CLG-PST5.02		Page 1 of 39
Title: Screening for Pesticides by LC/MS/MS and GC/MS/MS		
Revision: .02	Replaces: CLG-PST5.01	Effective: 8/06/2012

Contents

A. INTRODUCTION

1. Summary of Procedure

   Various classes of pesticides are extracted from muscle tissue with high speed dispersion in ethyl acetate followed by solvent exchange to acetonitrile and clean-up using ultra-low temperature freezing, centrifugation, and solid phase extraction. Detection of pesticide residues is performed by gas chromatography with tandem mass spectrometry (GC/MS/MS) and liquid chromatography with tandem mass spectrometry (LC/MS/MS).

2. Applicability

   This method is suitable for screening the listed pesticides in ovine, caprine, poultry, porcine, and bovine muscle at levels ≥ the levels listed in Appendix J.4.

   Note: Refer to 40CFR for tolerance values set by EPA.

B. EQUIPMENT

Note: Equivalent equipment may be substituted.

1. Apparatus
   a. A Food processor - Robot Coupe model RSI6Y-1, Robot Coupe USA Inc.
   b. Sample cups - eValue 4.5 oz specimen containers w/caps, Cat. No. C686550, E&K Scientific.
   c. Analytical Balance - Readable to 0.20 g, Model 2000, Mettler.
   d. 50 mL centrifuge tubes - Cat. 62-548-004 PP, Sarstedt, Inc.
   e. Shaker - Model E6010.00, Eberbach Corp.
   f. Freezer capable of -20 °C - Isotemp Freezer, Cat. No. 13-986-149, Fisher Scientific.
   g. Centrifuge - Sorvall RC-4, Thermo Scientific.
   h. Micro Centrifuge - Micro Centrifuge 5424, Cat. No. 22620461, Eppendorf.
   i. Nitrogen Evaporator Apparatus with Heated Water Bath - N-Evap, Cat. No. 11250, Organomation.
   j. Multi Tube Vortex - VWR Signature Multi Tube Vortexer, Cat. No. 14005-826, VWR International.
   k. Freezer capable of -70 °C - Isotemp Freezer Ultra-Low Temperature, Cat. No. 13-990-14, Fisher Scientific.
   l. Positive Pressure Manifold - Cat. No. VMFPPM16, UCT, LLC.

m. 50 mL glass centrifuge tubes - Pyrex Centrifuge Tubes w/ stopper, Cat. No. CLS808450-12EA, Sigma-Aldrich.

n. 15 mL glass centrifuge tubes - Kimax Centrifuge Tube w/ glass stopper, Cat. No. 89002-1984, VWR International.

o. 1000 mg C_{18} SPE Columns - Cat. No. BJ9008, VWR International.

p. Filter paper - Whatman #4, Cat. No. 28460-120, VWR International.

q. 0.2 µm Nylon Syringe Filter - Cat. No. 28143-242, VWR International.

r. Micro centrifuge tubes (150 mg $MgSO_4$ & 50 mg PSA) - QuEChERS micro centrifuge tubes (150 mg $MgSO_4$ & 50 mg PSA), Cat. No. RK26124, VWR International.

s. 6 mL SPE cartridge (500 mg PSA) - Cat. No. 26195, Restek.

t. Variable volume dispensers - VWR Digital Easy Calibration Dispenser, Cat. No. 18901-130, VWR International.

u. Variable volume pipetters capable of accurately delivering 100 - 2500 µL – Eppendorf.

v. Eppendorf adjustable volume pipetter, 500-2500 µL - Cat. No. 022470353, Fisher.

w. Disposable Pasteur Pipettes - Cat. No. 13-678-20D, Fisher.

x. 3 mL Plastic Syringe - Luer Lok Plastic Disposable Syringes, Becton Dickinson,Cat. No. 301073, VWR International.

y. Glass Autosampler Vials & Caps - 2 mL, Cat. No. E251036, amber Cat. No. E251011, caps with septa Cat. No. E416209, E&K Scientific.

z. Glass Volumetric Flasks - Class A.

aa. Graduated cylinders - Class A.

2. Instrumentation

a. Waters UPLC Acquity TQ Detector.

b. Waters Acquity UPLC HSS/T3, 1.8 µm particle size, 2.1 x 100 mm column, part # 186003539.

c. Bruker (formerly Varian) 450 GC equipped with Bruker 300 triple quadruple mass spectrometer. Bruker MS Workstation 7 Software.

d. Bruker VF 5ms 30 m x 0.25 mm ID GC analytical column, part # CP8944.

C. REAGENTS AND SOLUTIONS

Note: Equivalent reagents / solutions may be substituted. The stability time frame of the solution is dependant on the expiration date of the components used or the listed expiration date, whichever is soonest.

1. Reagents
   a. QuEChERS Salts Packets (8g $MgSO_4$ & 2 g NaCl) - Cat. No. ECQUVIN50CT-MP, UCT.
   b. Magnesium Sulfate, Anhydrous - Cat. No. BDH0246-500G, VWR International.
   c. Acetic Acid, ACS grade - Cat. No. EM-AX0073-75, VWR International.
   d. Ethyl Acetate, HPLC grade - Cat. No. BJLP100-4, VWR International.
   e. Acetonitrile, HPLC grade - Cat. No. BJLP014-4, VWR International.
   f. Acetone, HPLC grade - Cat. No. BJ010-4, VWR International.
   g. Toluene, HPLC grade - Cat. No. BJLP347-4, VWR International.
   h. Methanol, HPLC grade - Cat. No. BJLP230-4, VWR International.
   i. Ammonium acetate - Cat. No. BDH0204-500G, VWR International.
   j. Formic acid, ACS grade - Cat. No. EM-FX0440-7, VWR International.
   k. Water, HPLC grade - Millipore water (deionized distilled).

