Validation Data of 127 Pesticides Using a Multiresidue Method by LC-MS/MS and GC-MS/MS in Olive Oil

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1. Aim and Scope

This report describes a validation data of 127 pesticides using a multiresidue method by LC-MS/MS and GC-MS/MS in olive oil.

2. Short Description

The homogeneous sample is diluted with n-hexane and extracted with acetonitrile. The purification is carried out using a SPE cartridge with C18 (500 mg) as sorbent. The extract obtained is analysed by GC-MS/MS and LC-MS/MS.

3. Apparatus and Consumables

- Automatic pipettes, suitable for handling volumes of 10 μL to 500 μL and 1 mL to 3 mL.
- 50 ml centrifuge tubes with screw caps (e.g. Sharlab S. L, Spain, article-no 027 – 409926).
- Centrifuge, suitable for the centrifuge tubes employed in the procedure and capable of achieving at least 1000 rpm.
- C18 SPE cartridges (e.g. Scharlau Extrabond C18 500 mg 6mL).
- Syringes, e.g. 2 mL disposable syringes.
- Syringe filters, 0.45 μm pore size.
- Injection vials, 2 ml, suitable for LC and GC auto-sampler.
- Inserts of 300 μL suitable for injection vials (e.g. Waters insert 300 μL 6X29 mm with preinstalled plastic spring).
- Test tubes.
- Volumetric flasks.
- Concentration Workstation, e.g. TurboVap LV, Zymark.

4. Chemicals

- n-Hexane 96% HPLC grade
- Acetonitrile HPLC grade
- Methanol HPLC grade
- Cyclohexane GC grade
- Ultrapure water
- Pesticides Standards, e.g. Dr. Ehrenstorfer, Sigma Aldrich.

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5. Procedure

5.1 Sample preparation

Samples were prepared according to the procedure described in the document *"Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed" (Document N° SANCO/12495/2011)*. The samples were homogenised by shaking and were stored at room temperature before analysis. As olive oil is a processed sample it should be analysed within the stated shelf life.

5.2 Recovery Experiments for Method Validation

The olive oil employed did not contain any of the pesticides analysed. Olive oil obtained from organically grown olives is recommended for the analysis.

The validation method was performed at two fortification levels (0.50 mg/Kg and 0.05 mg/Kg). Five spiked samples were analyzed at each level.

Working standard solutions containing all the pesticides used for the validation method were prepared in two different solvents, acetonitrile for LC-MS/MS and cyclohexane for GC-MS/MS.

5.3 Extraction

1. Weigh 1.5 g ± 0.1 g sample in 50 mL centrifuge tube.
2. Add 1.5 mL of n-hexane. Shake the tube for 20 seconds.
3. Add 6 mL of acetonitrile.
4. Shake vigorously for 10 minutes.
5. Centrifuge for 2 min at 1000 rpm .
6. Condition a C18 SPE cartridge with 5 mL acetonitrile (ACN)
7. Introduce 3 mL of the extract from the upper phase (ACN) into the C18 SPE cartridge.
8. Elute with 3 mL of ACN.
9. Collect the eluate and repeat the elution with 3 mL of ACN.
10. Take 1 mL of the eluate and evaporate to dryness.

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11. Reconstitute with 1 mL of ACN: H2O 1:9 (v:v). Sake the sample in the vortex and filter with a 0.45 μm syringe filter into an injection vial suitable for HPLC-MS/MS. This extract contains 0.083 g of sample per mL.
12. Transfer 1.5 mL eluate into a test tube. Evaporate to dryness
13. Add 0.5 mL cyclohexane
14. Sake the sample in the vortex.
15. Filter into an injection vial suitable for GC-MS/MS. This extract contains 0.249 g of sample per mL.

5.4 Measurement

Both LC and GC systems were operated in multiple reaction monitoring mode (SRM). SRM experiments were carried out to obtain the maximum sensitivity for the detection of the target molecules. For confirmation of the studied compounds, two SRM transitions and a correct ratio between the abundances of the two optimised SRM transitions (SRM2/SRM1) were used, along with retention time matching.

The mass transitions used are presented in Appendix I.

5.5 Instrumentation and analytical conditions for the LC- MS/MS system

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

- Column: Atlantis T3 3 μm 2.1x200 mm
- Column temperature: 40 ºC
- Mobile phase A: 2 mM ammonium formate in water, 0.1% formic acid.
- Mobile phase B: methanol
- Injection volume: 5 μL
- Autosampler temperature: 10 ºC

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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-MS/MS system

- 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	Hold Time (min)	Run Time (min)
Initial		70	2	2
Ramp 1	25	150	0	5.2
Ramp 2	3	200	0	21.867
Ramp 3	8	280	10	41.867

- 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: 280 ºC
- Quadrupole temperature: Q1 and Q" = 150 ºC
- Gas flows: Nitrogen at 1.5 mL/min, Helium at 25 ml/min

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6 Validation of the method

6.1 Recoveries and within-laboratory reproducibility

The results corresponding to the mean recovery and within-laboratory reproducibility in terms of relative standard deviation (RSD) at both fortification levels are summarized in Appendix II.

