQ (MS/MS)
ACRINATHRIN	103	12	91	13	GC/QqQ (MS/MS)
ALDICARB(RD)	105	13	98	5	HPLC/QqQ (MS/MS)
AMITRAZ(RD)	89	8	80	7	HPLC/QqQ (MS/MS)
DMPF	84	7	92	5	HPLC/QqQ (MS/MS)
DMF	75	5	103	7	HPLC/QqQ (MS/MS)
AZINPHOS-METHYL	86	17	100	5	HPLC/QqQ (MS/MS)
AZOXYSTROBIN	87	6	104	4	HPLC/QqQ (MS/MS)
BIFENTHRIN	95	9	92	10	GC/QqQ (MS/MS)
BITERTANOL	118	11	103	8	HPLC/QqQ (MS/MS)
BOSCALID	98	8	100	4	HPLC/QqQ (MS/MS)
BROMOPROPYLATE	95	11	94	12	GC/QqQ (MS/MS)
BUPIRIMATE	96	6	94	10	GC/QqQ (MS/MS)
BUPROFEZIN	87	8	89	8	GC/QqQ (MS/MS)
CADUSAFOS	88	16	96	6	HPLC/QqQ (MS/MS)
CAPTAN	76	11	85	9	GC/QqQ (MS/MS)
CARBARYL	110	9	97	5	HPLC/QqQ (MS/MS)
CARBENDAZIM(RD)	96	6	95	5	HPLC/QqQ (MS/MS)
CARBOFURAN(RD)	91	14	103	4	HPLC/QqQ (MS/MS)
CHLORFENVINPHOS	99	8	86	27	GC/QqQ (MS/MS)
CHLOROTALONIL	56	4	67	3	GC/QqQ (MS/MS)
CHLORPROPHAM(RD)	99	7	95	7	GC/QqQ (MS/MS)
CHLORPYRIPHOS	98	6	92	7	GC/QqQ (MS/MS)
CHLORPIRIPHOS-METHYL	96	5	93	7	GC/QqQ (MS/MS)
CLOFENTEZIN(RD)	93	27	88	9	HPLC/QqQ (MS/MS)
CLOTHIANIDIN	109	8	98	7	HPLC/QqQ (MS/MS)
CYFLUTHRIN(RD)	104	13	97	16	GC/QqQ (MS/MS)
CYPERMETHRIN(RD)	109	11	109	16	GC/QqQ (MS/MS)
CYPROCONAZOLE	97	13	95	5	HPLC/QqQ (MS/MS)
CYPRODINIL	97	7	91	9	GC/QqQ (MS/MS)
DELTAMETHRIN	106	14	95	16	GC/QqQ (MS/MS)
DIAZINON	99	7	91	7	GC/QqQ (MS/MS)
DICHLOFLUANID	68	5	71	2	GC/QqQ (MS/MS)
DICHLORVOS	85	9	98	6	HPLC/QqQ (MS/MS)
DICLORAN	111	17	97	8	GC/QQQ (MS/MS)
DIFENOCONAZOLE	94	9	99	5	HPLC/QqQ (MS/MS)
DIMETHOATE(RD)	86	11	99	5	HPLC/QqQ (MS/MS)
DIMETHOMORPH	107	10	97	5	HPLC/QqQ (MS/MS)
DIPHENYLAMINE	101	8	86	7	GC/QqQ (MS/MS)
ENDOSULFAN(RD)	92	10	89	10	GC/QqQ (MS/MS)
EPOXICONAZOLE	86	8	101	3	HPLC/QqQ (MS/MS)
ETHION	114	9	102	10	GC/QqQ (MS/MS)
ETOFENPROX	95	13	94	14	GC/QqQ (MS/MS)
ETOPROFOS	98	4	92	6	GC/QqQ (MS/MS)
FENARIMOL	98	12	90	13	GC/QqQ (MS/MS)