2. Solutions
   a. 1% Acetic Acid/Acetonitrile (by volume)

      Using a class A graduated cylinder, measure 20 mL of acetic acid and 1980 mL of acetonitrile into a two liter bottle and mix well. Solution expires one year from preparation date.

   b. LC/MS/MS Mobile Phase A (5 mM ammonium acetate/0.1% formic acid in water by volume)

      Dissolve 0.771 g ammonium acetate in a small amount of water and pour into a two liter class A graduated cylinder, add 2 mL of formic acid and bring to volume with water and mix well. Solution expires one year from preparation date.

      LC/MS/MS Mobile Phase B (0.1% formic acid in methanol by volume)

      Using a class A graduated cylinder measure 2 mL of formic acid into a class A two liter graduated cylinder and bring to volume with methanol and mix well. Solution expires one year from preparation date.

   c. 3:1 v/v Acetone/Toluene

      Using a class A graduated cylinder measure 1500 mL of acetone and 500 mL of

toluene into a two liter bottle and mix well. Solution expires one year from preparation date.

D. STANDARD(S)

Note: Equivalent standards / solutions may be substituted. Purity and counterions are to be taken into account when calculating standard concentrations. The stability time frame of the solution is dependant on the expiration date of the components used or the listed expiration date, whichever ends sooner.

1. Standard Information
   a. Trichloronate, 1,000 µg/mL in Ethyl Acetate- Ultra Scientific
   b. Ethoprophos, 500 µg/mL in Ethyl acetate- Ultra Scientific
   c. GC Mixed Pesticide Standard- Accustandard

Table 1 – Example GC Mixed Pesticide Standard composition

Cmpd #	Name	CAS #	Spiking Solution (D.2.b) Conc. (µg/mL ethyl acetate)	Stock Solution Conc. (µg/mL ethyl acetate)
1	Alachlor	15972-60-8	2	20
2	Aldrin	309-00-2	5	50
3	Azinphos methyl	86-50-0	2	20
4	Bifenthrin	82657-04-3	1	10
5	Boscalid	188425-85-6	3	30
6	Carfentrazone ethyl	128639-02-1	1	10
7	Chlordane cis	5103-71-9	1	10
8	Chlordane trans	5103-74-2	1	10
9	Chlorpyrifos	2921-88-2	1.5	15
10	Chlorpyrifos methyl	5598-13-0	1	10
11	Cyhalothrin (Cyhalothrin-L)	91465-08-6	1	10
12	Cypermethrin	52315-07-8	3	30
13	Deltamethrin	52918-63-5	2	20
14	Dichlorvos (DDVP)	62-73-7	3	30
15	Dieldrin	60-57-1	5	50
16	Difenoconazole	119446-68-3	3	30
17	Endosulfan I	959-98-8	4.5	45
18	Endosulfan II	33213-65-9	4.5	45
19	Endosulfan sulfate	1031-07-8	1.5	15

Cmpd #	Name	CAS #	Spiking Solution (D.2.b) Conc. (µg/mL ethyl acetate)	Stock Solution Conc. (µg/mL ethyl acetate)
20	Fipronil	120068-37-3	1	10
21	Heptachlor	76-44-8	5	50
22 & 23	Heptachlor epoxide (cis & trans)	1024-57-3 & 28044-83-9	5	50
24	Mirex	2385-85-5	2	20
25	Nonachlor, trans-	39765-80-5	1	10
26	Oxychlordane	27304-13-8	2	20
27	Permethrin (cis & trans)	52645-53-1	3	30
28	Piperonyl butoxide	51-03-6	4.5	45
29	Pronamide	23950-58-5	1	10
30	Propanil	709-98-8	1.2	12
31	Propiconazole	60207-90-1	3	30
32	Tefluthrin	79538-32-2	1	10
33	Tetrachlorvinphos	961-11-5	2	20
34	Tetraconazole	112281-77-3	1	10

d. LC Mixed Pesticide Standard- Accustandard

Table 2 – Example LC Mixed Pesticide Standard composition

Cmpd #	Name	CAS #	Spiking Solution (D.2.b) Conc. (µg/mL ethyl acetate)	Stock Solution Conc. (µg/mL ethyl acetate)
35	3-Hydroxycarbofuran	16655-82-6	4	40
36	Acephate	30560-19-1	2	20
37	Carbaryl	63-25-2	5	50
38	Carbofuran	1563-66-2	2	20
39	Clofentezine	74115-24-5	5	50
40	Diflubenzuron	35367-38-5	5	50
41	Diuron	330-54-1	16	160
42	Ethofumesate	26225-79-6	4	40
43	Imazalil	35554-44-0	1	10
44	Imidacloprid	138261-41-3	5	50

Cmpd #	Name	CAS #	Spiking Solution (D.2.b) Conc. (µg/mL ethyl acetate)	Stock Solution Conc. (µg/mL ethyl acetate)
45	Indoxacarb	144171-61-9	10	100
46	Linuron	330-55-2	5	50
47	Metalaxyl	57837-19-1	2	20
48	Methomyl	16752-77-5	6	60
49	Methoxyfenozide	161050-58-4	2	20
50	Myclobutanil	88671-89-0	2	20
51	Norflurazon	27314-13-2	2	20
52	Pyridaben	96489-71-3	1.8	18
53	Simazine	122-34-9	2	20
54	Tebufenozide	112410-23-8	8	80
55	Thiabendazole	148-79-8	3	30
56	Thiamethoxam	153719-23-4	2	20