Document N° SANCO/12495/2011 recommends mean recovery values within the range 70-120% and RSD<20%. The majority of the validation results fulfil the criteria for the acceptance mentioned above.

6.2 Limits of Quantification

The limits of quantification (LOQ) of the pesticides analysed in olive oil are 0.050 mg/kg as maximum, taking into account the dilution factor applied during the extraction process.

6.3 Linearity

Linearity was evaluated in matrix, using matrix-matched calibration curves.

A) Pesticides analysed by LC-QqQ-MS/MS

A matrix-matched calibration curve was constructed for each pesticide at five calibration levels; 4, 10, 20, 50 and 100 μg/L.

The criterion for the acceptance of the linearity ($R^2 \geq 0.95$) was fulfilled for all analytes in the method. Figures 1 and 2 show some examples of calibration curves in olive oil.

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Figure 1: Calibration curve for dimethoate

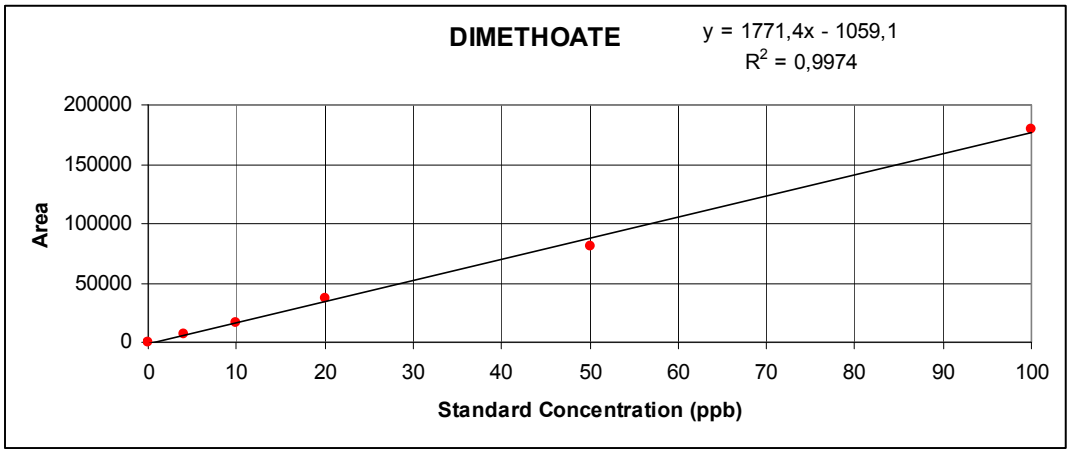
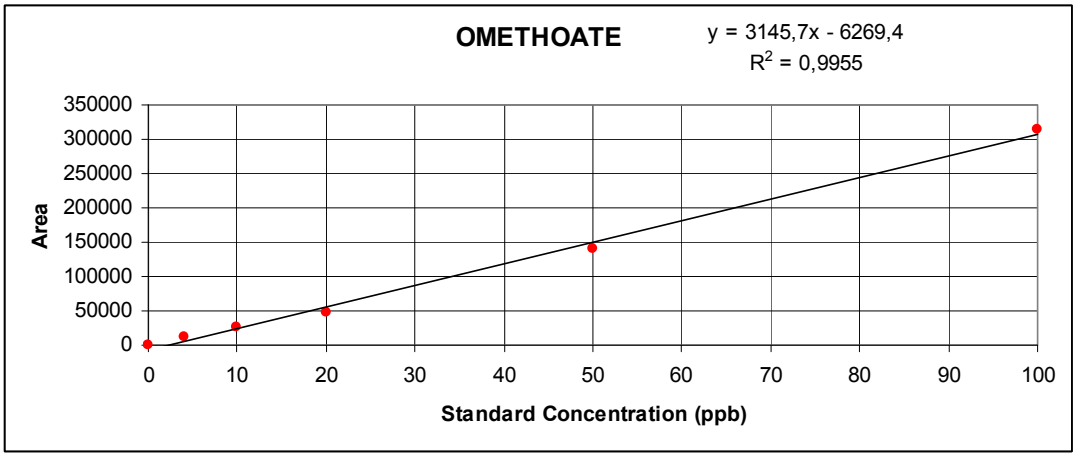


Figure 2: Calibration curve for omethoate



B) Pesticides analysed by GC-MS/MS

A calibration curve was constructed for each pesticide at five calibration levels, 10, 20, 50, 100 and 200 µg/L. The criterion for the acceptance of the linearity ($R^2 \geq 0.95$) was fulfilled for all analytes in the method. Figures 3 and 4 show some examples of calibration curves in olive oil.

