EURL-FV

Analysis of pesticide residues in fruit and vegetables with ethyl acetate extraction using gas and liquid chromatography with tandem mass spectrometric detection 0.1

CONTENTS

1. Introduction

The Swedish National Food Administration has since 1989 employed a multi residue method that is based on extraction with ethyl acetate followed by LC and GC determination[1]. The multi residue method has been revised continuously resulting in an improved and simplified methodology for analysis of pesticides residues. For example, the need of clean up has been eliminated entirely and to improve the recovery of basic pesticides the addition of sodium hydrogen carbonate has been used to all matrices. The use of LC-MS/MS and GC-MS/MS has further enhanced the analytical quality and performance. A previous drawback of the method has been the relatively large sample size (75 g) and the large volume of extraction solvent (200 ml), which made the sample preparation rather cumbersome and limiting to the sample throughput. Recent developments of the method enable the use of a smaller sample size of 10 g following a volume of 20 ml of ethyl acetate. Before extraction in 50 ml Falcon tubes a reduced amount of $NaHCO_3$ and Na_2SO_4 was added to all matrices. Furthermore, in improving the analytical step, the chromatographic aspects were taken into consideration including the use of columns with small particles (1.7 µm UPLC column) resulting in the reduction of analytical time in LC-MS/MS from 30 minutes to 16 minutes. Finally, the previously employed solvent switch from ethyl acetate to methanol has been eliminated saving time and reducing the number of analytical steps.

2. Application area/matrices

The method is used for analysis of pesticide residues in fruit and vegetables by means of LC-MS/MS and GC-MS/MS detection and has been validated according to SANCO 10684/2009[2] for three selected commodity groups (see Annex 1) 1) high water content. 2) high acid content and high water content and 3) high sugar and low water content.

3. Principles

Residues are extracted from food matrix with ethyl acetate. Sodium hydrogen carbonate is added to well homogenised crop sample which is extracted with ethyl acetate. After centrifugation and filtration the extract is injected to GC-MS/MS and LC-MS/MS. No clean up is needed.
For more details see Figure 1 Analytical flow scheme.

4. Limit of Quantification

The Limit of Quantification (LOQ) of the method is 0.01 mg/kg for most of the analytes. Appendix 3.

5. Reagents and chemicals

- Methanol, gradient grade
- Ethyl acetate, pestiscan grade.
- Acetone, pestiscan grade
- Acetic acid 100 %.
- Ammonium, ca 25 % NH_3 (ca 13.4 M
- Sodium sulphate, water free. p.a.
- Sodium hydrogen carbonate, water free. p.a.

6. Apparatus

- Sample processing equipment. for example Cut-O-MAT H10/4 Standard 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 Sarstedt.114x28 mm PP
- 25 mL volumetric cylinder for ethyl acetate.
- Syringes, e.g. 10 mL disposable syringes.
- Syringes filters, 0.20 µm pore size.
- Injection vials: 1.5 ml suitable for LC and GC auto-sampler.
- Centrifuge for example Hettich Rotanta/AP (Germany)
- Ultrasonic bath for example Sonorex RK100

7. Extraction

1) Weigh 3.0 g sodium hydrogen carbonate ($NaHCO_3$) to 10 ± 0.1g sample in a 50 mL centrifuge tube
2) Add 10 g sodium sulphate (Na_2SO_4) and 20 ± 0.1ml ethyl acetate and extract by shaking (30 sec) and ultrasonication (3 min), max 35°C
3) Centrifuge 3 minutes at 3200 g.
4) Filtrate the crude extract through a 0.20 µm PTFE filter
5) Inject to GC-MS/MS and LC-MS/MS

For analysis of dried fruits (water content of ca 20%) addition of water is needed before extraction. Add 750 g cold water (4 °C) to 500 g dried fruits and homogenate the sample. Weigh 25 g sample corresponding 10 g dried fruit and add 20 ml ethyl acetate as described above.

8. Determination

LC -MS/MS: Instrumentation and settings

Any suitable LC -MS/MS conditions may be used. More detailed information of the LC-MS/MS measurement conditions is available in the validation report below.

Instrumentation

Agilent 6410 triple quad LC-MS system
Agilent 1200 HPLC

Proposed settings for mass spectrometry

Cycle time	500ms
Total MRMs	212
Concurrent MRM	60
Min/Max Dwell	4.83ms/246.50ms
Pressure start	600bar
Pressure max	880bar
Gas Temp:	350°C

Gas flow:	5 l/min
Nebulizer:	45 psi
Sheath Gas Temp:	250°C
Sheath Gas Flow:	11 l/min
Capillary:	3500 V
Nozzle voltage:	500 V

Proposed UPLC conditions for chromatographic separation were following:

Column:

- Waters HSS T3, 150x 2.1mm , 1.7 µm
- Column temperature: 45 °C
- Mobile phase A: 10 mM ammonium formiate. pH 4
- Mobile phase B: methanol
- Injection volume: 2 µL
- Total run time: 16 min.

Table 1. Flow rate and elution gradient

Time (min)	Flow Rate (µl/min)	A (%)	B (%)
0	450	95	5
11	450	5	95
13	450	5	95
13.1	450	95	5
16	450	95	5

GC-MS/MS: Instrumentation and settings
Any suitable GC-MS/MS conditions may be used. More detailed information of the GC-MS/MS measurement conditions is available in the validation report.

Used/proposed instrumentation/GC conditions are presented below.

Instrumentation:
Varian 1200 Quadrupole MS/MS
Varian CP-3800 Gas Chromatograph
Varian 1079 GC injector
Varian CP-8400 Autosampler

Electron ionisation at 70 eV and an ion source temperature of 320°C were applied. Collision energies are optimised for each pesticide. See settings in Appendix 2.

GC Column:
FactorFour VF-5ms w/EZ-Guard (30+10m. 0.25 mm ID. 0.25 µm df), P/N: CP9013
Gas flow: 1.00 ml/min (constant flow mode)
Carrier gas: Helium

Gas: Helium, Alphagaz 2 (Air Liquid)
Argon, Alphagaz 1 (Air Liquid)

Varian 1200 Quadrupole MS/MS detector:
Collision gas: Argon
Solvent Delay: 3.5 min

Varian CP-3800 GC:
Initial Temperature: 90 °C
Initial Time: 1.0 min

GC oven ramp:

Rate (°C/min)	Final temp (°C)	Hold Time (min)	Total Time (min)
30.00	180	0.50	4.50
5.00	280	5.50	30.00

Post-run temperature: 320 °C
Post-run time: 10 min

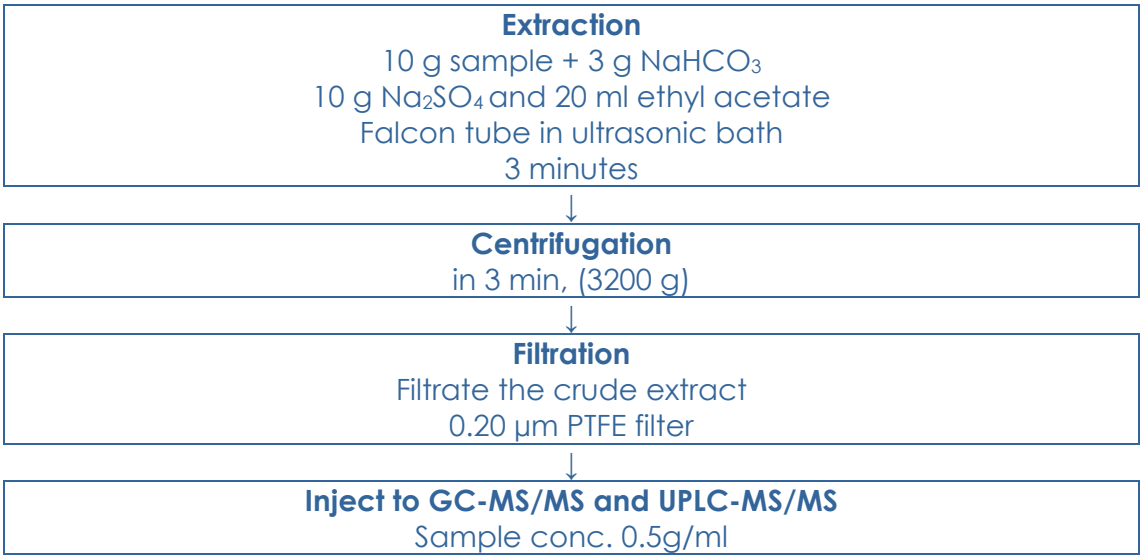
Varian 1079 GC injector:
Initial Temperature: 170 °C
Initial Time: 0.10 min

Injector oven ramp:

Rate (°C/min)	Final temp (°C)	Hold Time (min)	Total Time (min)
180.00	280	39.3	40

Varian CP-8400 Autosampler
Syringe volume: 10.0 µl
Injection Volume: 2.00 µl
Air Volume: 1.00 µl
Solvent plug: 0.5 µl (ethyl acetate)
Pre Clean with Solvent1: 3 (acetone)
Pre Clean with Solvent2: 3 (ethyl acetate)
Pre Clean with sample: 0
Filling Speed: 2.0 µl/s
Filling Strokes: 3
Injection Speed: 10.0 µl/s
Pre Inject Delay: 3000 ms (hot needle injection)
Post Inject Delay: 500 ms
Post Clean with Solvent1: 3 (acetone)
Post Clean with Solvent2: 3 (ethyl acetate)

9. Figure1. The analytical flow scheme of the ethyl acetate method



10. Validation design

The method is validated for at least one commodity from each commodity group as far the commodities are applicable to samples analysed in the laboratory. The analysis of other matrices within the same commodity category is directly applicable.

Please refer to the EU-RL Data Pool for single validation results.
http://www.crl-pesticides-datapool.eu/ Registration and login is required.

Recovery results
The method is validated for all analytes within the scope of the method (Appendix 1). The validation is performed with five recovery values for two concentration levels 0.01 and 0.05 mg/kg in three different commodities, orange, raisins and leek.
The mean recovery and the within-laboratory reproducibility (RSD) are determined for each matrix /level/commodity combination. Quantification has been done using matrix matched standards. In the majority of cases the quantitative results (70-120 %) with RSD <20% for most analytes/matrix combinations were obtained.

Mean recovery for all included analytes at 0.01 mg/kg (n=5 per analyte) :
Orange 92 %
Raisins 93 %
Leek 93 %

Mean recovery for all analytes in all matrices at 0.01 mg/kg was found to be 93 %, n=15 per analyte.