2. Preparation of Standard Solution(s)

   a. Internal Standard Spiking Solution (20 µg/mL Trichloronate & 10 µg/mL Ethoprofos):

      Pipet 1.0 mL of the 1000 µg/mL Trichloronate and 500 µg/mL Ethoprofos mixed stock solution into a 50 mL class A volumetric flask and dilute to volume with ethyl acetate. Mix well. All spiking solutions are stored at ≤ -10 °C and expire one year from the preparation date.

   b. Mixed Pesticide Spiking Solution:

      Pipet 5 mL of LC compound stock solution and 5 mL of GC compound stock solution into a 50 mL class A volumetric flask, and dilute to volume with ethyl acetate. All spiking solutions are stored at ≤ -10 °C and expire one year from the preparation date,

   c. Injection Standard for LC compounds:

      Pipet 200 µL of internal standard spiking solution (D.2.a) and 200 µL of mixed pesticide spiking solution (D.2.b) into a 10 mL class A volumetric flask, and dilute to volume with acetonitrile. Injection standards are stored at ≤ -10 °C and expire in 1 month.

   d. Injection Standard for GC compounds:

      Pipet 200 µL of internal standard spiking solution (D.2.a) and 200 µL of mixed pesticide spiking solution (D.2.b) into a 10 mL class A volumetric flask, and dilute

to volume with toluene. Injection standards are stored at ≤ -10 °C and expire in 1 month.

Table 3 - Concentration of LC and GC injection standard.

Cmpd #	Name	ppb (ng of pest./ g sample)	µg/mL (µg of pest./mL of extract)
	GC Mixed Standard		
1	Alachlor	10	0.04
2	Aldrin	25	0.1
3	Azinphos methyl	10	0.04
4	Bifenthrin	5	0.02
5	Boscalid	15	0.06
6	Carfentrazone ethyl	5	0.02
7	Chlordane cis	5	0.02
8	Chlordane trans	5	0.02
9	Chlorpyrifos	7.5	0.03
10	Chlorpyrifos methyl	5	0.02
11	L-Cyhalothrin	5	0.02
12	Cypermethrin	15	0.06
13	Deltamethrin	10	0.04
14	Dichlorvos (DDVP)	15	0.06
15	Dieldrin	25	0.1
16	Difenoconazole	15	0.06
17	Endosulfan I	22.5	0.09
18	Endosulfan II	22.5	0.09
19	Endosulfan sulfate	7.5	0.03
20	Fipronil	5	0.02
21	Heptachlor	25	0.1
22 & 23	Heptachlor epoxide, cis & trans	25	0.1
24	Mirex	10	0.04
25	Nonachlor trans	5	0.02
26	Oxychlordane	10	0.04
27	Permethrin (cis & trans)	15	0.06
28	Piperonyl butoxide	22.5	0.09
29	Pronamide	5	0.02

Cmpd #	Name	ppb (ng of pest./ g sample)	µg/mL (µg of pest./mL of extract)
30	Propanil	6	0.024
31	Propiconazole	15	0.06
32	Tefluthrin	5	0.02
33	Tetrachlorvinphos	10	0.04
34	Tetraconazole	5	0.02
	LC Mixed Standard		
35	3-Hydroxycarbofuran	20	0.08
36	Acephate	10	0.04
37	Carbaryl	25	0.1
38	Carbofuran	10	0.04
39	Clofentezine	25	0.1
40	Diflubenzuron	25	0.1
41	Diuron	80	0.32
42	Ethofumesate	20	0.08
43	Imazalil	5	0.02
44	Imidacloprid	25	0.1
45	Indoxacarb	50	0.2
46	Linuron	25	0.1
47	Metalaxyl	10	0.04
48	Methomyl	30	0.12
49	Methoxyfenozide	10	0.04
50	Myclobutanil	10	0.04
51	Norflurazon	10	0.04
52	Pyridaben	9	0.036
53	Simazine	10	0.04
54	Tebufenozide	40	0.16
55	Thiabendazole	15	0.06
56	Thiamethoxam	10	0.04
	Internal Standards		
57	Trichloronate	100	0.4
58	Prophos	50	0.2

E. SAMPLE PREPARATION

1. Chop 0.5 -1 lb of muscle tissue into small pieces and homogenize with an equal amount of dry ice in a large food processor. The resulting sample homogenate will be a frozen powder.

2. Transfer a portion of the homogenized sample into a loosely capped sample cup until the dry ice has sublimed. Excess sample from step E.1 may be discarded.

3. Tighten the caps and store sample cups at ≤ -10 ºC for short term storage or ≤ -70 ºC for long term storage

F. ANALYTICAL PROCEDURE

1. Preparation of Controls

   a. Prepare positive and negative control samples by weighing two 20 ± 0.20 g blank homogenized samples and then fortifying one at the screening levels with 100 µL of the mixed pesticide spiking solution (D.2.b). Allow the sample to dry (about 5 minutes) before continuing at step F.2.b.

2. Extraction Procedure

   a. Weigh 20.0 ± 0.20 g of homogenized sample into a 50 mL polypropylene centrifuge tube. Make sure the sample is all the way down in the tube.

   b. Add 30 mL of ethyl acetate to each sample.

   c. Fortify each sample and the positive control with 100 µL of the internal standard spiking solution (D.2.a.) and cap centrifuge tube. Do not add internal standard to the negative control so the extract may be used to dilute samples for re-injection on the mass spectrometer if necessary.

   d. Place samples on the shaker for 1 minute to mix.

   e. Add 8 g of $MgSO_4$ and 2 g NaCl (pre-weighed QuEChERS salts) to each sample and cap tube.

   f. Shake vigorously for 5 minutes on the shaker.