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Figure 3: Calibration curve for benfluralin

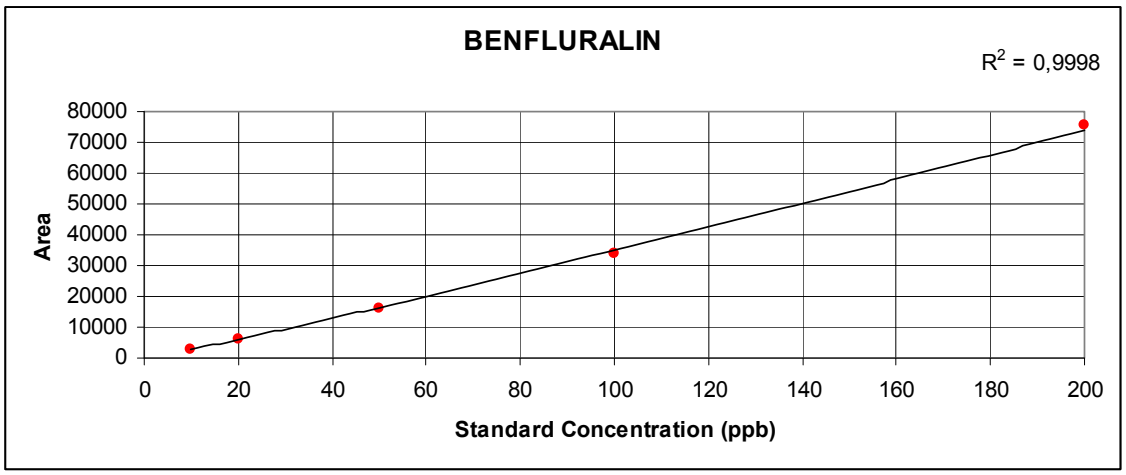
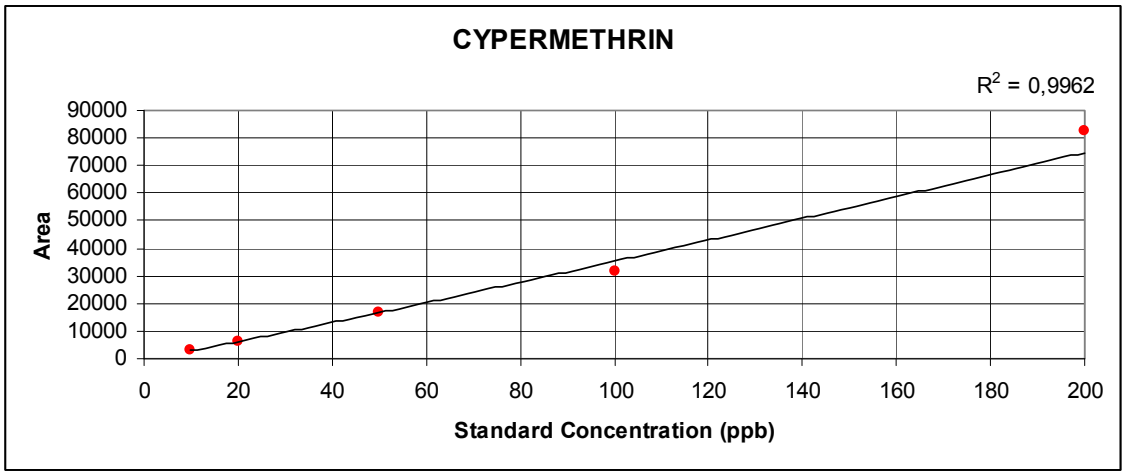


Figure 4: Calibration curve for cypermethrin



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7 Conclusions

In spite of the fact that there are some recoveries and RSD values slightly lower or higher than the values recommended by the SANCO document of method validation, the results obtained are considered acceptable within the studied range, as in certain justified cases, typically with multi-residue methods, recoveries outside this range may be accepted, especially if they are consistent. Due to the high complexity of the matrix and considering the good repeatability of the method, we accepted those recoveries in the range 60–140%, which is the range proposed by the guideline for routine analysis working with multiresidue methods.

This report aims to provide information to laboratories that analyse pesticide residues in olive oil or are interested in it.