Mean recovery for all included analytes at 0.05 mg/kg (n=5 per analyte).
Orange 94 %
Raisins 99 %
Leek 99 %

Mean recovery for all analytes in all matrices at 0.05 mg/kg was found to be 97 %, n=15 per analyte.

11. Precision-repeatability

Detection with LC-MS/MS
Repeatability is expressed as the relative standard deviation (RSD %) on the results from five replicates for all included analytes.

	RSD %, n=5 per analyte	
	0.01 mg/kg	0.05 mg/kg
Orange	10	8.9
Raisin	7.7	5.8
Leek	8.1	7.5

RSD calculated for all matrices 9.1 % at 0.01 mg/kg (n=15) and 8.4 % at 0.05 mg/kg (n=15).

Detection med GC-MS/MS
Repeatability is expressed as the relative standard deviation (RSD %) on the results from five replicates for all included analytes.

	RSD %, n=5 per analyte	
	0.01 mg/kg	0.05 mg/kg
Orange	12	13
Raisin	18	16
Leek	19	17

RSD calculated for all matrices is 16 % at 0.01 mg/kg (n=15) and 15 % at 0.05 mg/kg (n=15).

12. Linearity test and calibration curve

For monitoring purposes the quantification is done in standard dissolved in generic matrix (cucumber for GC-MS/MS and carrot for LC-MS/MS). Therefore, linearity test is carried out in generic matrix. The method showed to be linear up to 0.3 mg/kg for all analytes/ matrices with LC-MS/MS and up to 0.4 mg/kg for GC-MS/MS as well.
A criterion for the acceptance of the linearity ($R2 \geq 0.95$) is fulfilled for all analytes in the method.

13. Stability of standards

Some pesticides especially LC pesticides, have shown somewhat low stability in working solutions of pure methanol or ethyl acetate and a better stability in solvents diluted with matrix. Therefore, a stability test of the working standards dissolved in generic matrices was performed. The "old" working standard, which was stored sealed in darkness (at 6 °C) was analyzed and controlled against the new prepared standard.
As can be seen in Appendix 4 the LC working standard solutions were stable over the period of five weeks except for Methiocarb and DMPF (metabolite to amitraz) which were degradated ≥20%. The stability study for GC analytes was performed over three weeks so far.

Analyte	Degradation
Methiocarb	20%
DMPF	46 %

14. Robustness

The proposed method is a multi residue method for different type of pesticides and matrices. In order to test the robustness of the method the matrix effect was studied. The matrix effect, expressed as the signal from the standard in matrix compared to the signal in generic matrix was tested at 0.05 mg/kg. In general, the measured matrix effect is small (<20% suppression or enhancement of the signal). As shown in Figure 2 and Table 2, only 6% of analytes in raisin with LC-MS/MS showed matrix effects >20% (suppression of the signal). Citrus fruits have a well known matrix effect showing 20-50 % suppression for 11% of analytes, Figure 2 and Table 3.
However, the majority of analytes detected with GC-MS/MS showed a significant enhancement of the signal in raisin. As a result, 77 % of the analytes had a matrix effect >20% and 8% of the analytes have matrix effects >50%. However, orange matrix had no influence on the signal with GC-MS/MS.

Table 2. Analytes with >20 % suppression in raisin extract with LC-MS/MS-detection

Analyte	Matrixeffect (%)
Atrazindesisopropyl	-22.7
DMPF	-41.1
Etofenprox	-25.0
Fenazakin	-28.4
Flufenoxuron	-22.0
Chlorfluasuron	-29.2
Quinoxyfen	-21.2
Lufenuron	-20.7
Paraoxonmethyl	-23.3
Pyriproxifen	-21.3
Teflubensuron	-29.9

Table 3. Analytes with >20 % suppression in orange extract with LC-MS/MS-detection

Analyte	Matrixeffect (%)
Atrazin	-22.0
Atrazindesethyl	-41.7
Azoxystrobin	-38.0
Bentazon	-41.4
Cyproconazole	-33.1
Etofumesate	-44.6
Linuron	-48.2
Mekarbam	-23.7
Methoxyfenozide	-23.2
Propetamphos	-38.5
Pyridafention	-41.5
Tepraloxydim	-33.4
Terbuphossulfon	-37.0
Terbuphossulfoxid	-29.3
Tetraconazole	-20.5
Tiachloprid	-23.9
Tiofanatmethyl	-22.0
Triadimefon	-29.3
Triadimenol	-29.2

Figure 2. Histogram of matrix effects of all analytes in raisin and orange.

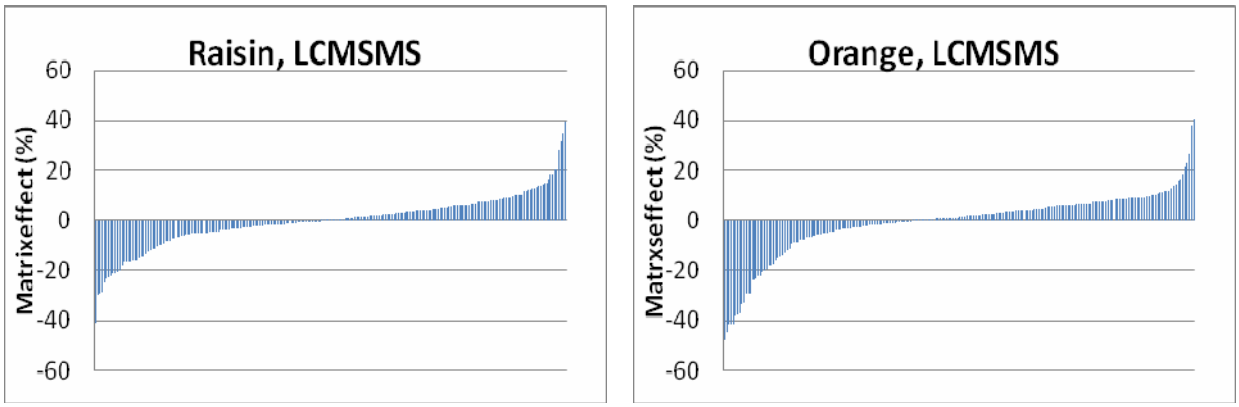
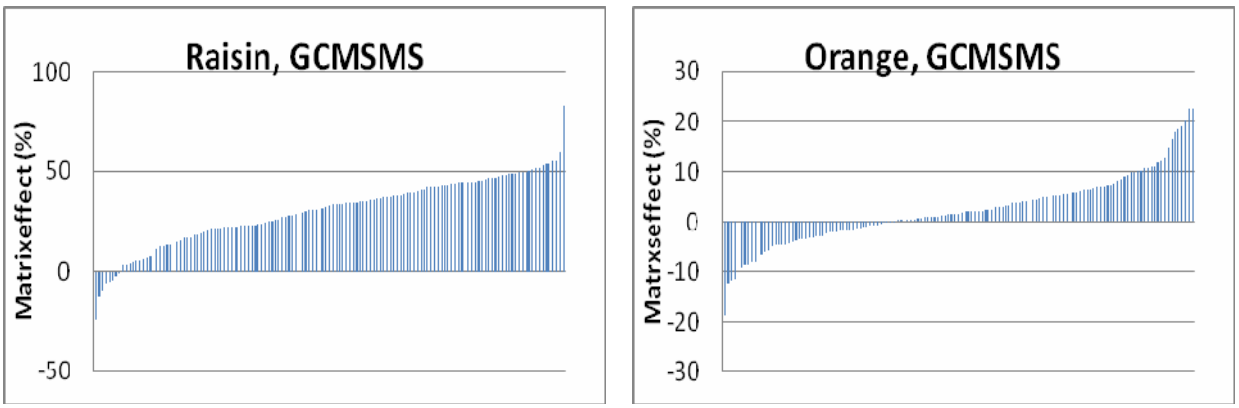


Figure 3. Histogram of matrix effects of all analytes in raisin and orange with GC-MS/MS detection.



15. References

1. T. Pihlström *et al.*. Anal Bioanal. Chem. (2007) 389:1773-1789
2. Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed (Document No. SANCO/10684/2009)

16. Contact information

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18. Appendix 1. Mass transitions LC-MSMS (ES+)

Pesticide	Rt min	Precursor	Product	DP	CE	Product	CE
Abamectin	12.19	890.6	305.2	150	20	567.1	10
Acefate	2.57	184.0	143.0	100	0	95.0	20
Acetamiprid	5.6	223.0	126.0	110	20	99.1	45
AcibenzolarSmetyl	9.4	211.0	136.2	130	30	91.1	15
Aldicarb	6.56	208.0	116.0	70	0	89.1	10
Aldicarbsulfon	3.21	223.0	148.0	100	0	86.0	10
Aldicarb-sulfoxid	3.04	207.0	132.0	100	0	89.0	8
Aminocarb	5.3	209.0	137.0	100	20	152.0	10
Amitraz	12.2	294.2	163.2	100	10	122.1	35
Aspon	11.73	379.1	114.9	100	35	210.9	15
Atrazin	8.47	216.0	174.1	120	15	104.1	30
Atrazindesethyl	6.13	188.1	146.0	120	15	104.0	25
Atrazindesisopropyl	4.75	174.0	68.0	110	28	104.1	20
Azoxystrobin	9.09	404.0	372.0	100	10	344.0	23
Benalaxyl	10.52	326.0	148.0	100	20	294.0	5
Bendiocarb	7.4	224.0	109.0	100	15	167.0	5
Benfuracarb	11.24	411.1	190.2	100	5	102.0	25
Bitertanol	10.57	338.0	70.0	80	5	269.0	1
Boscalid	9.36	343.3	307.0	100	15	139.9	20
Bupirimate	10.21	317.2	166.1	150	20	108.0	25
Buprofezin	11.36	306.0	201.0	100	5	116.1	10
Butocarboximsulfoxid	2.9	207.0	132.0	100	5	75.0	10
Butokarboxim Na	6.46	213.0	75.0	100	10	156.0	10
Butoxycarboxim	3.15	223.0	166.0	100	0	106.0	5
Butralin	11.87	296.2	240.4	100	5	222.1	20
Carbaryl	7.76	202.0	145.0	100	5	127.0	25
Carbendazim	5.71	192.1	160.0	100	15	132.0	30
Carbofenothion	11.6	343.0	157.1	80	5	199.1	5
Carbofuran	7.47	222.0	165.0	100	10	123.0	20
Carbofuran3OH	5.51	238.0	163.0	100	10	181.0	5
Carbosulfan	12.33	381.1	160.1	130	10	118.0	20
Carfentrazonethyl	10.25	412.1	346.0	150	20	365.8	15
Chlorbromuron	9.38	295.0	206.0	120	15	125.1	30
CHlorfenvinfos	10.6	359.0	154.9	100	5	98.8	30
Clofentezin	10.67	303.0	138.0	80	10	102.0	40
Clomazon	8.91	240.0	125.0	100	20	89.0	50
Clothianidin	5.11	250.0	169.0	90	5	132.0	15
Coumafos	10.61	363.0	227.1	150	25	307.1	15
Cyanazin	7.15	241.0	214.1	100	15	104.1	30