      Note: Make sure the solvent interacts well with the entire sample and the crystalline agglomerates are broken up sufficiently.

   g. Place samples into the ≤ -20 °C freezer for 30 minutes.

   h. Remove samples from freezer and centrifuge at 5100 RCF for 12 minutes.

   i. Decant more than 18 mL of the ethyl acetate layer into a 50 mL graduated glass centrifuge tube using a funnel and filter paper.

   j. Adjust the volume to 18 mL, discarding the excess.

k. Concentrate the extract under nitrogen in a 65 ± 5 °C water bath until the volume remains constant. This volume is typically 0.5 mL to 2.0 mL.

l. Dilute to 15 mL with acetonitrile, cap glass tube and vortex for 1 minute.

m. Place samples in ≤ -70 °C freezer for 30 minutes.

n. Centrifuge the extract while frozen for 3 minutes at 1500 RCF.

Note: Acetonitrile will thaw during centrifugation.

o. Prepare a solid phase extraction (SPE) column containing 1000 mg C_{18} by adding approximately 2 g anhydrous $MgSO_4$ to the top of the C_{18}.

Note: SPE columns containing $MgSO_4$ may be prepared ahead of time and stored in a desiccator.

p. Using a positive pressure SPE manifold (PPM), condition the SPE cartridge with 5 mL of 1% acetic acid/acetonitrile and elute to waste.

q. Place properly labeled 15 mL graduated glass tubes in the collection rack below SPE cartridges.

r. Transfer 10 mL of sample extract into the SPE column and pass the extract through the column using a regulated flow pressure of approximately 35 psi.

s. After the extract has completely passed through the column add 2 aliquots of 2.5 mL of 1% acetic acid/acetonitrile to elute the sample from the column. (Change gas flow to full flow for approximately 1 minute to completely elude the extract from the column.)

Note: Be careful not to overfill the SPE columns.

Note: Samples may be capped and stored in the ≤ -20 °C freezer overnight at this point.

t. Concentrate each sample to under 2 mL (final sample volume) under nitrogen in a 65 ± 5 °C water bath. Adjust all samples to 2 mL with acetonitrile

3. Extract preparation for LC/MS/MS analysis

a. Transfer 1 mL of the extract from step F.1.u to a 2 mL mini-centrifuge tube that contains 50 mg PSA (primary secondary amine) and 150 mg of $MgSO_4$.

b. Vortex the mini-centrifuge tubes for 1 minute.

c. Centrifuge the mini-centrifuge tubes for 2 minutes at 10,000 RCF.

d. Transfer the sample extract to a 3 mL plastic syringe with a 0.2 µm Nylon syringe filter and filter extract into a labeled autosampler vial. Analyze vial by LC/MS/MS.

4. Extract preparation for GC/MS/MS analysis

   a. Use a PPM, condition a 500 mg PSA SPE column with 4 mL of 3:1 v/v acetone/toluene and elute to waste.

   b. Place properly labeled 15 mL graduated glass tubes in the collection rack below SPE columns.

   c. Using a Pasteur pipette, transfer the remainder of the sample extract from step F.2.t. to the SPE column.

   d. Elute the extract through the column using a regulated flow pressure of 35 psi with 4 mL of 3:1 v/v acetone/toluene.

   e. Collect the eluate while washing the SPE column two times with 4 mL of 3:1 v/v acetone/toluene (eluant). Do not allow the SPE column to go dry.

   f. After the last 4 mL portion of eluant has passed through the column move the switch of the PPM from “Regulated flow” to “Full Flow/Dry” and dry the column for 1 minute.

   g. Evaporate the sample to approximately 0.5 mL under nitrogen in a 65 ± 5 °C water bath.

   h. Add 3 mL of toluene to centrifuge tube and vortex.

   i. Evaporate again to less than 0.5 mL to insure all other solvents have been removed.

   j. Bring the volume to 1.0 mL with toluene and vortex to mix.

   k. Transfer the sample to a labeled autosampler vial. Analyze by GC/MS/MS.

5. LC/MS/MS Instrumental Settings

   Note: The instrument parameters may be optimized to ensure system suitability.

   a. UPLC Conditions:

      Aqueous Mobile Phase: 5 mM ammonium acetate/0.1% formic acid in water

      Organic Mobile Phase: 0.1% formic acid in methanol

      Flow rate: 0.5 mL/min

      Column Temperature: 50 ºC

      Injection Volume: 1 µL

      Run Time: 10 minutes.

b. UPLC Mobile Phase Gradient:

Table 4 – UPLC gradient

Time (minute)	% Aqueous	% Organic
initial	90%	10%
0.25	90%	10%
7.75	2%	98%
8.50	2%	98%
8.51	90%	10%

c. Interface Conditions

Ion Mode: ES+

Source Temperature: 150 ºC

Desolvation Temperature: 450 ºC

Cone Gas Flow: 25 L/hr

Desolvation Gas Flow: 850 L/hr

Collision Gas Flow: 0.25 mL/min

d. MRM parameters

Table 5 – LC MRM parameters

Cmpd #	Name	RT (min.)	Cone (V)	1º Trace *	Coll En (eV)	2º Trace	Coll En (eV)
1	3-hydroxycarbofuran	3.46	15	255.2 > 163	18	255.2 > 181	15
2	acephate	1.44	20	184.1 > 143	12	184.1 > 125	16
3	carbaryl	4.91	20	202.2 > 145	15	202.2 > 127	28
4	carbofuran	4.76	25	222.2 > 165	13	222.2 > 123	23
5	clofentezine	6.96	20	303 > 138	13	303 > 102.1	40
6	diflubenzuron	6.51	23	311 > 158.2	15	311 > 141.1	32
7	diuron	5.44	25	233 > 72.1	15	233 > 160	24