8 References

- Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed (Document N° SANCO/12495/2011)
- http://www.eurl-pesticides.eu

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APPENDIX I: MASS TRANSITIONS

MASS TRANSITIONS FOR LC-MS/MS (3200 Q TRAP, Applied Biosystems)

PESTICIDE	R.T. (min)	TRANSITION
ACETAMIPRID	11.50	223.1 > 126.2 223.1 > 72.8
ALDICARB	12.70	208.2 > 116.2 208.2 > 89.1
ALDICARB SULFONE	8.80	240.1 > 223.3 240.1 > 86.1
ALDICARB SULFOXIDE	8.40	207.2 > 89.1 207.2 > 132.1
AZOXYSTROBIN	15.70	404.1 > 372.3 404.1 > 344.2
CARBENDAZIM	9.10	192.1 > 160.2 192.1 > 105.2
CARBOFURAN	13.80	222.0 > 165.1 222.0 > 123.0
CARBOFURAN 3-OH	11.30	238.0 > 163.2 238.0 > 181.0
CARFENTRAZONE-ETHYL	17.20	412.0 > 365.9 412.0 > 345.9
CHLORIDAZON	11.60	222.1 > 104.0 222.1 > 77.1
CHLOROXURON	14.70	291.0 > 72.0 291.0 > 46.0
CLOTHIANIDIN	11.00	250.0 > 169.1 250.0 > 132.0
CLORTOLURON	14.70	213.1 > 72.1 213.1 > 46.0
CYMOXANIL	12.10	199.1 > 128.2 199.1 > 111.2
DESMETHYL PIRIMICARB	10.00	225.1 > 72.0 225.1 > 168.0
DICROTOPHOS	1.30	238.1 > 112.2 238.1 > 126.7
DIFENOCONAZOLE	17.80	406.1 > 251.1 406.1 > 75.0
DIMEFURON	15.50	339.0 > 72.0 339.0 > 167.1
DIMETHACHLOR	15.40	256.1 > 224.2 256.1 > 148.2

PESTICIDE	R.T. (min)	TRANSITION
DIMETHENAMID	16.10	276.2 > 244.2 276.2 > 168.2
DIMETHOATE	11.50	230.1 > 199.1 230.1 > 125.1
DIMETHOMORPH	16.00	388.2 > 301.1 388.2 > 165.2
DIMOXYSTROBIN	17.10	327.1 > 205.1 327.1 > 116.1
DINICONAZOLE	17.90	326.1 > 70.0 326.1 > 43.1
DMST	13.90	215.2 > 106.3 215.2 > 79.1
EPOXICONAZOLE	16.90	330.1 > 121.0 330.1 > 74.9
ETACONAZOL	16.80	328.1 > 159.0 328.1 > 55.2
FENAMIPHOS	17.00	304.1 > 217.1 304.1 > 202.0
FENAMIPHOOS-SULPHONE	13.90	336.1 > 249.1 336.1 > 202.0
FENAMIPHOS-SULPHOXIDE	13.70	320.1 > 233.1 320.1 > 202.0
FENOBUCARB	15.80	208.1 > 95.1 204.1 > 152.2
FENPYROXIMATE	19.30	422.2 > 366.3 422.2 > 138.1
FENURON	11.20	165.0 > 72.1 165.0 > 120.0
FLAZASULFURON	15.40	408.1 > 182.0 408.1 > 227.0
FLUFENACET	16.70	364.0 > 152.2 364.0 > 124.1
FLUOPICOLIDE	16.90	383.1 > 173.0 383.1 > 109.0
FLUOXASTROBIN	16.50	459.1 > 427.2 459.1 > 188.1
FLUQUINCONAZOLE	16.70	376.0 > 307.2 376.0 > 108.1

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PESTICIDE	R.T. (min)	TRANSITION
FLURTAMONE	15.80	334.0 > 247.3 334.0 >178.3
FLUTRIAFOL	14.80	222.3 > 165.5 222.3 > 120.3
FORCHLORFENURON	15.30	284.1 > 104.0 284.1 > 228.2
HEXYTHIAZOX	18.90	353.0 > 168.0 353.0 > 228.0
IMIDACLOPRID	10.80	255.9 > 208.9 255.9 > 175.0
IPROVALICARB	16.60	321.0 > 119.0 321.0 > 90.9
LINURON	16.00	248.9 > 159.9 248.9 > 132.9
MALAOXON	13.80	315.0 > 99.0 315.0 > 127.1
METAMITRON	11.30	203.1 > 175.0 203.1 > 104.1
METCONAZOLE	17.60	320.1 > 70.1 320.1 > 125.2
METHIOCARB	16.00	225.9 > 169.0 225.9 > 121.1
METHIOCARB SULPHONE	11.70	258.0 > 122.0 258.0 > 201.0
METHIOCARB SULPHOXIDE	11.00	241.9 > 185.0 241.9 > 122.0
METHOMYL	9.40	163.0 > 88.0 163.0 > 106.0
METOSULAM	13.80	417.9 > 175.0 417.9 > 140.1
MONOCROTOPHOS	9.80	224 .0 > 127.0 224.0 > 193.0
NEBURON	17.20	275.1 > 88.1 275.1 > 114.1
OMETHOATE	8.10	213.9 > 125.0 213.9 > 183.0
OXAMYL	9.00	237.0 > 72.1 237.0 > 90.0