Pesticide	Rt min	Precursor	Product	DP	CE	Product	CE
Cyazofamid	9.96	325.0	108.0	90	10	261.0	5
Cypermethrin	11.89	433.0	191.0	70	10	193.0	10
Cyproconazole	9.7	292.2	70.0	120	15	125.0	30
Daniphos	10.42	327.0	157.0	90	5	121.2	35
Demeton	8.95	259.1	89.0	70	10	61.0	40
DemetonSmethylsulfon	3.8	263.0	169.0	120	10	125.0	20
DemetonSmethylsulfoxid	3.6	247.0	169.0	90	10	109.0	25
DemetonSmetyl	7.52	230.9	89.0	70	0	61.0	30
Desmetryn	8.42	214.1	172.0	120	15	82.0	35
Dialiphos	10.8	394.0	208.0	100	10	187.0	5
Diazinon	10.52	305.0	169.0	150	20	153.0	20
Dichlorvos	7.3	221.0	108.9	135	12	79.1	24
Dicrotophos	4.7	238.0	112.0	100	5	127.0	15
Dietofencarb	9.2	268.0	225.9	100	5	124.0	35
Difenamide	8.74	240.0	134.0	100	20	167.0	20
Difenoconazole	10.75	406.0	251.0	150	25	337.0	15
Dimethoate	5.48	230.0	125.0	70	20	199.0	5
Dimetomorf	9.5	388.0	165.0	130	30	301.0	20
Disulfoton	10.72	275.1	89.0	60	15	60.9	45
Disulfotonsulfon	8.27	307.0	97.0	100	30	125.0	10
DMF	7.0	150.0	107.2	120	20	106.2	35
DMPF	4.0	163.1	107.1	120	20	122.2	15
DMSA	6.78	201.1.	92.1	100	15	137.1	5
DMST	7.73	215.0.	106.0.	100	10	151.2	5
Epoxiconazole	10.02	330.1	121.1	130	25	100.9	50
Ethion	11.41	385.0	199.0	100	5	143.0	20
Ethofumesate	9.19	287.0	121.0	130	10	259.0	5
Etiofencarb	7.97	226.0	107.0	100	10	77.05	50
EtiofencarbsulfonNH3	4.7	275.0	107.0	80	15	201.0	5
Etiofencarbsulfoxid	5.0	242.2	107.0	80	15	185.0	5
Etofenprox	12.51	394.0	177.0	100	10	359.0	5
Etoprophos	9.97	243.1	130.9	100	15	173.0	10
Etrimphos	10.39	293.1	124.9	100	25	264.9	10
Famoxadon	10.42	392.2	331.0	80	5	238.0	10
Fenamifossulfon	7.75	336.1	266.0	100	15	308.0	10
Fenamiphossulfoxid	7.66	337.2	320.1	80	5	171.1	20
Fenarimol	9.89	331.0	268.2	150	20	81.1	30
Fenazaquin	11.8	307.0	57.0	120	25	161.1	15
Fenbuconazole	9.98	337.0	70.0	150	15	125.0	40
Fenhexamide	9.9	302.0	96.9	100	25	55.0	30
Fenmedifam	8.94	318.1	168.2	100	5	301.1	5
Fenothrin	12.31	351.1	183.1	110	15	333.4	5

Pesticide	Rt min	Precursor	Product	DP	CE	Product	CE
Fenoxycarb	10.07	302.0	88.0	90	15	116.0	5
Fenpiclonil	8.9	254.0	202.0	80	25	140.1	50
Fenpropimorf	11.24	305.0	147.3	150	30	117.2	50
Fenpyroximate	11.78	422.2	366.2	130	10	135.0	30
Fensulfothionoxon	6.6	293.1	236.9	100	15	265.0	10
Fensulfothionoxonsulfon	6.8	309.0	253.0	100	10	174.9	20
Fensulfothionsulfon	8.69	325.1	268.9	100	10	297.0	5
Fenthion	10.42	279 .0	168.9	120	15	247.0	5
Fenthion-oxon	8.93	263.1	231.3	140	10	216.1	20
Fenthion-oxon-sulfone	5.91	295.1	217.2	150	15	78.1	40
Fenthion-oxon-sulfoxide	5.7	279.1	264.2	130	15	104.2	25
Fenthionsulfon	7.99	311.0	125.0	150	20	109.1.	25
Fenthionsulfoxid	7.68	295.0	280.0	140	15	109.0	30
FluazifopPbutyl	11.13	384.0	282.0	120	20	328.0	15
Flucytrinate	11.59	469.2	412.3	120	5	199.4	15
Fludioxonil	9.32	266.0	158.0	90	35	185.1	20
Flumetralin	11.77	422.0	143.0	100	35		
Fluquinkonazole	9.86	376.0	307.1	100	25	349.1	15
Flusilazole	10.05	316.0	247.0	120	15	165.0	25
Fonophos	10.51	247.0	109.1	70	15	137.1	5
Furalaxyl	9.19	302.2	94.9	100	25	242.2	10
Furathiocarb	11.26	383.0	195.0	90	15	252.0	5
Haloxyfop	9.5	362.0	316.2	130	15	288.2	30
Haloxyfop2etoxyethyl	11.12	434.0	91.0	100	40	316.0	15
HaloxyfopRmetyl_	10.82	376.0	316.0	120	15	288.0	25
Heptenophos	8.65	251.0	126.9	100	10	124.9	10
Hexaconazole	10.49	314.0	70.1	130	20	159.1	40
Hexazinon	7.58	253.0	171.1	120	10	71.1	35
Hexythiasox	11.52	353.0	228.0	120	10	168.0	20
Imazalile	9.36	297.0	201.0	140	12	159.0	20
Imidacloprid	5.03	256.1	175.1	100	15	209.0	10
Indoxacarb	10.78	528.0	150.0	120	20	203.0	40
Iprovalicarb	9.81	321.0	119.0	80	15	203.0	5
Isocarbofos	8.56	312.1	270.0	120	10	236.0	10
Isofenfosmetyl	10.35	332.1	231.1	80	5	273.1	5
Isofenphos	10.71	346.1	244.8	70	5	286.8	5
Isoprocarb	8.3	194.0	95.0	100	10	152.0	5
Isopropalin	11.91	310.3	226.1	120	15	206.1	15
Isoproturon	8.54	207.1	72.1	100	20	165.2	10
Isoxaben	9.39	333.1	165.1	100	15	107.0	50
Kresoximmetyl	10.3	314.0	116.0	90	10	267.0	0
Linuron	9.11	248.9	181.9	110	10	160.1	15

Pesticide	Rt min	Precursor	Product	DP	CE	Product	CE
Malathion	9.43	331.0	127.0	110	5	284.8	5
MalathionOanalog	7.64	315.0	99.0	100	20	127.0	5
Mecarbam	9.91	330.0	227.0	90	5	199.0	10
Mepanipyrim	9.78	224.0	77.0	120	45	106.0	25
Mephosfolan	7.38	270.0	139.9	100	20	196.0	10
Metabenztiazuron	8.42	222.0	165.0	90	10	150.0	35
Metaflumizone	11.23	507.2	178.2	140	24	116.2	50
Metalaxyl	8.65	280.1	220.0	100	10	191.9	15
Metamidophos	2.15	142.0	94.0	100	10	125.0	10
Metconazole	10.3	320.2	70.1	140	25	43.2	50
Methomyl	3.41	163.1	88.1	70	4	106.0	4
Methoxyfenozide	9.62	369.3	149.1	90	10	313.3	0
Metidathion	8.8	303.0	145.0	100	0	85.0	15
Metiocarb	9.2	226.0	121.0	100	15	169.0	5
Metiocarbsulfon	5.91	258.1	122.2	130	15	201.2	0
Metiokarbsulfoxid	5.45	242.0	185.2	100	5	122.2	30
Monocrotophos	4.0	224.0	127.0	100	10	193.0	0
Myclobutanil	9.62	289.0	70.0	120	15	125.0	40
Napropamid	9.89	272.0	129.0	100	10	171.0	15
Omethoate	2.87	214.0	125.0	90	16	183.0	4
Oxamyl	3.29	237.0	72.0	80	10	90.0	5
Oxamyloxim	2.89	163.1	72.1	80	5	90.0	15
Oxydisulfoton	8.24	291.0	185.0	70	5	157.0	20
Paclobutrazole	9.51	294.2	70.1	130	15	125.1	40
Paraoxon	8.35	276.0	220.0	110	10	174.0	20
Paraoxonmethyl	6.85	248.0	202.0	120	15	90.0	25
Penconazole	10.36	284.0	70.1	120	15	159.0	30
Pencycuron	10.72	329.2	125.0	140	25	218.0	15
Phorate	10.59	261.1	75.1	50	5	46.9	45
PhorateOanalogue	8.92	245.1	75.0	70	5	47.0	35
Phoratesulfon	8.3	293.0	171.0	100	5	247.0	0
Phoratesulfoxid	8.24	277.0	143.0	80	15	199.0	5
Phosfamidon	7.06	300.0	127.0	130	15	174.0	10
Phoxim	10.5	299.1	77.1	110	35	129.2	5
Piperonylbutoxid	11.37	356.2	149.0	100	35	147.0	30
Pirimicarb	8.2	239.1	72.1	110	20	182.1	10
Pirimicarb desmethyl	6.7	225.2	72.1	100	20	168.2	10
Prochloraz	10.66	376.0	308.0	100	5	266.0	10
Promecarb	9.33	208.0	109.0	100	10	151.0	5
Propamocarb	3.0	189.0	101.9	110	15	73.9	25
Propaquizafop	11.27	444.1	100.0	100	15	370.9	10
Propetamphos	9.57	282.1	138.1	100	10	156.0	5