Cmpd #	Name	RT (min.)	Cone (V)	1º Trace *	Coll En (eV)	2º Trace	Coll En (eV)
8	ethofumesate	5.9	13	304.1 > 121.1	20	304.1 > 161.2	25
9	imazalil	5.19	35	297 > 159	20	297 > 255	18
10	imidacloprid	3.06	25	256.1 > 209	14	256.1 > 175	18
11	indoxacarb	7.12	25	528 > 203.2	35	528 > 150.1	22
12	linuron	5.85	28	249 > 160	18	249 > 182	17
13	metalaxyl	5.56	18	280.1 > 220.1	13	280.1 > 192.2	18
14	methomyl	2.39	13	163.1 > 106	9	163.1 > 88	9
15	methoxyfenozide	6.24	15	369.1 > 149.2	18	369.1 > 91.1	47
16	myclobutanil	6.2	28	289.1 > 125.1	30	289.1 > 70.1	18
17	norflurazon	5.54	30	304.1 > 284.1	32	304.1 > 160.1	40
18 - ISTD	ethoprofos	6.49	23	243.1 > 173	22	-	-
19	pyridaben	8.01	25	365.2 > 147.1	28	365.2 > 309	13
20	simazine	4.72	35	202 > 124.1	20	202 > 132	20
21	tebufenozide	6.64	12	353.1 > 133.1	22	353.1 > 105	50
22	thiabendazole	3.15	45	202.1 > 175	24	202.1 > 131	33
23	thiamethoxam	2.5	23	292 > 211	13	292 > 181	18

*the most abundant ion is used to compare to the cutoff level

e. MS parameters

Dwell time: varied from 0.025 – 0.1 s

Capillary: 1.4 kV

Multiplier: -640 V

6. GC/MS/MS Instrumental Settings

Note: The instrument parameters may be optimized to ensure system suitability.

a. Gas Chromatograph Parameters:

Carrier Gas	Helium
Column Flow Rate	1.0 mL/min
Injector Temperature	260 ºC
Injection Volume	1 µL
Injection Mode	splitless

Temperature Program:

Initial temp	75 ºC
Initial hold time	2 min
Program rate up to 150 ºC	25 ºC/min
Program rate up to 225 ºC	3 ºC/min
Program rate up to 300 ºC	15ºC/min
Final hold time	10 min
Total Run time	45.0 min

b. Mass Spectrometer Parameters:

Ionization	Positive electron Impact
Detector Voltage	1250 V
Collision Gas	Argon @ 1.5 mTorr
Collision Energy	Optimized for each compound
MS Source temperature	200 ºC
Transferline temperature	280 ºC
Acquisition delay	5.0 min

Note: Autotune the instrument as needed.

c. Summary of Multiple Reaction Monitoring (MRM) transitions and parameters selected for each compound:

Table 6 – GC MRM Parameters

Cmpd #	Name	RT (min)	First transition (m/z)	Coll En (V)	Second transition (m/z)	Coll En (V)	Third transition (m/z)	Coll En (V)	Quant Ion*
1	Alachlor	17.79	188 > 160	10	188 > 130	40			160
2	Aldrin	19.90	263 > 191	40	293 > 193	30	293 > 228	20	191
3	Azinphos methyl	33.15	160 > 77	20	160 > 132	5	160 > 104	15	77
4	Bifenthrin	32.21	181 > 166	15	181 > 153	15	165 > 115	30	166
5	Boscalid	35.32	342 > 140	20	205 > 169	10			140
6	Carfentrazone ethyl	29.75	340 > 312	10	312 > 151	20	312 > 195	15	312
7	Chlordane, cis	24.18	375 > 266	10	373 > 337	10			266

Cmpd #	Name	RT (min)	First transition (m/z)	Coll En (V)	Second transition (m/z)	Coll En (V)	Third transition (m/z)	Coll En (V)	Quant Ion*
8	Chlordane, trans	23.45	375 > 266	10	373 > 337	10			266
9	Chlorpyrifos	19.95	314 > 260	15	314 > 286	10	314 > 258	25	286
10	Chlorpyrifos methyl	17.38	286 > 93	20	286 > 271	15	286 > 208	15	93
11	Cyhalothrin-L	33.50	197 > 141	10	181 > 152	10	181 > 127	30	141
12	Cypermethrin	35.22	181 > 152	20	181 > 127	30			152
13	Deltamethrin	37.11	181 > 152	20	253 > 172	10	181 > 127	30	152
14	Dichlorvos	5.83	185 > 93	15	185 > 109	20			93
15	Dieldrin	25.76	277 > 241	10	263 > 193	25			241
16	Difenoconazole	36.75	323 > 265	20	265 > 202	20	323 > 267	15	265
17	Endosulfan I	24.19	241 > 206	20	339 > 160	20			206
18	Endosulfan II	27.63	241 > 206	20	339 > 160	20			206
19	Endosulfan sulfate	29.88	272 > 237	20	272 > 235	25	272 > 143	30	237
20	Fipronil	22.21	367 > 213	30	367 > 255	20			213
21	Heptachlor	18.04	272 > 237	20	337 > 266	20			237
22 & 23	Heptachlor epoxide (cis & trans)	22.35	272 > 237	20	183 > 119	20	353 > 282	15	237
24	Mirex	33.47	272 > 237	20	272 > 167	40	272 > 140	40	237
25	Nonachlor, trans	24.35	409 > 302	10	409 > 263	20			302
26	Oxychlordane	22.11	187 > 123	10	185 > 149	20	389 > 355	5	123
27	Permethrin (cis & trans)	34.53	183 > 153	12	183 > 165	20	183 > 127	10	153
28	Piperonyl butoxide	31.39	176 > 131	10	176 > 103	25	176 > 149	20	131
29	Pronamide	14.91	173 > 145	20	173 > 109	20			145
30	Propanil	17.27	217 > 161	20	161 > 126	20			161
31	Propiconazole	29.99	259 > 191	10	259 > 173	20			191
32	Tefluthrin	15.82	177 > 127	20	177 > 137	20			127
33	Tetrachlorvinphos	24.00	329 > 109	20	329 > 79	30	329 > 314	15	109
34	Tetraconazole	20.74	336 > 218	15	336 > 204	30			218
35	Trichloronate (method ISTD)	20.86	297 > 269	20	299 > 271	20			269