PESTICIDE	R.T. (min)	TRANSITION
PACLOBUTRAZOLE	16.20	294.1 > 70.0 294.1 > 125.0
PARAOXON - METHYL	12.90	248.0 > 202.1 248.0 > 90.1
PENCYCURON	17.80	329.0 > 125.0 329.0 > 89.0
PETHOXAMID	16.80	296.2 > 91.0 296.2 > 131.2
PHOSMET	15.60	318.0 > 160.2 318.0 > 77.0
PICOXISTROBIN	16.90	367.9 > 145.0 367.9 > 145.0
PYMETROZINE	7.80	218.1 > 105.2 218.1 > 78.0
PYRACLOSTROBIN	17.50	387.9 > 194.0 387.9 > 163.0
TERBUTRYN	16.10	242.1 > 186.1 242.1 > 68.1
THIABENDAZOLE	9.90	201.9 > 175.0 201.9 > 131.0
THIACLOPRID	12.10	252.9 > 126.0 252.9 > 73.0
THIAMETHOXAM	9.80	291.8 > 211.0 291.8 > 181.0
TRIADIMEFON	16.40	293.9 > 69.0 293.9 > 197.1
TRIADIMENOL	16.50	295.9 > 70.0 295.9 > 227.2
TRIFLOXYSTROBIN	17.90	408.9 > 186.0 408.9 > 145.0
TRIFLUMIZOLE	18.00	346.0 > 278.2 346.0 > 43.1
TRITICONAZOLE	16.80	318.1 > 70.0 318.1 > 125.1
ZOXAMIDE	17.60	336.0 > 187.0 336.0 > 159.0

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MASS TRANSITIONS FOR GC-MS/MS (Agilent 7000B Series)

PESTICIDE	R.T. (min)	TRANSITION
BENALAXYL	26.74	266 > 148 148 > 105
BENFLURALIN	11.72	292 > 264 292 > 160
BIFENOX	29.18	311 > 279 311 > 216
BROMOPROPYLATE	28.62	341 > 185 183 > 155
BUPIRIMATE	24.81	273 > 193 273 > 108
CHLORFENVINPHOS	20.98 - 21.57	323 > 267 267 > 159
CHLORFENAPYR	25.22	247 > 227 247 > 197
CHLORPYRIFOS	19.23	197 > 169 197 > 107
CHLORPYRIFOS - METHYL	16.59	286 > 271 286 > 93
CHLORTAL-DIMETHYL	19.43	299 > 221 291 > 109
CHLORTHIOPHOS	26.12	268 > 205 325 > 269 269 > 205
CHLOZOLINATE	21.38	188 > 147 331 > 259
CYFLUTHRIN	32.2 - 32.5	206 > 151 163 > 127 163 > 91
CYPERMETHRIN	32.69 - 33.02	181 > 152 163 >127 163 > 91
DELTAMETHRIN	36.00	253 > 93 181 > 152
DIAZINON	14.47	304 > 179 179 > 137

PESTICIDE	R.T. (min)	TRANSITION
DICLORAN	12.56	206 > 176 206 > 124 176 > 148
DIFLUFENICAM	27.78	394 > 266 266 > 218
ENDOSULFAN (ALPHA ISOMER)	22.64	241 > 206 239 > 204
ENDOSULFAN (BETA ISOMER)	26.16	241 > 206 239 > 204
ENDOSULFAN SULPHATE	26.76	387 > 253 387 > 217
ESFENVALERATE	34.69	125 > 89 125 > 99
ETHION	26.00	231 > 175 231 > 129
ETHOPROPHOS	10.74	158 > 97 200 > 158
FENARIMOL	30.40	251 > 139 139 > 111
FENITROTHION	18.07	277 > 125 277 > 109
FENPROPATHRIN	28.99	265 > 210 181 > 152 181 > 127
FLUSILAZOLE	24.59	233 > 165 233 > 152
FLUVALINATE-TAU	34.70 – 34.85	250 > 200 250 > 55
FURALAXYL	21.92	242 > 95 301 > 225
IPRODIONE	28.39	314 > 245 314 > 56
ISOCARBOPHOS	19.60	136 > 108 230 > 212
ISOFENPHOS-METHYL	20.72	199 > 121 241 > 199

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PESTICIDE	R.T. (min)	TRANSITION
LAMBDA - CYHALOTHRIN	30.37	181 > 152 163 > 127 163 > 91
LINDANE	13.46	181 > 145 219 > 183 219 > 145
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
NUARIMOL	27.44	235 > 139 314 > 139
o-PHENYLPHENOL	8.78	170 > 141 170 > 115
OXYFLUORFEN	24.73	252.1 > 252 252 > 196
PARATHION	19.27	291 > 109 291 > 79
PARATHION – METHYL	16.59	263 > 109 263 > 81
PENDIMETHALIN	20.99	252 > 162 252 > 161
PHENTHOATE	21.71	274 > 125 274 > 121
PHOSALONE	29.67	182 > 111 182 > 138
PICOLINAFEN	28.79	238 > 145 238 > 190
PIRIMICARB	15.68	238 > 166 166 > 96
PIRIMIPHOS - METHYL	18.31	305 > 290 290 > 125