Pesticide	Rt min	Precursor	Product	DP	CE	Product	CE
Propiconazole	10.51	342.1	159.2	140	25	69.0	20
Propoxur	7.46	210.0	111.0	80	10	168.0	5
Prosulfocarb	11.1	252.0	91.1	100	25	128.1	5
Prothioconazoledesthio	10.1	312.1	125.2	140	40	89.1	76
Pymetrozine	3.8	218.0	105.0	120	20	78.12	48
Pyraclostrobin	10.6	388.0	194.1	100	5	163.0	20
Pyrazophos	10.67	374.0	222.0	100	20	194.0	35
Pyridafenthion	9.58	341.1	189.1	100	20	205.0	20
Pyrifenox	9.9	295.1	93.2	130	20	263.2	15
Pyriproxifen	11.46	322.1	95.9	100	10	227.0	10
Quinoxyfen	11.52	308.0	197.0	120	35	272.0	30
QuisalofopEtyl	11.14	373.1	299.0	120	15	271.0	25
Simazin	7.47	202.1	124.0	100	15	131.9	15
SpinosynA	11.02	732.4	142.0	150	30	98.0	50
SpinosynD	11.34	746.0	142.0	140	30	98.0	55
Spiroxamin	9.35	298.0	144.0	130	20	100.0	30
Sulfentrazon	7.77	386.9	306.9	150	20	308.9	20
Taufluvalinate	12.13	503.1	208.1	100	5	181.1	20
Tebuconazole	10.39	308.2	70.1	140	20	124.9	35
Tebufenozide	10.16	353.0	133.0	90	15	297.0	0
Tebufenpyrad	11.28	334.0	145.0	130	25	117.0	40
TEPP	7.05	291.0	178.9	100	15	235.0	5
Tepraloxydim	9.56	342.1	250.1	100	5	166.1	15
Terbuphos	11.3	289.1	57.1	70	20	103.1	5
Terbuphosoxon	9.95	273.1	57.1	80	15	103.1	5
Terbuphosoxonsulfon	7.21	305.1	203.1	130	10	99.1	20
Terbuphosoxonsulfoxid	6.9	289.0	171.1	90	5	115.1	25
Terbuphossulfon	9.06	321.0	171.0	100	5	114.9	25
Terbuphossulfoxid	9.15	305.0	187.0	80	5	131.0	25
Terbuthylazine	9.42	230.2	174.0	120	15	68.0	40
Terbutryn	10.0	242.0	186.0	120	15	91.0	25
Tetrachlorvinphos	10.25	364.9	127.1	130	10	239.0	15
Tetraconazole	9.88	372.0	159.1	100	25	70.2	20
Thiabendazole	6.63	202.0	175.0	100	24	131.0	35
Thiachloprid	6.18	253.0	126.0	90	20	99.0	50
Thiametoxam	4.0	292.0	211.0	90	10	210.1	5
Thiodicarb	8.18	355.0	88.0	90	10	108.0	10
Thiofanatmethyl	7.47	343.1	151.1	100	15	311.2	5
Thiometon	8.33	247.0	89.1	60	5	61.0	40
Thiometonsulfon	6.93	279.0	143.1	120	5	125.1	15
Thiometonsulfoxid	6.75	263.0	157.1	80	10	185.1	5
Triadimefon	9.62	294.0	197.0	80	10	225.2	5

Pesticide	Rt min	Precursor	Product	DP	CE	Product	CE
Triadimenol	9.74	296.0	70.0	80	10	43.0	35
Triamiphos	8.57	295.2	135.2	130	20	92.1	45
Triazamate	9.97	315.1	72.1	90	20	226.3	5
Trichlorfon	5.4	257.0	109.2	120	15	221.0	10
Trifloxystrobin	10.85	409.2	186.0	100	15	206.1	10
Triflumeron	10.65	359.0	156.1	100	10	139.1	40
Trimethacarb -2,3,5	8.58	194.0	137.0	100	5	122.0	25
Trimethacarb- 3,4,5	8.58	194.1	137.0	100	5	122.0	25
Trithiconazole	9.97	318.2	70.1	110	15	125.2	40
Vamidothion	5.5	288.2	146.1	90	5	118.0	20
Vamidothionsulfon	4.0	320.1	178.1	130	10	169.0	15
Vamidothionsulfoxid	3.7	304.0	169.1	90	10	201.1	5
Zoxamide	10.58	336.1	187.1	120	20	159.1	45

Mass transitions LC-MSMS (ES^-)

Pesticide	Rt min	Precursor	Product	DP	CE	Product	CE
Bentazon	2.01	239.1	197.1	140	15	175.2	15
Diflubensuron	5.40	309.1	289.0	100	0	156.1	0
Dinocap	5.40	295.1	209.2	150	25	193.1	25
Dinoseb	3.80	239.1	193.1	140	20	194.1	15
Dinoterb	4.10	239.1	207.0	150	20	177.0	30
DNOC	2.30	197.1	180.1	120	15	137.0	15
Flufenoxuron	6.73	487.1	156.2	140	10	304.2	15
Hexaflumuron	5.94	460.1	440.2	90	5	276.2	15
Chlorfluasuron	7.03	538.0	518.1	110	5	355.0	20
Lufenuron	6.38	509.0	339.1	110	5	326.1	15
Teflubensuron	6.44	379.1	339.0	90	5	359.1	5

19. Appendix 2. Mass transitions of GC-MSMS

Pesticide	R t min	m/z quant	Selected transitions and collision energies (V)
Aclonifen	17.73	193.8	212.0>182.0 [-10.0V] + 264.0>194.0 [-14.0V]
Acrinathrin 2	21.20	152.0	181.0>152.0 [-18.0V] + 208.0>181.0 [-10.0V]
Acrinatrin 2	21.47	152.0	181.0>152.0 [-18.0V] + 208.0>181.0 [-10.0V]
Aldrin	12.05	193.0	263.0>193.0 [-30.0V] + 292.9>257.9 [-20.0V]
Azinphos-ethyl	21.95	77.0	132.0>77.0 [-12.0V] + 160.0>132.0 [-4.0V]
Azinphos-methyl	20.86	77.0	132.0>77.0 [-12.0V] + 160.0>132.0 [-4.0V]
Beta-cyfluthrin 1	24.45	91.0	163.0>91.0 [-11.0V] + 163.0>127.0 [-5.0V] + 226.0>206.0 [-12.0V]
Beta-cyfluthrin 2	24.66	91.0	163.0>91.0 [-11.0V] + 163.0>127.0 [-5.0V] + 226.0>206.0 [-12.0V]
Beta-cyfluthrin 3	24.66	91.0	163.0>91.0 [-11.0V] + 163.0>127.0 [-5.0V] + 226.0>206.0 [-12.0V]
Beta-cyfluthrin 4	24.86	91.0	163.0>91.0 [-11.0V] + 163.0>127.0 [-5.0V] + 226.0>206.0 [-12.0V]
Bifenthrin	19.31	165.0	165.0>115.0 [-31.0V] + 181.0>165.0 [-12.0V]
Binapacryl	15.54	55.0	83.0>55.0 [-9.0V] + 83.0>83.0 [-1.0V]
Biphenyl	5.30	153.1	154.0>128.0 [-20.0V] + 154.0>153.0 [-7.0V]
Bromophos	12.54	316.0	329.0>314.0 [-16.0V] + 331.0>316.0 [-16.0V]
Bromophos-ethyl	13.80	303.0	358.9>330.8 [-10.0V] + 359.0>303.0 [-20.0V]
Bromopropylate	19.48	157.0	185.0>157.0 [-12.0V] + 341.0>185.0 [-14.0V]
Bromuconazole I	19.34	145.0	173.0>145.0 [-14.0V] + 295.0>173.0 [-10.0V]
Bromuconazole II	20.14	145.0	173.0>145.0 [-14.0V] + 295.0>173.0 [-10.0V]
Cadusaphos	7.89	96.9	159.0>97.0 [-15.0V] + 159.0>131.0 [-10.0V]
Captafol	19.92	77.0	79.0>51.0 [-25.0V] + 79.0>77.0 [-15.0V]
Captan	13.57	105.0	149.0>105.0 [-8.0V] + 149.0>70.0 [-15.0V] + 149.0>79.0 [-16.0V]
Chlorbensilate	16.12	139.0	251.0>139.0 [-13.0V] + 253.0>141.0 [-15.0V]
Chlordan-alpha	14.41	237.0	272.0>237.0 [-14.0V] + 373.0>266.0 [-20.0V]
Chlordan-gamma	13.99	266.0	272.0>237.0 [-14.0V] + 373.0>266.0 [-20.0V]
Chlordimeform	7.66	117.0	152.0>117.0 [-11.0V] + 196.0>181.0 [-8.0V]
Chlorfenapyr	15.57	31.0	59.0>31.0 [-6.0V] + 247.0>227.0 [-10.0V]
Chlorfenson	14.76	111.0	175.0>111.0 [-12.0V] + 302.0>175.0 [-10.0V]
Chlormefos	5.61	121.0	154.0>121.0 [-7.0V] + 234.0>121.0 [-14.0V]
Chlorprofam	7.59	65.0	127.0>65.0 [-19.0V] + 171.0>127.0 [-8.0V]
Chlorpropylate	16.12	139.0	251.0>139.0 [-13.0V] + 253.0>141.0 [-15.0V]
Chlorpyriphos	11.81	258.0	314.0>194.0 [-29.0V] + 314.0>258.0 [-14.0V]
Chlorpyriphos-methyl	10.49	93.0	125.0>79.0 [-6.0V] + 286.0>93.0 [-23.0V]
Chlorpyriphos-O-analogue	11.62	123.0	224.0>123.0 [-12.0V] + 298.0>242.0 [-15.0V]