* The Quant Ion listed above is not being used for quantitfication in this method. It is the most abundant product ion of those listed for each analyte, under the stated instrument conditions.

7. Injection sequence /Sample Set
   a. External Standard
   b. Positive Control
   c. Solvent Blank (optional)
   d. Negative Control
   e. Intra-laboratory check sample (if needed)
   f. Samples, up to a maximum of 14
   g. Re-injection of the external standard or positive control (for system suitability)

G. CALCULATIONS / IDENTIFICATION

1. Calculations
   a. Relative Response Factor (RRF)

      This is the internal standard corrected analyte response. The MS instruments can be programmed to automatically do this calculation.

      A = B / C

      where

      A = Relative Response Factor (unitless)

      B = Quant Ion Peak Area of Analyte (counts)

      C = Quant Ion Peak Area of Internal Standard (counts)

   b. Estimated Amount Found

      This is a quantitative estimate calculated for comparison to the screen cutoff level. It is based on a one point calibration with the positive control as the reference. The MS instruments can be programmed to automatically do this calculation.

      D = E * A sample / A pos. ctrl.

      where

      D = Estimated Amount Found in the Sample (ppb)

      E = Positive Control Fortification Level (ppb)

A sample = Relative Response Factor in the Sample (unitless)

A pos. ctrl. = Relative Response Factor in the Positive Control (unitless)

c. Screen Cutoff Level

This level is used to determine if a sample is screen positive or negative. It includes two safety factors so that potential violations are not missed.

F = 0.5 * G * H

where

F = Screen Cutoff Level (ppb)

G = Tolerance (ppb)

The tolerance or action level will need to be looked up for the analyte in the product of interest.

For zero and no tolerance, samples are screened at the positive control fortification level, which makes G = 2 * E, and F = E * H.

Screening at half tolerance is the first safety factor.

H = Minimum / Maximum Recovery (unitless)

Take values from the Tables 7 and 8 below.

Note: Values may be updated as more data becomes available.

This is the second safety factor to ensure that violations are not missed due to variation in recovery. These values are based on the positive control having the maximum recovery and the sample having the minimum recovery.

Table 7 – Minimum / Maximum Recovery Values for LC/MS/MS Analytes

Cmpd #	Name	min/max recovery
1	3-hydroxycarbofuran	0.60
2	Carbaryl	0.59
3	Carbofuran	0.64
4	Imazalil	0.33
5	Methoxyfenozide	0.46
6	Imidacloprid	0.61
7	Myclobutanil	0.49
8	Clofentezine	0.58
9	Thiabendazole	0.26
10	Diflubenzuron	0.68

Cmpd #	Name	min/max recovery
11	Ethofumesate	0.42
12	Tebufenozide	0.48
13	Linuron	0.55
14	Indoxacarb	0.56
15	Acephate	0.62
16	Methomyl	0.59
17	Simazine	0.60
18	Metalaxyl	0.56
19	Thiamethoxam	0.58
20	Norflurazon	0.59
21	Pyridaben	0.66
22	Diuron	0.63

Table 8 - Minimum / Maximum Recovery Values for GC/MS/MS Analytes

Cmpd #	Name	min/max recovery
1	Alachlor	0.48
2	Aldrin	0.73
3	Azinophos methyl	0.34
4	Bifenthrin	0.53
5	Boscalid	0.48
6	Carfentrazone ethyl	0.49
7	Chlordane, cis-	0.36
8	Chlordane, trans-	0.48
9	Chlorpyrifos	0.62
10	Chlorpyrifos methyl	0.71
11	Cyhalothrin-L	0.38
12	Cypermethrin	0.50
13	Deltamethrin	0.32
14	Dichlorvos	0.49
15	Dieldrin	0.49
16	Difenoconazole	0.29
17	Endosulfan I	0.58
18	Endosulfan II	0.45
19	Endosulfan sulfate	0.65

Cmpd #	Name	min/max recovery
20	Fipronil	0.46
21	Heptachlor	0.76
22 & 23	Heptachlor Epoxide (cis & trans)	0.69
24	Mirex	0.50
25	Nonachlor, trans-	0.40
26	Oxychlordane	0.45
27	Permethrin (cis & trans)	0.41
28	Piperonyl butoxide	0.39
29	Pronamide	0.66
30	Propanil	0.65
31	Propiconazole	0.37
32	Tefluthrin	0.78
33	Tetrachlorvinphos	0.37
34	Tetraconazole	0.58

2. Screening Criteria

   a. Retention time for the samples must match the retention time of the positive control or the injection standard injected at the beginning of the relevant sample set within 5% for LC and 5% for GC.