PESTICIDE	R.T. (min)	TRANSITION
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
PYRAZOPHOS	30.71	221 > 193 232 > 204
PYRIDABEN	31.53	147 > 132 147 > 117
PYRIDAFENTHION	28.51	340 > 199 340 > 97
PYRIPROXYFEN	29.86	136 > 96 136 > 78
QUINALPHOS	21.64	146 > 118 146 > 91
TEBUCONAZOLE	27.43	252 > 127 250 > 125
TEFLUTHRIN, CIS-	15.08	197 > 141 177 > 127
TERBUFOS	13.79	231 > 175 231 >129
TETRACONAZOLE	18.86	336 > 218 336 > 204
TOLCLOFOS - METHYL	16.81	265 > 250 265 > 93
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

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APPENDIX II: VALIDATION RESULTS

PESTICIDE	MEAN RECOVERY% (Spiking Level 0,05 mg/Kg)	RSD% (n = 5)	MEAN RECOVERY% (Spiking Level 0,5 mg/Kg)	RSD% (n = 5)	TECHNIQUE	R^2
ACETAMIPRID	64%	3%	84%	4%	LC-MS/MS	0.9922
ALDICARB *(RD)*	89%	24%	76%	7%	LC-MS/MS	0.9988
ALDICARB SULFOXIDE	89%	19%	82%	5%	LC-MS/MS	0.9900
ALDICARB SULFONE	95%	16%	85%	11%	LC-MS/MS	0.9958
AZOXYSTROBIN	99%	6%	91%	2%	LC-MS/MS	0.9999
BENALAXYL	73%	8%	85%	3%	GC-MS/MS	0.9988
BENFLURALIN	71%	8%	76%	2%	GC-MS/MS	0.9996
BIFENOX	73%	8%	84%	6%	GC-MS/MS	0.9952
BROMOPROPYLATE	66%	7%	72%	6%	GC-MS/MS	0.9990
BUPIRIMATE	80%	7%	84%	5%	GC-MS/MS	0.9990
CARBENDAZIM	101%	9%	74%	4%	LC-MS/MS	0.9940
CARBOFURAN *(RD)*	62%	2%	72%	5%	LC-MS/MS	0.9999
CARBOFURAN 3-OH	70%	16%	79%	5%	LC-MS/MS	0.9952
CARFENTRAZONE ETHYL	74%	18%	70%	5%	LC-MS/MS	0.9931
CHLOFENVINPHOS	82%	11%	96%	10%	GC-MS/MS	0.9970
CHLORFENAPYR	84%	14%	91%	8%	GC-MS/MS	0.9933
CHLORIDAZON	73%	10%	81%	4%	LC-MS/MS	0.9996
CHLOROXURON	68%	13%	86%	2%	LC-MS/MS	0.9980
CHLORPYRIPHOS	72%	5%	74%	3%	GC-MS/MS	0.9969
CHLORPYRIPHOS METHYL	74%	9%	88%	7%	GC-MS/MS	0.9970
CHLORTAL-DIMETHYL	73%	4%	79%	3%	GC-MS/MS	0.9985
CHLORTHIOPHOS	68%	7%	75%	7%	GC-MS/MS	0.9987
CHLOZOLINATE	73%	12%	87%	7%	GC-MS/MS	0.9997
CLORTOLURON	67%	7%	67%	1%	LC-MS/MS	0.9998
CYFLUTHRIN	108%	8%	93%	6%	GC-MS/MS	0.9930
CYHALOTHRIN LAMBDA	88%	6%	88%	4%	GC-MS/MS	0.9957
CYMOXANIL	82%	5%	78%	7%	LC-MS/MS	0.9966
CYPERMETHRIN	98%	6%	88%	4%	GC-MS/MS	0.9930
DELTAMETHRIN	96%	7%	90%	4%	GC-MS/MS	0.9990
DIAZINON	76%	6%	82%	6%	GC-MS/MS	0.9999
DICLORAN	79%	7%	79%	8%	GC-MS/MS	0.9981
DICROTOPHOS	87%	6%	81%	7%	LC-MS/MS	0.9996
DIFENOCONAZOLE	88%	5%	102%	6%	LC-MS/MS	0.9980
DIFLUFENICAN	73%	9%	87%	2%	GC-MS/MS	0.9995
DIMEFURON	85%	10%	96%	1%	LC-MS/MS	0.9998
DIMETHACHLOR	79%	15%	69%	5%	LC-MS/MS	0.9974
DIMETHENAMID	78%	12%	82%	5%	LC-MS/MS	0.9978