Pesticide	R t min	m/z quant	Selected transitions and collision energies (V)
Chlortaldimetyl	12.00	221.0	299.0>221.0 [-25.0V] + 301.0>223.0 [-25.0V]
Chlorthalonil	9.55	231.0	264.0>229.0 [-15.0V] + 266.0>231.0 [-17.0V]
Chlozolinate	13.51	145.0	186.0>145.0 [-17.0V] + 259.0>188.0 [-15.0V]
Cyanofenphos	17.45	141.0	169.0>141.0 [-9.0V] + 185.0>157.0 [-10.0V]
Cyanophos	9.08	109.0	109.0>79.0 [-9.0V] + 243.0>109.0 [-15.0V]
Cyfluthrin 1	23.82	91.0	163.0>91.0 [-11.0V] + 163.0>127.0 [-5.0V]
Cyfluthrin 2	24.02	91.0	163.0>91.0 [-11.0V] + 163.0>127.0 [-5.0V]
Cyfluthrin 3	24.13	91.0	163.0>91.0 [-11.0V] + 163.0>127.0 [-5.0V]
Cyfluthrin 4	24.22	91.0	163.0>91.0 [-11.0V] + 163.0>127.0 [-5.0V]
Cyprodinil	12.92	208.0	224.0>197.0 [-21.0V] + 224.0>208.0 [-18.0V]
DEET	6.78	91.0	190.0>91.0 [-30.0V] + 191.0>190.0 [-5.0V]
Deltamethrin 1	27.92	152.0	181.0>152.0 [-17.0V] + 253.0>174.0 [-8.0V]
Deltamethrin 2	28.50	152.0	181.0>152.0 [-17.0V] + 253.0>174.0 [-8.0V]
Dichlofluanid	11.63	123.0	224.0>123.0 [-12.0V]
Dichloran	8.61	176.0	206.0>124.0 [-25.0V] + 206.0>176.0 [-15.0V]
Dichloranilin-3.5	5.45	99.0	161.0>90.0 [-21.0V] + 161.0>99.0 [-22.0V]
Dichlorbenzofenon-o.p	11.44	111.0	139.0>111.0 [-12.0V] + 251.0>139.0 [-16.0V]
Diclobenil	5.03	136.0	171.0>100.0 [-26.0V] + 171.0>136.0 [-14.0V]
Diclobenzofenon-p.p	12.39	111.0	139.0>111.0 [-11.0V] + 251.0>139.0 [-16.0V]
Dicofol-o.p	19.47	139.0	139.0>111.0 [-10.0V] + 251.0>111.0 [-30.0V] + 251.0>139.0 [-16.0V]
Dieldrin	15.32	193.0	263.0>193.0 [-35.0V] + 279.0>243.0 [-10.0V]
Dinobuton	13.21	117.0	211.0>163.0 [-8.0V] + 211.1>117.0 [-18.0V]
Dioxathion 2	23.11	97.0	125.0>97.0 [-5.0V] + 270.0>97.0 [-30.0V]
Dioxathion I	8.95	97.0	125.0>97.0 [-5.0V] + 197.0>141.0 [-15.0V]
Diphenylamine	7.39	167.0	168.0>140.0 [-29.0V] + 168.0>167.0 [-20.0V]
Endosulfan-alpha	14.43	206.0	195.0>159.0 [-8.0V] + 241.0>206.0 [-20.0V]
Endosulfan-beta	16.42	206.0	195.0>159.0 [-8.0V] + 241.0>206.0 [-20.0V] + 277.0>241.0 [-10.0V]
Endosulfan-sulfate	17.71	237.0	272.0>237.0 [-14.0V] + 274.0>239.0 [-11.0V]
Endrin	16.43	243.0	263.0>193.0 [-35.0V] + 279.0>243.0 [-10.0V]
EPN	19.48	141.0	157.0>110.0 [-14.0V] + 169.0>141.0 [-9.0V]
Esfenvalerate 1	26.42	89.0	125.0>89.0 [-16.0V] + 225.0>119.0 [-17.0V]
Esfenvalerate 2	26.95	89.0	125.0>89.0 [-16.0V] + 225.0>119.0 [-17.0V]
Fenamiphos	14.49	195.0	303.0>195.0 [-9.0V] + 303.1>288.1 [-15.0V]
Fenitrothion	11.38	109.0	125.0>79.0 [-10.0V] + 277.0>109.0 [-17.0V]
Fenchlorphos	10.97	270.0	285.0>270.0 [-14.0V] + 286.9>271.9 [-20.0V]
Fenpropathrin	19.71	152.0	181.0>127.0 [-20.0V] + 181.0>152.0 [-18.0V]
Fenson	12.60	77.0	141.0>77.0 [-10.0V] + 268.0>141.0 [-10.0V]

Pesticide	R t min	m/z quant	Selected transitions and collision energies (V)
Fensulfothion	16.40	97.0	293.0>97.0 [-22.0V] + 293.0>125.0 [-15.0V]
Fenthoate	13.33	125.0	246.0>121.0 [-10.0V] + 274.0>125.0 [-15.0V]
Fenvalerate 2	26.95	89.0	125.0>89.0 [-16.0V] + 225.0>119.0 [-17.0V]
Fenvalerate 1	26.42	89.0	125.0>89.0 [-16.0V] + 225.0>119.0 [-17.0V]
Fluacrypyrim	16.60	189.0	426.0>189.0 [-18.0V] + 426.0>204.0 [-5.0V]
Fluazinam	12.65	372.0	418.0>372.0 [-20.0V] + 420.0>339.0 [-18.0V]
Flutriafol	14.52	123.0	123.0>75.0 [-15.0V] + 219.1>123.0 [-15.0V]
Folpet	13.77	130.0	260.0>130.0 [-14.0V] + 262.0>130.0 [-9.0V]
Formothion	10.09	93.0	125.0>79.0 [-6.0V] + 170.0>93.0 [-10.0V]
Ftalimid	5.95	76.0	147.0>76.0 [-25.0V] + 147.0>103.0 [-25.0V]
HCH-alpha	8.29	145.0	181.0>145.0 [-11.0V] + 218.9>182.9 [-9.0V]
HCH-beta	9.10	145.0	181.0>145.0 [-11.0V] + 218.9>182.9 [-9.0V]
HCH-delta	9.84	145.0	181.0>145.0 [-11.0V] + 218.9>182.9 [-9.0V]
HCH-gamma	9.09	183.0	181.0>145.0 [-11.0V] + 218.9>182.9 [-9.0V]
Heptachlorepoxide	13.38	119.0	183.1>119.0 [-25.0V] + 352.8>252.9 [-15.0V]
Heptachlor	10.98	237.0	272.0>237.0 [-14.0V] + 336.8>301.9 [-12.0V]
Hexachlorbensen	8.41	249.0	284.0>249.0 [-16.0V] + 285.8>250.8 [-20.0V]
Iodofenphos	14.71	362.0	377.0>362.0 [-19.0V] + 387.9>363.9 [-16.0V]
Iprodione	19.15	245.0	314.0>245.0 [-11.0V] + 314.0>271.0 [-12.0V]
Chinomethionate	14.13	148.0	206.0>148.0 [-14.0V] + 234.1>206.1 [-10.0V]
Lambda-cyhalothrin	21.20	152.0	181.0>152.0 [-18.0V] + 197.0>141.0 [-12.0V]
Leptophos	20.69	362.0	374.9>360.0 [-26.0V] + 377.0>362.0 [-20.0V]
Methoxychlor	19.70	115.0	227.0>115.0 [-50.0V] + 227.0>184.1 [-20.0V]
Metribuzin	10.53	82.0	198.0>82.0 [-15.0V] + 198.0>110.0 [-10.0V]
Mevinphos	5.42	127.0	127.0>95.0 [-13.0V] + 192.0>127.0 [-9.0V]
Nitrofen	15.94	162.0	283.0>253.0 [-15.0V] + 283.0>162.0 [-22.0V]
Ortofenylphenol	6.40	141.0	170.0>115.0 [-30.0V] + 170.0>141.0 [-20.0V]
Oxadixyl	16.49	132.0	163.0>132.0 [-8.0V] + 233.0>146.0 [-11.0V]
Parathion	12.07	109.0	235.0>139.0 [-6.0V] + 291.0>109.0 [-13.0V]
Parathion-methyl	10.69	109.0	246.0>106.0 [-20.0V] + 263.0>109.0 [-12.0V]
Pendimethanil	12.85	162.0	252.0>162.0 [-13.0V] + 252.0>191.0 [-9.0V]
Pentachloraniline	10.28	192.0	263.0>192.0 [-22.0V] + 263.0>227.0 [-12.0V]
Pentachloranisole	8.49	237.0	265.0>237.0 [-12.0V] + 279.9>236.9 [-20.0V]
Pentachlorbensen	6.42	212.9	247.8>212.9 [-20.0V] + 250.0>215.0 [-17.0V]
Permethrin 1	22.78	153.0	183.0>153.0 [-8.0V] + 183.0>168.0 [-8.0V]
Permethrin 2	23.03	153.0	183.0>153.0 [-8.0V] + 183.0>168.0 [-8.0V]
Phosalone	20.65	111.0	182.0>111.0 [-15.0V] + 367.0>182.0 [-6.0V]

Pesticide	R t min	m/z quant	Selected transitions and collision energies (V)
Phosmet	19.43	133.0	160.0>77.0 [-21.0V] + 160.0>133.0 [-9.0V]
Phosmet-O-analogue	17.78	77.0	160.0>77.0 [-21.0V] + 160.0>133.0 [-9.0V]
Phosthiazate I	12.60	103.0	195.0>103.0 [-8.0V] + 195.0>139.0 [-6.0V]
Phosthiazate II	12.68	103.0	195.0>103.0 [-8.0V] + 195.0>139.0 [-6.0V]
Pirimiphos-ethyl	12.37	166.0	318.0>166.0 [-13.0V] + 333.1>168.1 [-20.0V]
Pirimiphos-methyl	11.20	125.0	290.0>125.0 [-22.0V] + 290.0>151.0 [-18.0V]
pp-DDD	16.52	165.0	235.0>165.0 [-23.0V] + 237.0>165.0 [-20.0V]
pp-DDD/op-DDT	16.52	165.0	235.0>165.0 [-23.0V] + 237.0>165.0 [-20.0V]
pp-DDE	15.08	176.0	246.0>176.0 [-28.0V] + 317.9>245.9 [-20.0V]
pp-DDT	17.79	165.0	235.0>165.0 [-23.0V]
pp-Dicofol	19.88	111.0	139.0>111.0 [-10.0V] + 251.0>111.0 [-30.0V] + 251.0>139.0 [-16.0V]
Procymidone	13.51	96.0	283.0>96.0 [-9.0V] + 285.0>96.0 [-9.0V]
Profam	5.73	93.0	137.0>93.0 [-10.0V] + 179.0>137.0 [-8.0V]
Profenophos	14.91	267.0	139.2>97.0 [-10.0V] + 337.0>267.0 [-15.0V]
Propargite 1	18.22	107.0	135.0>107.0 [-11.0V] + 173.0>105.0 [-15.0V]
Propargite 2	18.28	107.0	135.0>107.0 [-11.0V] + 173.0>105.0 [-15.0V]
Propyzamide	9.11	145.0	173.0>145.0 [-10.0V] + 175.0>147.0 [-14.0V]
Prothiophos	14.75	239.0	267.0>221.0 [-20.0V] + 309.0>239.0 [-12.0V]
Pyrachlofos	22.18	138.0	138.0>111.0 [-15.0V] + 194.0>138.0 [-15.0V]
Pyridaben	23.09	119.1	147.0>119.0 [-9.0V] + 147.0>132.0 [-10.0V]
Pyrimethanil	9.35	198.0	198.0>118.0 [-29.0V] + 199.0>198.0 [-9.0V]
Quinalphos	13.38	118.0	146.0>118.0 [-8.0V] + 298,1>156,0 [-10.0V]
Quintozene	8.97	237.0	295.0>237.0 [-16.0V] + 237.0>119.0 [-10.0]
Sulfotep	7.67	146.0	238.0>146.0 [-15.0V] + 322.0>97.0 [-35.0V]
TCNB-2,3,4,5	7.78	178.9	215.0>179.0 [-12.0V] + 260.9>202.9 [-15.0V]
Tecnazene	7.07	179.0	203.0>143.0 [-21.0V] + 215.0>179.0 [-12.0V]
Tefluthrin	9.33	127.0	177.0>127.0 [-16.0V] + 197.0>141.0 [-10.0V]
Tetrachloraniline (2,3,5,6-TCA)	7.47	158.0	229.0>158.0 [-21.0V] + 230.9>159.9 [-15.0V]
Tetradifon	20.50	199.0	227.0>199.0 356.0 [-13.0V] >159.0 [-10.0V]
Tetrahydroftalimid	6.13	79.1	151.0>79.0 [-12.0V] + 151.0>122.0 [-5.0V]
Tetrasul	17.00	182.0	252.0>182.0 [-35.0V] + 253.9>218.9 [-20.0V]
Thionazin	7.03	106.1	107.0>106.0 [-10.0V] + 143.0>79.0 [-10.0V]
Tolclofos-methyl	10.71	93.0	265.0>93.0 [-24.0V] + 267.0>252.0 [-13.0V]
Tolylfluanid	13.16	137.0	137.0>91.0 [-15.0V] + 238.0>137.0 [-12.0V]
Triazophos	17.00	77.0	161.0>77.0 [-21.0V]] + 161.0>134.0 [-5.0V]
Tribromanisole	7.40	301.0	327.0>299.0 [-11.0V] + 329.0>301.0 [-11.0V]
Trichloronate	12.35	269.0	297.0>269.0 [-14.0V] + 298.9>270.9 [-12.0V]