PESTICIDE	MEAN% (0,01 mg/Kg)	RSD% (0,01 mg/Kg)	MEAN% (0,1 mg/Kg)	RSD% (0,1 mg/Kg)	TECHNIQUE
FENAZAQUIN	89	9	88	11	GC/QqQ (MS/MS)
FENBUTATIN OXIDE	-	-	78	4	HPLC/QqQ (MS/MS)
FENBUCONAZOLE	106	12	100	5	HPLC/QqQ (MS/MS)
FENHEXAMID	79	9	94	5	HPLC/QqQ (MS/MS)
FENITROTHION	116	10	103	7	GC/QqQ (MS/MS)
FENOXYCARB	105	24	98	8	HPLC/QqQ (MS/MS)
FENPROPATHRIN	99	10	96	11	GC/QqQ (MS/MS)
FENPROPIMORPH	81	7	99	3	HPLC/QqQ (MS/MS)
FENTHION *(RD)*	92	7	90	8	GC/QqQ (MS/MS)
FENTHION SULFOXIDE	86	15	92	10	HPLC/QqQ (MS/MS)
FENVALERATE	96	15	93	15	GC/QqQ (MS/MS)
FIPRONIL *(RD)*	98	5	91	11	GC/QqQ (MS/MS)
FLUDIOXONIL	132	3	96	2	HPLC/QqQ (MS/MS)
FLUFENOXURON	83	18	110	10	HPLC/QqQ (MS/MS)
FLUQUINCONAZOLE	94	21	99	7	HPLC/QqQ (MS/MS)
FLUSILAZOLE	98	8	93	10	GC/QqQ (MS/MS)
FLUTRIAFOL	99	8	102	5	HPLC/QqQ (MS/MS)
FOLPET	59	21	65	13	GC/QqQ (MS/MS)
FORMETANATE *(RD)*	87	10	95	4	HPLC/QqQ (MS/MS)
FOSTHIAZATE	79	20	114	8	HPLC/QqQ (MS/MS)
HEXACONAZOLE	95	12	96	4	HPLC/QqQ (MS/MS)
HEXYTHIAZOX	104	15	97	12	HPLC/QqQ (MS/MS)
IMAZALIL	88	6	97	6	HPLC/QqQ (MS/MS)
IMIDACLOPRID	96	17	100	6	HPLC/QqQ (MS/MS)
INDOXACARB *(RD)*	90	40	113	9	HPLC/QqQ (MS/MS)
IPRODIONE	106	13	94	13	GC/QqQ (MS/MS)
IPROVALICARB	105	8	99	4	HPLC/QqQ (MS/MS)
KRESOXIM-METHYL	103	14	107	5	HPLC/QqQ (MS/MS)
LAMBDA-CYHALOTHRIN *(RD)*	108	12	96	13	GC/QqQ (MS/MS)
LINURON	97	29	99	6	HPLC/QqQ (MS/MS)
LUFENURON	132	16	110	12	HPLC/QqQ (MS/MS)
MALATHION *(RD)*	107	6	100	9	GC/QqQ (MS/MS)
MEPANIPYRIM *(RD)*	103	12	95	12	GC/QqQ (MS/MS)
METALAXYL *(RD)*	111	11	94	8	GC/QqQ (MS/MS)
METCONAZOLE	101	9	95	4	HPLC/QqQ (MS/MS)
METHAMIDOPHOS	91	13	89	6	HPLC/QqQ (MS/MS)
METHIDATHION	115	6	101	9	GC/QqQ (MS/MS)
METHIOCARB *(RD)*	109	33	104	15	HPLC/QqQ (MS/MS)
METHOMYL *(RD)*	109	7	106	5	HPLC/QqQ (MS/MS)
METHOXYFENOZIDE	125	12	99	13	HPLC/QqQ (MS/MS)
MONOCROTOPHOS	79	10	98	6	HPLC/QqQ (MS/MS)
MYCLOBUTANIL	89	11	91	11	GC/QqQ (MS/MS)
OXADIXYL	94	12	88	9	GC/QqQ (MS/MS)
OXAMYL	96	8	96	5	HPLC/QqQ (MS/MS)
OXYDEMETON-METHYL *(RD)*	94	7	97	4	HPLC/QqQ (MS/MS)
PACLOBUTRAZOLE	91	13	100	5	HPLC/QqQ (MS/MS)
PARATHION	119	6	101	9	GC/QqQ (MS/MS)
PARATHION-METHYL *(RD)*	109	6	100	7	GC/QqQ (MS/MS)