   b. All ions for a given analyte must be present. The required ions for each compound are listed in Table 5 and 6.

   c. All ions must have a signal-to-noise ratio ≥ 3.

   d. For findings of analytes with a tolerance more than 10 times greater than the positive control fortification level (G > 10 * E), dilution and re-injection may be required to determine if the sample is screen positive. If the estimated amount found is greater than 10 times the positive control fortification level (D > 10 * E), dilute the sample 10-fold with blank matrix extract not fortified with ISTD (negative control extract) and re-inject on the appropriate mass spectrometer.

   e. The sample is screen positive if the estimated amount found equals or exceeds the screen cutoff level (D ≥ F).

   f. All quant ion peak areas in the blank must be less than 10% of the positive control injected at the beginning of the relevant sample set.

   g. The external standard and positive control injections at the beginning and end of the sample set must all be positive for 95% of the analytes according to criteria b.-c. above. If a sample shows a positive response for a compound which did not meet screening criteria in the associated QC samples, then further testing of

that sample is warranted.

H. SAFETY INFORMATION AND PRECAUTIONS

1. Required Protective Equipment — Safety glasses, laboratory coat and gloves.

2. Hazards

Procedure Step	*Hazard*	*Recommended Safe Procedures*
Organic solvents (Ethyl Acetate, Acetonitrile, Methanol)	Flammable, vapors are corrosive to the skin, eyes and respiratory system.	Use only in an efficient chemical fume hood, away from any electrical or heating devices.
Toluene	Flammable, carcinogen, mutagen, vapors are corrosive to the skin, eyes and respiratory system.	Use only in an efficient chemical fume hood, away from any electrical or heating devices.
Pesticides	Persistent, bioaccumulative, carcinogenic, irritation to eyes, skin and respiratory system	Avoid direct contact, work in properly vented areas and use good personal hygiene.

3. Disposal Procedures

   Follow local, state and federal guidelines for disposal.

I. QUALITY ASSURANCE PLAN

1. Performance Standard

   a. Screening Criteria

      i. For set acceptance, 95% of the monitored analytes in the positive control must meet screening criteria. For sample reporting purposes, screen positive analytes must meet screening criteria in the positive control, or else further testing is warranted.

      ii. The blank (negative control) must be negative using the criteria in Section G.

2. Critical Control Points and Specifications

Record	*Acceptable Control*
a. Grinding sample with dry ice	Ground samples in powder form.
b. Sample weight	20.0 ± 0.2 g
c. Addition of QuEChERS salts	Make sure the salts mix thoroughly with the sample
d. Evaporation steps	Do not let the sample evaporate to dryness at any of the evaporation steps

3. Intralaboratory Check Samples
   a. System, minimum contents.
      i. Frequency: One per week per analyst when samples analyzed.
      ii. Records are to be maintained.
   b. Acceptability criteria.
      Refer to I. 1.
      If unacceptable values are obtained, then:
      i. Investigate following established procedures.
      ii. Take corrective action as warranted.

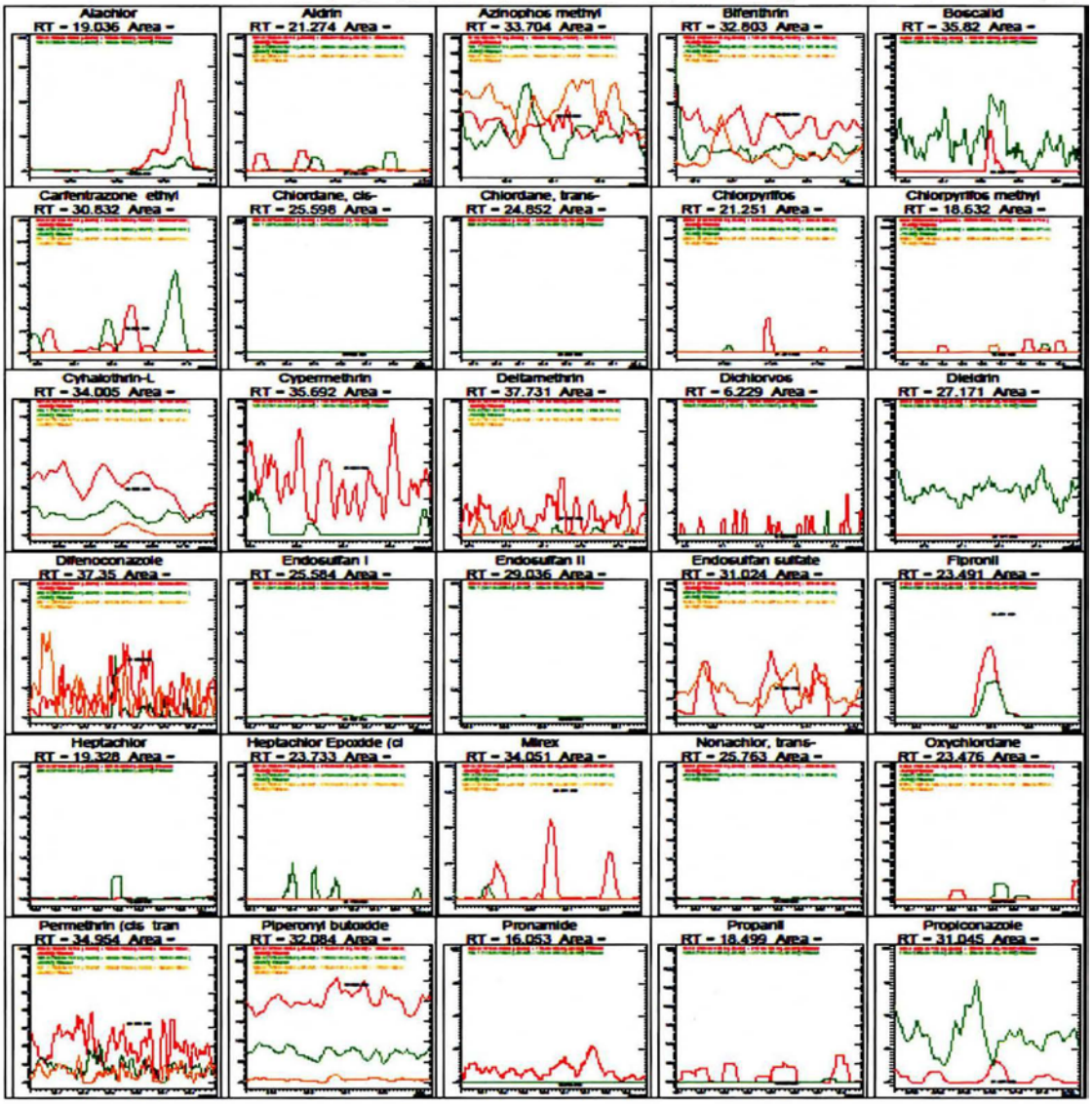
4. Sample Condition Upon Receipt: Cold or Frozen