Pesticide	R t min	m/z quant	Selected transitions and collision energies (V)
Trichlorphenol	5.10	132.0	196.0>132.0 [-15.0V] + 198.0>134.0 [-15.0V]
Triflumizole	13.49	179.0	179.0>144.0 [-15.0V] + 206.0>179.0 [-14.0V]
Vinclozolin	10.56	124.0	187.0>124.0 [-19.0V] + 198.0>145.0 [-16.0V]

20. Appendix 3 . Limit of Quantification (LOQ) and detection technique

Pesticide	Detection	LOQ (mg/kg)
Abamectin	LC-MSMS	0.05
Acephate	LC-MSMS	0.01
Acetamiprid	LC-MSMS	0.01
Acibenzolar-S-methyl	LC-MSMS	0.01
Aclonifen	GC-MSMS	0.01
Acrinathrin	GC-MSMS	0.01
Aldicarb	LC-MSMS	0.01
Aldicarb-sulfone	LC-MSMS	0.01
Aldicarb-sulfoxid	LC-MSMS	0.01
Aminocarb	LC-MSMS	0.01
Amitraz	LC-MSMS	0.01
Aspon	LC-MSMS	0.01
Atrazine	LC-MSMS	0.01
Atrazine-desethyl	LC-MSMS	0.01
Atrazine-desisopropyl	LC-MSMS	0.01
Azinphos-ethyl	GC-MSMS	0.01
Azinphos-methyl	GC-MSMS	0.01
Azoxystrobin	LC-MSMS	0.01
Benalaxyl	LC-MSMS	0.01
Bendiocarb	LC-MSMS	0.01
Benfuracarb	LC-MSMS	0.01
Bentazone	LC-MSMS(-)	0.01
Bifenthrin	GC-MSMS	0.01
Binapacryl	GC-MSMS	0.05
Biphenyl	GC-MSMS	0.01
Bitertanol	LC-MSMS	0.01
Boscalid	LC-MSMS	0.01
Bromophos	GC-MSMS	0.01
Bromophos-ethyl	GC-MSMS	0.01
Bromopropylate	GC-MSMS	0.01
Bromuconazole I	GC-MSMS	0.01
Bromuconazole II	GC-MSMS	0.01
Bupirimate	LC-MSMS	0.01
Buprofezin	LC-MSMS	0.01
Butocarboxim	LC-MSMS	0.01
Butocarboxim-sulfoxid	LC-MSMS	0.01
Butoxycarboxim	LC-MSMS	0.01
Butralin	LC-MSMS	0.01
Cadusafos	GC-MSMS	0.01
Captafol	GC-MSMS/GC-ECD	0.05
Captan	GC-MSMS/GC-ECD	0.05
Carbaryl	LC-MSMS	0.01
Carbendazim	LC-MSMS	0.01

Pesticide	Detection	LOQ (mg/kg)
Carbofuran	LC-MSMS	0.01
Carbofuran-3OH	LC-MSMS	0.01
Carbophenothion	LC-MSMS	0.01
Carbosulfan	LC-MSMS	0.01
Carfentrazone-ethyl	LC-MSMS	0.01
Chinomethionat	GC-MSMS	0.01
Chlordane, cis-	GC-MSMS	0.01
Chlordane, trans-	GC-MSMS	0.01
Chlordimeform	GC-MSMS	0.01
Chlorfenapyr	GC-MSMS	0.01
Chlorfenson	GC-MSMS	0.01
Chlorfenvinphos	LC-MSMS	0.01
Chlorfluazuron	LC-MSMS(-)	0.01
Chlormephos	GC-MSMS	0.01
Chlorobenzilate	GC-MSMS	0.01
Chlorobromuron	LC-MSMS	0.01
Chloropropylate	GC-MSMS	0.01
Chlorothalonil	GC-MSMS	0.01
Chlorpropham	GC-MSMS	0.01
Chlorpyrifos	GC-MSMS	0.01
Chlorpyrifos-methyl	GC-MSMS	0.01
Chlorpyrifos-O-Analogue	GC-MSMS	0.01
Chlorthal-dimethyl	GC-MSMS	0.01
Chlozolinate	GC-MSMS	0.01
Clofentezine	LC-MSMS	0.01
Clomazone	LC-MSMS	0.01
Clothianidin	LC-MSMS	0.01
Coumaphos	LC-MSMS	0.01
Cyanazin	LC-MSMS	0.01
Cyanofenfos	GC-MSMS	0.01
Cyanofos	GC-MSMS	0.01
Cyazofamid	LC-MSMS	0.01
Cyfluthrin (sum)	GC-MSMS	0.01
Cyfluthrin, beta- (sum)	GC-MSMS	0.01
Cypermethrin	LC-MSMS	0.01
Cyproconazole	LC-MSMS	0.01
Cyprodinil	GC-MSMS	0.01
Danifos	LC-MSMS	0.01
DDD, p,p-/DDT, o,p-	GC-MSMS/GC-ECD	0.01
DDE, p,p-	GC-MSMS/GC-ECD	0.01
DDT, p,p-	GC-MSMS/GC-ECD	0.01
DEET	GC-MSMS	0.01
Deltamethrin 1	GC-MSMS	0.01
Deltamethrin 2	GC-MSMS	0.01
Demeton	LC-MSMS	0.01
Demeton-S-methyl	LC-MSMS	0.01
Demeton-S-methyl-sulfone	LC-MSMS	0.01

Pesticide	Detection	LOQ (mg/kg)
Demeton-S-methyl-sulfoxid	LC-MSMS	0.01
Desmethyl pirimicarb	LC-MSMS	0.01
Desmetryn	LC-MSMS	0.01
Dialifos	LC-MSMS	0.01
Diazinon	LC-MSMS	0.01
Dichlobenil	GC-MSMS	0.01
Dichlofluanid	GC-MSMS	0.01
Dichloroaniline, 3,5-	GC-MSMS	0.01
Dichlorobenzophenone, 2,4`-	GC-MSMS	0.01
Dichlorobenzophenone, 4,4`-	GC-MSMS	0.01
Dichlorvos	LC-MSMS	0.01
Dicloran	GC-MSMS	0.01
Dicofol	GC-MSMS/GC-ECD	0.05
Dicrotophos	LC-MSMS	0.01
Dieldrin	GC-MSMS	0.01
Diethofencarb	LC-MSMS	0.01
Difenoconazole	LC-MSMS	0.01
Diflubenzuron	LC-MSMS(-)	0.01
Dimethoate	LC-MSMS	0.01
Dimethomorph	LC-MSMS	0.01
Dinobuton	GC-MSMS	0.01
Dinocap	LC-MSMS(-)	0.01
Dinoseb	LC-MSMS(-)	0.01
Dinoterb	LC-MSMS(-)	0.01
Dioxathion 1	GC-MSMS	0.01
Dioxathion 2	GC-MSMS	0.01
Diphenamid	LC-MSMS	0.01
Diphenylamine	GC-MSMS	0.01
Disulfoton	LC-MSMS	0.01
Disulfoton-Sulfon	LC-MSMS	0.01
Disulfoton-sulfoxid	LC-MSMS	0.01
DMF	LC-MSMS	0.01
DMPF	LC-MSMS	0.01
DMSA	LC-MSMS	0.01
DMST	LC-MSMS	0.01
DNOC	LC-MSMS(-)	0.01
Endosulfan, alpha-	GC-MSMS	0.01
Endosulfan, beta-	GC-MSMS	0.01
Endosulfansulfate	GC-MSMS	0.01
Endrin	GC-MSMS	0.01
EPN	GC-MSMS	0.01
Epoxiconazole	LC-MSMS	0.01
Esfenvalerate	GC-MSMS	0.01
Ethiofencarb	LC-MSMS	0.01
Ethiofencarb-sulfone NH3-add	LC-MSMS	0.01
Ethiofencarb-sulfoxid	LC-MSMS	0.01
Ethion	LC-MSMS	0.01