PESTICIDE	MEAN% (0,01 mg/Kg)	RSD% (0,01 mg/Kg)	MEAN% (0,1 mg/Kg)	RSD% (0,1 mg/Kg)	TECHNIQUE
PENCYCURON	100	18	101	6	HPLC/QqQ (MS/MS)
PENCONAZOLE	97	11	97	5	HPLC/QqQ (MS/MS)
PENDIMETHALIN	116	8	96	8	GC/QqQ (MS/MS)
PERMETHRIN(RD)	98	12	93	13	GC/QqQ (MS/MS)
PHENTHOATE	109	7	99	8	GC/QqQ (MS/MS)
PHOSALONE	111	14	99	14	GC/QqQ (MS/MS)
PHOSMET(RD)	100	10	99	7	HPLC/QqQ (MS/MS)
PYRACLOSTROBIN	95	11	110	4	HPLC/QqQ (MS/MS)
PIRIMICARB(RD)	92	6	94	7	GC/QqQ (MS/MS)
PIRIMIPHOS-METHYL	111	8	94	9	GC/QqQ (MS/MS)
PROCHLORAZ(RD)	88	8	95	5	HPLC/QqQ (MS/MS)
PROCYMIDONE	94	8	93	8	GC/QqQ (MS/MS)
PROFENOFOS	100	10	97	10	GC/QqQ (MS/MS)
PROPAMOCARB(RD)	68	9	69	6	HPLC/QqQ (MS/MS)
PROPARGITE	112	10	104	7	HPLC/QqQ (MS/MS)
PROPICONAZOLE	94	9	91	10	GC/QqQ (MS/MS)
PROPYZAMIDE	99	5	96	7	GC/QqQ (MS/MS)
PROTHIOCONAZOLE	78	24	33	12	HPLC/QqQ (MS/MS)
PYRIDABEN	95	14	92	13	GC/QqQ (MS/MS)
PYRIMETHANYL	119	13	95	6	GC/QqQ (MS/MS)
PYRIPROXYFEN	103	16	95	13	GC/QqQ (MS/MS)
QUINOXYFEN	114	8	87	10	HPLC/QqQ (MS/MS)
SPINOSAD(RD)	97	11	98	4	HPLC/QqQ (MS/MS)
SPIROXAMINE	124	15	80	15	HPLC/QqQ (MS/MS)
TAUFLUVALINATE	102	13	96	17	GC/QqQ (MS/MS)
TEBUCONAZOLE	113	11	95	11	GC/QqQ (MS/MS)
TEBUFENOZIDE	124	45	97	13	HPLC/QqQ (MS/MS)
TEBUFENPYRAD	92	11	94	12	GC/QQQ (MS/MS)
TEFLUBENZURON	96	31	103	14	HPLC/QqQ (MS/MS)
TEFLUTHRIN	89	5	89	7	GC/QqQ (MS/MS)
TETRACONAZOLE	107	10	91	8	GC/QqQ (MS/MS)
TETRADIFON	87	12	90	13	GC/QqQ (MS/MS)
THIABENDAZOLE	92	9	93	8	HPLC/QqQ (MS/MS)
THIAMETHOXAM(RD)	84	16	101	5	HPLC/QqQ (MS/MS)
THIACLOPRID	86	8	105	4	HPLC/QqQ (MS/MS)
THIOPHANATE-MEHYIL	69	13	104	6	HPLC/QqQ (MS/MS)
TOLCLOFOS-METHYL	91	4	97	5	GC/QqQ (MS/MS)
TOLYFLUANID(RD)	69	9	72	10	GC/QqQ (MS/MS)
TRIADIMENOL(RD)	-	-	105	29	HPLC/QqQ (MS/MS)
TRIAZOPHOS	117	7	102	11	GC/QqQ (MS/MS)
TRICHLORFON	75	19	106	7	HPLC/QqQ (MS/MS)
TRIFLOXYSTROBIN	93	13	103	7	HPLC/QqQ (MS/MS)
TRIFLUMURON	-	-	121	6	HPLC/QqQ (MS/MS)
TRIFLURALIN	92	3	88	6	GC/QqQ (MS/MS)
TRITICONAZOLE	104	14	97	5	HPLC/QqQ (MS/MS)
VINCLOZOLIN(RD)	97	7	95	7	GC/QqQ (MS/MS)
ZOXAMIDE	79	17	112	5	HPLC/QqQ (MS/MS)