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PESTICIDE	MEAN RECOVERY% (Spiking Level 0,05 mg/Kg)	RSD% (n = 5)	MEAN RECOVERY% (Spiking Level 0,5 mg/Kg)	RSD% (n = 5)	TECHNIQUE	R^2
DIMETHOATE *(RD)*	90%	3%	75%	7%	LC-MS/MS	0.9972
OMETHOATE	105%	4%	95%	7%	LC-MS/MS	0.9934
DIMETHOMORPH	81%	8%	89%	4%	LC-MS/MS	0.9992
DIMOXYSTROBIN	62%	8%	71%	6%	LC-MS/MS	0.9999
DINICONAZOLE	69%	14%	86%	7%	LC-MS/MS	0.9954
DMST	69%	14%	79%	5%	LC-MS/MS	0.9992
ENDOSULFAN SULPHATE *(RD)*	84%	8%	90%	12%	GC-MS/MS	0.9985
ENDOSULFAN (ALPHA ISOMER)	53%	9%	56%	4%	GC-MS/MS	0.9985
ENDOSULFAN (BETA ISOMER)	62%	15%	71%	6%	GC-MS/MS	0.9995
EPOXICONAZOLE	85%	21%	92%	6%	LC-MS/MS	0.9992
ESFENVALERATE/FENVALERATE	91%	7%	89%	5%	GC-MS/MS	0.9921
ETACONAZOL	71%	7%	83%	5%	LC-MS/MS	0.9992
ETHION	83%	9%	95%	7%	GC-MS/MS	0.9983
ETHOPROPHOS	69%	7%	83%	2%	GC-MS/MS	0.9997
FENAMIPHOS *(RD)*	75%	12%	82%	3%	LC-MS/MS	0.9990
FENAMIPHOS SULFOXIDE	77%	10%	85%	3%	LC-MS/MS	0.9980
FENAMIPHOS SULFONE	75%	13%	89%	2%	LC-MS/MS	0.9998
FENARIMOL	67%	6%	74%	6%	GC-MS/MS	0.9983
FENITROTHION	105%	10%	104%	12%	GC-MS/MS	0.9963
FENOBUCARB	76%	7%	80%	4%	LC-MS/MS	0.9936
FENPROPATHRIN	72%	7%	77%	5%	GC-MS/MS	0.9969
FENPYROXIMATE	83%	4%	70%	2%	LC-MS/MS	0.9936
FENURON	82%	4%	80%	2%	LC-MS/MS	0.9996
FLAZASULFURON	110%	11%	102%	7%	LC-MS/MS	0.9996
FLUFENACET	75%	20%	86%	4%	LC-MS/MS	0.9942
FLUOPICOLIDE	81%	16%	78%	4%	LC-MS/MS	0.9998
FLUOXASTROBIN	92%	9%	86%	3%	LC-MS/MS	0.9964
FLUQUINCONAZOLE	94%	18%	87%	7%	LC-MS/MS	0.9984
FLURTAMONE	91%	9%	92%	3%	LC-MS/MS	0.9996
FLUSILAZOLE	80%	8%	81%	11%	GC-MS/MS	0.9992
FLUTRIAFOL	78%	16%	72%	5%	LC-MS/MS	0.9999
FLUVALINATE	107%	6%	102%	6%	GC-MS/MS	0.9980
FORCHLORFENURON	105%	10%	82%	2%	LC-MS/MS	0.9960
FURALAXYL	68%	10%	82%	10%	GC-MS/MS	0.9986
HEXYTHIAZOX	89%	11%	68%	4%	LC-MS/MS	0.9976
IMIDACLOPRID	65%	8%	74%	3%	LC-MS/MS	0.9998
IPRODIONE	94%	14%	97%	20%	GC-MS/MS	0.9947
IPROVALICARB	98%	19%	99%	6%	LC-MS/MS	0.9980
ISOCARBOPHOS	95%	11%	110%	18%	GC-MS/MS	0.9967
ISOFENPHOS-METHYL	78%	7%	93%	6%	GC-MS/MS	0.9993
LINDANE	74%	7%	79%	10%	GC-MS/MS	0.9991
LINURON	87%	15%	88%	8%	LC-MS/MS	0.9970
MALATHION *(RD)*	91%	11%	111%	8%	GC-MS/MS	0.9909
MALAOXON	76%	11%	74%	4%	LC-MS/MS	0.9973
MEPANIPYRIM	74%	9%	84%	5%	GC-MS/MS	0.9987