Pesticide	Detection	LOQ (mg/kg)
Ethofumesate	LC-MSMS	0.01
Ethoprophos	LC-MSMS	0.01
Etofenprox	LC-MSMS	0.01
Etrimfos	LC-MSMS	0.01
Famoxadone	LC-MSMS	0.01
Fenamiphos	GC-MSMS	0.01
Fenamiphos-Sulfon	LC-MSMS	0.01
Fenamiphos-Sulfoxid	LC-MSMS	0.01
Fenarimol	LC-MSMS	0.01
Fenazaquin	LC-MSMS	0.01
Fenbuconazole	LC-MSMS	0.01
Fenchlorphos	GC-MSMS	0.01
Fenhexamid	LC-MSMS	0.01
Fenitrothion	GC-MSMS	0.01
Fenoxycarb	LC-MSMS	0.01
Fenpiclonil	LC-MSMS	0.01
Fenpropathrin	GC-MSMS	0.01
Fenpropimorph	LC-MSMS	0.01
Fenpyroximate	LC-MSMS	0.01
Fenson	GC-MSMS	0.01
Fensulfothion	GC-MSMS	0.01
Fensulfothion-oxon	LC-MSMS	0.01
Fensulfothion-oxon-sulfone	LC-MSMS	0.01
Fensulfothion-sulfone	LC-MSMS	0.01
Fenthion	LC-MSMS	0.01
Fenthion-oxon	LC-MSMS	0.01
Fenthion-oxon-sulfone	LC-MSMS	0.01
Fenthion-oxon-sulfoxide	LC-MSMS	0.01
Fenthion-sulfon	LC-MSMS	0.01
Fenthion-sulfoxid	LC-MSMS	0.01
Fenvalerate 1	GC-MSMS	0.01
Fenvalerate 2	GC-MSMS	0.01
Fipronil	GC-MSMS	0.01
Fluacrypyrim	GC-MSMS	0.01
Fluazifop-P-butyl	LC-MSMS	0.01
Fluazinam	GC-MSMS	0.01
Flucythrinate	LC-MSMS	0.01
Fludioxinil	LC-MSMS(-)	0.01
Fludioxonil	LC-MSMS	0.01
Flufenoxuron	LC-MSMS(-)	0.01
Flumetralin	LC-MSMS	0.01
Fluquinconazole	LC-MSMS	0.01
Flusilazole	LC-MSMS	0.01
Flutriafol	GC-MSMS	0.01
Folpet	GC-MSMS/GC-ECD	0.05
Fonofos	LC-MSMS	0.01
Formothion	GC-MSMS	0.01

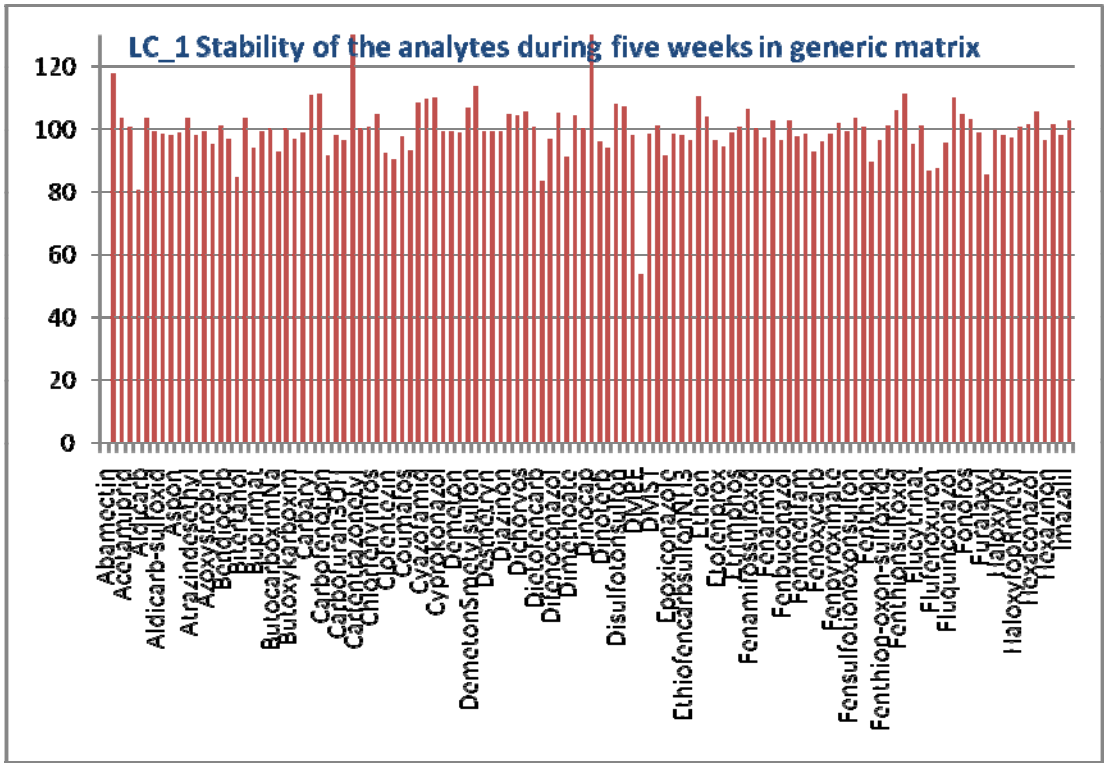
Pesticide	Detection	LOQ (mg/kg)
Fosthiazate 1+2	GC-MSMS	0.01
Ftalimid	GC-MSMS	0.01
Furalaxyl	LC-MSMS	0.01
Furathiocarb	LC-MSMS	0.01
Haloxyfop	LC-MSMS	0.01
Haloxyfop-Ethoxyethylester	LC-MSMS	0.01
Haloxyfop-Methyl	LC-MSMS	0.01
HCH, alpha-	GC-MSMS	0.01
HCH, beta-	GC-MSMS	0.01
HCH, delta-	GC-MSMS	0.01
HCH, gamma-	GC-MSMS	0.01
Heptachlor	GC-MSMS	0.01
Heptachlor epoxide	GC-MSMS	0.01
Heptenophos	LC-MSMS	0.01
Hexachlorobenzene	GC-MSMS	0.01
Hexaconazole	LC-MSMS	0.01
Hexaflumuron	LC-MSMS(-)	0.01
Hexazinone	LC-MSMS	0.01
Hexythiazox	LC-MSMS	0.01
Imazalil	LC-MSMS	0.01
Imidacloprid	LC-MSMS	0.01
Indoxacarb	LC-MSMS	0.01
Iprodione	GC-MSMS	0.01
Iprovalicarb	LC-MSMS	0.01
Isofenphos	LC-MSMS	0.01
Isofenphos-methyl	LC-MSMS	0.01
Isoprocarb	LC-MSMS	0.01
Isopropalin	LC-MSMS	0.01
Isoproturon	LC-MSMS	0.01
Isoxaben	LC-MSMS	0.01
Jodfenphos	GC-MSMS	0.01
Kresoxim-methyl	LC-MSMS	0.01
Kvinoxyfen	LC-MSMS	0.01
Lambda-Cyhalothrin 2	GC-MSMS	0.01
Leptophos	GC-MSMS	0.01
Linuron	LC-MSMS	0.01
Lufenuron	LC-MSMS(-)	0.01
Malaoxon	LC-MSMS	0.01
Malathion	LC-MSMS	0.01
Mecarbam	LC-MSMS	0.01
Mepanipyrim	LC-MSMS	0.01
Mephosfolan	LC-MSMS	0.01
Metaflumizone	LC-MSMS	0.01
Metalaxyl	LC-MSMS	0.01
Metconazole	LC-MSMS	0.01
Methabenzthiazuron	LC-MSMS	0.01
Methamidophos	LC-MSMS	0.01

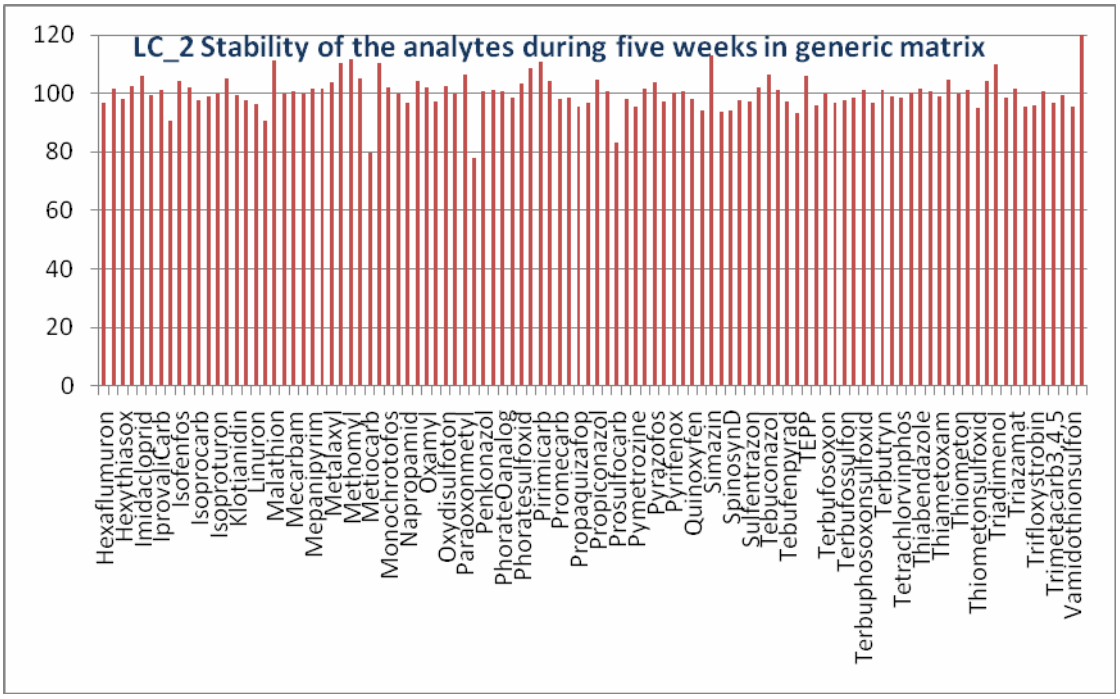
Pesticide	Detection	LOQ (mg/kg)
Methiocarb	LC-MSMS	0.01
Methiocarb-sulfon	LC-MSMS	0.01
Methiocarb-sulfoxid	LC-MSMS	0.01
Methomyl	LC-MSMS	0.01
Methoxychlor	GC-MSMS	0.01
Methoxyfenozide	LC-MSMS	0.01
Metidathion	LC-MSMS	0.01
Metribuzin	GC-MSMS	0.01
Mevinphos	GC-MSMS	0.01
Monocrotophos	LC-MSMS	0.01
Myclobutanil	LC-MSMS	0.01
Napropamide	LC-MSMS	0.01
Nitrofen	GC-MSMS	0.01
Omethoate	LC-MSMS	0.01
Orthophenylphenol	GC-MSMS	0.01
Oxadixyl	GC-MSMS	0.01
Oxamyl	LC-MSMS	0.01
Oxamyl-Oxime	LC-MSMS	0.01
Paclobutrazol	LC-MSMS	0.01
Paraoxon	LC-MSMS	0.01
Paraoxon-Methyl	LC-MSMS	0.01
Parathion	GC-MSMS	0.01
Parathion-methyl	GC-MSMS	0.01
Penconazole	LC-MSMS	0.01
Pencycuron	LC-MSMS	0.01
Pendimethalin	GC-MSMS	0.01
Pentachloroaniline	GC-MSMS	0.01
Pentachloroanisole	GC-MSMS	0.01
Pentachlorobenzene	GC-MSMS	0.01
Permethrin	GC-MSMS	0.01
Phenmedipham	LC-MSMS	0.01
Phenothrin	LC-MSMS	0.01
Phenthoate	GC-MSMS	0.01
Phorate	LC-MSMS	0.01
Phorate-O-Analogue	LC-MSMS	0.01
Phorate-Sulfon	LC-MSMS	0.01
Phorate-Sulfoxid	LC-MSMS	0.01
Phosalone	GC-MSMS	0.01
Phosmet	GC-MSMS	0.01
Phosmet oxon	GC-MSMS	0.05
Phosphamidon	LC-MSMS	0.01
Phoxim	LC-MSMS	0.01
Piperonyl Butoxide	LC-MSMS	0.01
Pirimicarb	LC-MSMS	0.01
Pirimiphos-Ethyl	GC-MSMS	0.01
Pirimiphos-methyl	GC-MSMS	0.01
Prochloraz	LC-MSMS	0.01