APPENDIX II
MASS TRANSITION FOR HPLC-MS/MS

PESTICIDE	R.T. (min)	TRANSITION
ACEPHATE	5.50	184.1 > 143.1 184.1 > 113.2
ACETAMIPRID	8.30	223.1 > 126.2 223.1 > 72.8
ALDICARB	9.20	208.2 > 116.2 208.2 > 89.1
ALDICARB SULFONE	6.70	240.1 > 223.3 240.1 > 86.1
ALDICARB SULFOXIDE	6.50	207.2 > 89.1 207.2 > 132.1
AMITRAZ	13.80	294.1 > 163.2 294.1 > 122.1
DMPF (N-2,4-DIMETHYLPHENYL-N-METHYL.FORMAMIDINE)	6.80	163.1 > 107.1 163.1 > 122.1
DMF (2,4 DIMETHYLFORMANILIDE)	8.70	150.2 > 107.1 150.0 > 132.1
AZINPHOS-METHYL	11.10	318.0 > 132.1 318.0 > 105.0
AZOXYSTROBIN	11.30	404.1 > 372.3 404.1 > 344.2
BITERTANOL	12.70	338.2 > 99.1 338.2 > 69.8
BOSCALID	11.60	343.0 > 307.1 343.0 > 140.1
CADUSAFOS	12.90	271.0 > 159.0 271.0 > 131.0
CARBARYL	10.20	202.2 > 145.3 202.2 > 127.0
CARBENDAZIM	6.80	192.1 > 160.2 192.1 > 105.2
CARBOFURAN	9.90	222.0 > 165.1 222.0> 123.0
CARBOFURAN 3OH	8.20	238.0 > 163.2 238.0 > 181.0
CLOTHIANIDIN	7.90	250.0 > 169.1 250.0 > 132.0
CLOFENTEZIN	12.70	303.1 > 138.1 303.1 > 130.1
CYPROCONAZOLE	11.90	292.1 > 69.8 292.1 > 125.0

PESTICIDE	R.T. (min)	TRANSITION
DICHLORVOS	9.80	221.1 > 127.1 221.1 > 109.2
DIFENOCONAZOLE	12.80	406.1 > 251.1 406.1 > 75.0
DIMETHOATE	8.30	230.1 > 199.1 230.1 > 125.1
DIMETHOMORPH	11.60	388.2 > 301.1 388.2 > 165.2
EPOXICONAZOLE	12.10	330.1 > 121.0 330.1 > 74.9
FENBUCONAZOLE	12.10	337.1 > 125.1 337.1 > 70.1
FENBUTATIN OXIDE	16.00	519.2 > 196.9 519.2 > 120.1
FENHEXAMID	12.00	302.1 > 97.2 302.1 > 55.2
FENOXYCARB	12.20	301.9 > 88.1 301.9 > 116.1
FENPROPIMORPH	10.30	304.0 > 117.0 304.0 > 147.1
FENTION SULFOXIDE	10.10	295.0 > 280.1 295.0 > 109.0
FLUFENOXURON	13.50	488.8 > 158.0 488.8 > 141.0
FLUQUINCONAZOLE	11.90	376.0 > 307.2 376.0 > 108.1
FORMETANATE	6.00	222.3 > 165.5 222.3 > 120.3
FOSTHIAZATE	10.50	284.1 > 104.0 284.1 > 228.2
HEXACONAZOLE	12.60	313.9 > 70.0 313.9 > 159.1
HEXYTHIAZOX	13.50	353.0 > 168.0 353.0 > 228.0
IMAZALIL	9.60	296.9 > 69.2 296.9 > 158.8
IMIDACLOPRID	7.80	255.9 > 208.9 255.9 > 175.0
INDOXACARB	12.80	527.8 > 203.0 527.8 > 217.9
IPROVALICARB	11.90	321.0 > 119.0 321.0 > 90.9
KRESOXIM-METHYL	12.30	314.2 > 131.1 314.2 > 115.8