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METALAXYL	74%	13%	84%	6%	GC-MS/MS	0.9996
METAMITRON	68%	7%	83%	3%	LC-MS/MS	0.9978
METCONAZOLE	90%	5%	93%	6%	LC-MS/MS	0.9996
METHIDATHION	100%	11%	114%	17%	GC-MS/MS	0.9953
METHIOCARB (RD)	73%	12%	92%	6%	LC-MS/MS	0.9986
METHIOCARB SULFOXIDE	88%	9%	90%	4%	LC-MS/MS	0.9996
METHIOCARB SULFONE	78%	7%	78%	6%	LC-MS/MS	0.9996
METHOMYL	86%	11%	81%	10%	LC-MS/MS	0.9966
METOSULAM	85%	11%	106%	2%	LC-MS/MS	0.9978
MONOCROTOPHOS	72%	4%	93%	5%	LC-MS/MS	0.9990
MYCLOBUTANIL	77%	9%	75%	11%	GC-MS/MS	0.9991
NEBURON	66%	13%	74%	5%	LC-MS/MS	0.9990
NUARIMOL	67%	8%	76%	10%	GC-MS/MS	0.9979
o-PHENYLPHENOL	66%	7%	82%	4%	GC-MS/MS	0.9997
OXAMYL	61%	11%	95%	10%	LC-MS/MS	0.9938
OXYFLUORFEN	101%	10%	96%	4%	GC-MS/MS	0.9906
PACLOBUTRAZOLE	84%	10%	73%	2%	LC-MS/MS	0.9966
PARATHION-METHYL (RD)	95%	11%	108%	12%	GC-MS/MS	0.9904
PARAOXON METHYL	78%	8%	83%	2%	LC-MS/MS	0.9990
PENCYCURON	92%	5%	96%	2%	LC-MS/MS	0.9994
PENDIMETHALIN	77%	6%	78%	3%	GC-MS/MS	0.9988
PETHOXAMID	68%	8%	79%	4%	LC-MS/MS	0.9988
PHENTHOATE	83%	9%	99%	9%	GC-MS/MS	0.9957
PHOSALONE	102%	6%	107%	15%	GC-MS/MS	0.9981
PHOSMET	88%	13%	79%	7%	LC-MS/MS	0.9994
PICOLINAFEN	74%	7%	86%	2%	GC-MS/MS	0.9992
PICOXISTROBIN	116%	11%	103%	6%	LC-MS/MS	0.9994
PIRIDAFENTHION	95%	7%	108%	15%	GC-MS/MS	0.9984
PIRIMICARB (RD)	65%	13%	76%	9%	GC-MS/MS	0.9997
DESMETHYL PIRIMICARB	82%	3%	84%	4%	LC-MS/MS	0.9988
PROCYMIDONE	77%	9%	84%	6%	GC-MS/MS	0.9983
PROFENOFOS	81%	10%	94%	15%	GC-MS/MS	0.9899
PROPICONAZOLE	71%	8%	78%	5%	GC-MS/MS	0.9993
PROPYZAMIDE	72%	8%	84%	3%	GC-MS/MS	0.9998
PYMETROZINE	78%	9%	81%	3%	LC-MS/MS	0.9992
PYRACLOSTROBIN	84%	15%	96%	6%	LC-MS/MS	0.9942
PYRAZOPHOS	92%	7%	102%	12%	GC-MS/MS	0.9927
PYRIDABEN	68%	7%	71%	6%	GC-MS/MS	0.9984
PYRIPROXYFEN	65%	7%	72%	2%	GC-MS/MS	0.9987
QUINALPHOS	74%	8%	84%	7%	GC-MS/MS	0.9977
TEBUCONAZOLE	84%	9%	77%	11%	GC-MS/MS	0.9934
TEFLUTHRIN	66%	3%	73%	1%	GC-MS/MS	0.9996
TERBUFOS	65%	5%	75%	9%	GC-MS/MS	0.9999
TERBUTRYN	53%	12%	83%	5%	LC-MS/MS	0.9974
TETRACONAZOLE	75%	11%	81%	9%	GC-MS/MS	0.9991
THIABENDAZOLE	74%	10%	76%	6%	LC-MS/MS	0.9986

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THIACLOPRID	59%	4%	68%	1%	LC-MS/MS	0.9994
THIAMETHOXAM (RD)	80%	10%	93%	3%	LC-MS/MS	0.9982
CLOTHIANIDIN	59%	44%	80%	12%	LC-MS/MS	0.9972
TOLCLOFOS-METHYL	73%	6%	83%	2%	GC-MS/MS	0.992
TRIADIMEFON	100%	23%	96%	3%	LC-MS/MS	0.9978
TRIADIMENOL	44%	36%	101%	36%	LC-MS/MS	0.9955
TRIAZOPHOS	103%	9%	105%	15%	GC-MS/MS	0.9981
TRIFLOXYSTROBIN	104%	21%	116%	9%	LC-MS/MS	0.9580
TRIFLUMIZOLE	76%	9%	86%	4%	LC-MS/MS	0.9998
TRIFLURALIN	71%	8%	78%	5%	GC-MS/MS	0.9998
TRITICONAZOLE	71%	17%	80%	6%	LC-MS/MS	0.9984
VINCLOZOLIN	72%	13%	84%	6%	GC-MS/MS	0.9986
ZOXAMIDE	98%	14%	105%	9%	LC-MS/MS	0.9958

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