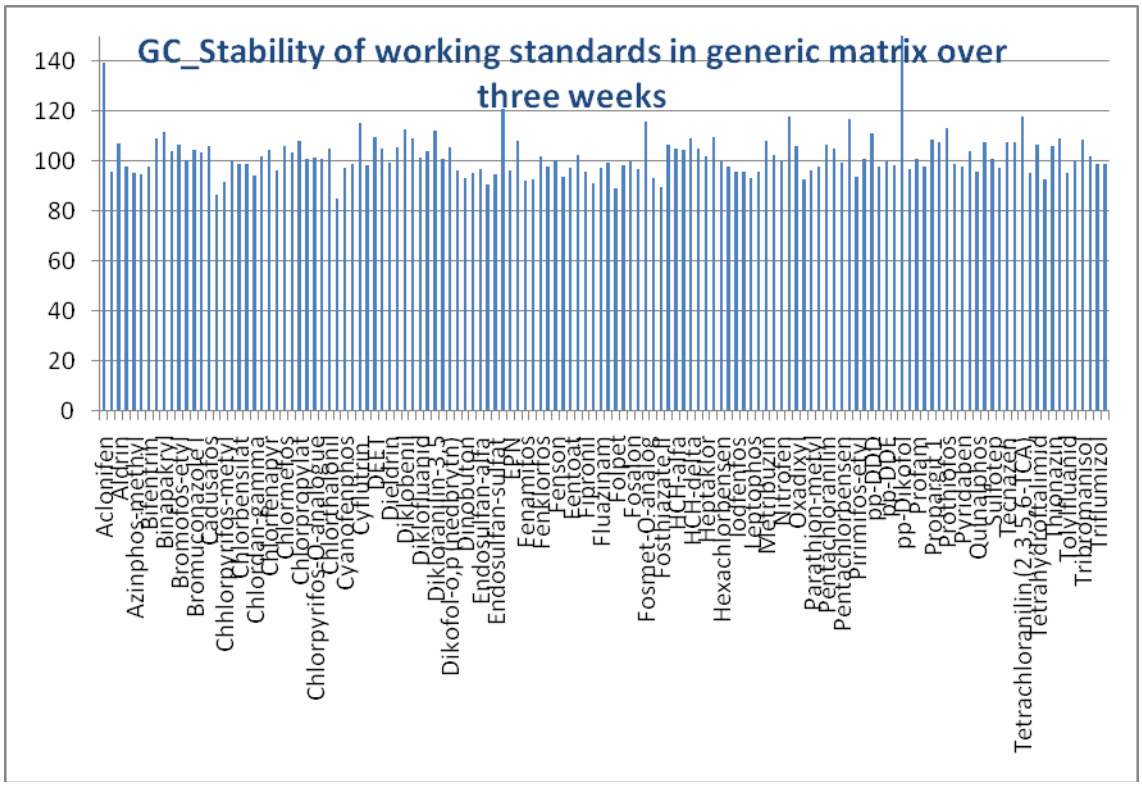
Pesticide	Detection	LOQ (mg/kg)
Procymidone	GC-MSMS	0.01
Profenofos	GC-MSMS	0.01
Promecarb	LC-MSMS	0.01
Propamocarb	LC-MSMS	0.01
Propaquizafop	LC-MSMS	0.01
Propargite (1+2)	GC-MSMS	0.01
Propetamphos	LC-MSMS	0.01
Propham	GC-MSMS	0.01
Propiconazole	LC-MSMS	0.01
Propoxur	LC-MSMS	0.01
Propyzamide	GC-MSMS	0.01
Prosulfocarb	LC-MSMS	0.01
Prothioconazole-desthio	LC-MSMS	0.01
Prothiofos	GC-MSMS	0.01
Pymetrozine	LC-MSMS	0.01
Pyraclofos	GC-MSMS	0.01
Pyraclostrobin	LC-MSMS	0.01
Pyrazophos	LC-MSMS	0.01
Pyridaben	GC-MSMS	0.01
Pyridaphenthion	LC-MSMS	0.01
Pyrifenox	LC-MSMS	0.01
Pyrimethanil	GC-MSMS	0.01
Pyriproxyfen	LC-MSMS	0.01
Quinalphos	GC-MSMS	0.01
Quintozene	GC-MSMS	0.01
Quizalofop	LC-MSMS	0.01
Simazine	LC-MSMS	0.01
Spinosyn A	LC-MSMS	0.01
Spinosyn D	LC-MSMS	0.01
Spiroxamine	LC-MSMS	0.01
Sulfentrazone	LC-MSMS	0.01
Sulfotep	GC-MSMS	0.01
tau-Fluvalinate	LC-MSMS	0.01
TCNB, 2,3,4,5-	GC-MSMS	0.01
Tebuconazole	LC-MSMS	0.01
Tebufenozide	LC-MSMS	0.01
Tebufenpyrad	LC-MSMS	0.01
Tecnazene	GC-MSMS	0.01
Teflubenzuron	LC-MSMS(-)	0.01
Tefluthrin	GC-MSMS	0.01
TEPP	LC-MSMS	0.01
Tepraloxydim	LC-MSMS	0.01
Terbufos	LC-MSMS	0.01
Terbufos Sulfone	LC-MSMS	0.01
Terbufos Sulfoxide	LC-MSMS	0.01
Terbufos-O-sulfone	LC-MSMS	0.01
Terbufos-oxon	LC-MSMS	0.01

Pesticide	Detection	LOQ (mg/kg)
Terbufos-oxon-sulphoxid	LC-MSMS	0.01
Terbuthylazine	LC-MSMS	0.01
Terbutryn	LC-MSMS	0.01
Tetrachloranilin, 2,3,5,6-	GC-MSMS	0.01
Tetrachlorvinphos	LC-MSMS	0.01
Tetraconazole	LC-MSMS	0.01
Tetradifon	GC-MSMS	0.01
Tetrahydroftalimid	GC-MSMS	0.01
Tetrasul	GC-MSMS	0.01
Thiabendazole	LC-MSMS	0.01
Thiacloprid	LC-MSMS	0.01
Thiametoxam	LC-MSMS	0.01
Thiodicarb	LC-MSMS	0.01
Thiometon	LC-MSMS	0.01
Thiometon-sulfone	LC-MSMS	0.01
Thiometon-sulfoxide	LC-MSMS	0.01
Thionazin	GC-MSMS	0.01
Thiophanate-methyl	LC-MSMS	0.01
Tolclofos-methyl	GC-MSMS	0.01
Tolylfluanid	GC-MSMS	0.01
Triadimefon	LC-MSMS	0.01
Triadimenol	LC-MSMS	0.01
Triamiphos	LC-MSMS	0.01
Triazamate	LC-MSMS	0.01
Triazofos	GC-MSMS	0.01
Tribromoanisole, 2,4,6-	GC-MSMS	0.01
Trichlorfon	LC-MSMS	0.01
Trichloronat	GC-MSMS	0.01
Trichlorophenol, 2,4,6-	GC-MSMS	0.01
Trifloxystrobin	LC-MSMS	0.01
Triflumizole	GC-MSMS	0.01
Triflumuron	LC-MSMS(-)	0.01
Trimethacarb, 2,3,5-	LC-MSMS	0.01
Triticonazole	LC-MSMS	0.01
Vamidothion	LC-MSMS	0.01
Vamidothion-sulfoxide	LC-MSMS	0.01
Vinclozolin	GC-MSMS	0.01
Zoxamide	LC-MSMS	0.01

21. Appendix 4. The stability of working standards






GC_Stability of working standards in generic matrix over three weeks
140
120
100
80
60
40
20
0
Aclonifen
Aldrin
Azinphos-methyl
Bifenthrin
Binapacryl
Bromophos-ethyl
Bromuconazole I
Cadusafos
Chlorpyrifos-methyl
Chlorbensilat
Chlordan-gamma
Chlorfenapyr
Chlormefos
Chlorpropylat
Chlorpyrifos-O-analogue
Chlorthalonil
Cyanofenphos
Cyhalothrin
DEET
Dieldrin
Dikloflanid
Diklobenil
Diklofol-o,p (hedbrytn)
Dikofol-o,p (hedbrytn)
Dinobuton
Endosulfan-alfa
Endosulfan-sulfat
EPN
Etrimfos
Fenklorfos
Fenson
Fenitoat
Fipronil
Fluazinam
Folpet
Fosalon
Fosmet-O-analog
Fosthiazate I
HCH-alfa
HCH-delta
Heptaklor
Hexachlorbensen
Iodfenfos
Leptophos
Metribuzin
Nitrofen
Oxadixyl
Parathion-methyl
Pentachloranilin
Pentachlorbensen
Pirimifos-ethyl
pp-DDD
pp-DDE
pp-Dikofol
Profam
Propargit 1
Prothiofos
Pyridaben
Quinalphos
Sulfotep
Tecnazen
Tetrachloranilin (2,3,5,6-TCA)
Tetrahydroftalimid
Thionazin
Tolylfluanid
Tribromanisol
Triflumizol