PESTICIDE	R.T. (min)	TRANSITION
LINURON	11.50	248.9 > 159.9 248.9 > 132.9
LUFENURON	13.30	510.6 > 141.1 510.6 > 158.2
MALAOXON	10.00	315.0 > 99.0 315.0 > 127.1
METCONAZOLE	12.60	320.1 > 70.1 320.1 > 125.2
METHAMIDOPHOS	3.40	142.0 > 93.9 142.0 > 112.0
METHIOCARB	11.50	225.9 > 169.0 225.9 > 121.1
METHIOCARB SULFONE	8.40	258.0 > 122.0 258.0 > 201.0
METHIOCARB SULFOXIDE	8.00	241.9 > 185.0 241.9 > 122.0
METHOMYL	7.10	163.0 > 88.0 163.0 > 106.0
METHOXYFENOZIDE	11.70	369.2 > 149.0 369.2 > 91.1
MONOCROTOPHOS	7.30	224 .0 > 127.0 224.0 > 193.0
OMETOATE	6.30	213.9 > 125.0 213.9 > 183.0
OXAMYL	6.80	237.0 > 72.1 237.0 > 90.0
OXYDEMETON-METHYL	7.10	263.0 > 169.2 263.0 > 127.2
DEMETON-S-METHYL SULFONE	7.00	247.1 > 169.1 247.1 > 127.0
PACLOBUTRAZOLE	11.60	294.1 > 70.0 294.1 > 125.0
PARAOXON - METHYL	9.40	248.0 > 202.1 248.0 > 90.1
PENCONAZOLE	12.40	284.0 > 159.2 284.0 > 70.1
PENCYCURON	12.80	329.0 > 125.0 329.0 > 89.0
PHOSMET	11.20	318.0 > 160.2 318.0 > 77.0
PHOSMETOXON	9.30	302.0 > 133.1 302.0 > 160.1
PROCHLORAZ	12.50	375.8 > 307.9 375.8 > 265.9

PESTICIDE	R.T. (min)	TRANSITION
PROPAMOCARB	6.00	189.2 > 102.2 189.2 > 144.1
PROPARGITE	13.60	368.1 > 175.1 368.1 > 231.2
PROTHIOCONAZOLE	12.60	344.0 > 326.2 344.0 > 125.2
PYRACLOSTROBIN	12.60	387.9 > 194.0 387.9 > 163.0
QUINOXYFEN	13.50	308.0 > 197.0 308.0 > 214.2
SPINOSAD (A)	11.50	732.0 > 142.2 732.0 > 97.6
SPINOSAD (D)	11.70	746.0 > 142.1 746.0 > 98.1
SPIROXAMINE	10.30	298.1 > 144.2 298.1 > 99.9
TEBUFENOZIDE	12.20	353.0 > 132.9 353.0 > 297.0
TEFLUBENZURON	13.30	383.1 > 140.9 383.1 > 158.2
THIABENDAZOLE	7.30	201.9 > 175.0 201.9 > 131.0
THIACLOPRID	8.80	252.9 > 126.0 252.9 > 73.0
THIAMETHOXAM	7.20	291.8 > 211.0 291.8 > 181.0
THIOPHANATE-MEHYIL	9.90	342.9 > 151.1 342.9 > 93.1
TRIADIMEFON	11.80	293.9 > 69.0 293.9 > 197.1
TRICHLORFON	8.30	256.9 > 109.1 256.9 > 127.1
TRIFLOXYSTROBIN	12.80	408.9 > 186.0 408.9 > 145.0
TRIFLUMURON	12.50	359.1 > 156.2 359.1 > 139.0
TRITICONAZOLE	12.00	318.1 > 70.0 318.1 > 125.1
ZOXAMIDE	12.50	336.0 > 187.0 336.0 > 159.0

MASS TRANSITION FOR GC-MS/MS

PESTICIDE	R.T. (min)	TRANSITION
ACRINATHRIN	30.72	289 > 93 181 > 152 208 > 181
BIFENTHRIN	28.84	181 > 166 181 > 165 181 > 153
BROMOPROPYLATE	28.62	341 > 185 183 > 155
BUPIRIMATE	24.81	273 > 193 273 > 108
BUPROFEZIN	24.58	172 > 57 105 > 104
CAPTAN	21.23	79 > 77 79 > 51
CHLORFENVINPHOS	20.98 - 21.57	323 > 267 267 > 159
CHLOROTHALONIL	14.78	266 > 231 266 > 168 264 > 168
CHLORPROPHAM	11.04	213 > 171 213 > 127
CHLORPYRIFOS	19.23	197 > 169 197 > 107
CHLORPYRIFOS METHYL	16.59	286 > 271 286 > 93
CYFLUTHRIN	32.2 - 32.5	206 > 151 163 > 127 163 > 91
CYPERMETHRIN	32.69 - 33.02	181 > 152 163 >127 163 > 91
CYPRODINIL	20.57	225 > 224 224 > 208
DELTAMETHRIN	36.00	253 > 93 181 > 152

PESTICIDE	R.T. (min)	TRANSITION
DIAZINON	14.47	304 > 179 179 > 137
DICHLOFLUANID	18.41	332 > 167 224 > 123
DICLORAN	12.56	206 > 176 206 > 124 176 > 148
DIPHENYLAMINE	10.52	169 > 77 169 > 115
ENDOSULFAN (ALPHA ISOMER)	22.64	241 > 206 239 > 204
ENDOSULFAN (BETA ISOMER)	26.16	241 > 206 239 > 204
ENDOSULFAN SULFATE	26.76	387 > 253 387 > 217
ETHION	26.00	231 > 175 231 > 129
ETHOFENPROX	33.20	163 > 135 163 > 107
FENARIMOL	30.40	251 > 139 139 > 111
FENAZAQUIN	29.08	160 > 145 145 > 115 145 > 91
FENITROTHION	18.07	277 > 125 277 > 109
FENPROPATHRIN	28.99	265 > 210 181 > 152 181 > 127
FENTHION	19.12	278 > 125 278 > 109
FENVALERATE/ ESFENVALERATE	34.68	125 > 99 125 > 89
FIPRONIL	21.81	367 > 228 367 > 213

PESTICIDE	R.T. (min)	TRANSITION
FLUSILAZOLE	24.59	233 > 165 233 > 152
FLUVALINATE-TAU	34.70 - 34.85	250 > 200 250 > 55
FOLPET	21.59	147 >103 147 > 76
IPRODIONE	28.39	314 > 245 314 > 56
LAMBDA - CYHALOTHRIN	30.37	181 > 152 163 > 127 163 > 91
MALATHION	18.80	173 > 117 173 > 99
MEPANIPYRIM	23.06	222 > 220 222 > 193
METALAXYL	17.34	206 > 162 206 > 132
METHIDATHION	22.30	145 > 85 145 > 58
MYCLOBUTANIL	24.44	179 > 152 179 > 125
OXADIXYL	25.90	163 > 132 163 > 117
PARATHION	19.27	291 > 109 291 > 81
PARATHION – METHYL	16.59	263 > 109 263 > 81
PENDIMETHALIN	20.99	252 > 162 252 > 161
PERMETHRIN	31.37 - 31.55	183 > 168 183 > 153 183 > 115
PHENTHOATE	21.71	274 > 125 274 > 121
PIRIMICARB	15.68	238 > 166 166 > 96

PESTICIDE	R.T. (min)	TRANSITION
PIRIMIPHOS METHYL	18.31	305 > 290 290 > 125
PROCYMIDONE	21.96	283 > 96 283 > 67
PROFENOFOS	23.90	337 > 267 208 > 63
PROPICONAZOLE	26.94 - 27.15	259 > 191 259 > 173 259 > 69
PROPYZAMIDE	13.95	173 > 145 173 > 109
PYRIDABEN	31.53	147 > 132 147 > 117
PYRIMETHANIL	14.13	199 > 184 199 > 158
PYRIPROXYFEN	29.86	136 > 96 136 > 78
TEBUCONAZOLE	27.43	252 > 127 250 > 125
TEBUFENPYRAD	29.09	333 > 276 333 > 171
TEFLUTHRIN, CIS-	15.08	197 > 141 177 > 127
TETRACONAZOLE	18.86	336 > 218 336 > 204
TETRADIFON	29.38	356 > 159 354 > 159 229 > 201
TOLCLOFOS METHYL	16.81	265 > 250 265 > 93
TOLYLFLUANID	21.25	137 > 91 137 > 65
TRIAZOPHOS	26.46	161 > 134 161 > 106
TRIFLURALIN	11.64	306 > 264 264 > 206 264 > 160
VINCLOZOLIN	16.63	212 > 172 212 > 145 212 > 109