J. APPENDIX

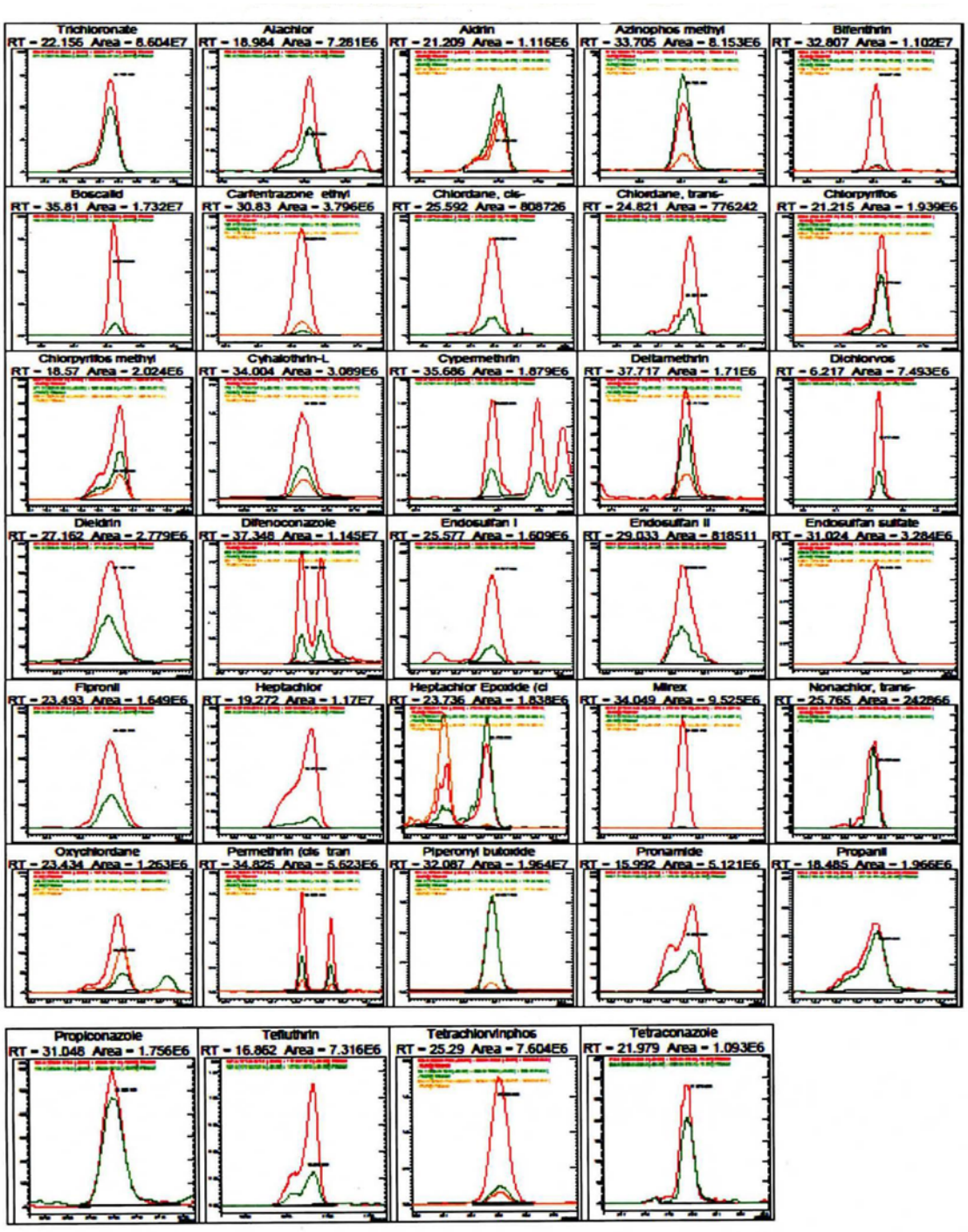
1. References
   a. Waters Application Note: Minimizing the Impact of the Sample Matrix During Routine Pesticide Residue Analysis in Food, July 2010.
   b. USDA, AMS, MET-100 Pesticide Method, WI-MET100-01 & WI-MET100-02 Work Instrutions.
   c. CLG-PST2.01, Screen and Confirmation of Pesticides by HPLC-MS-MS.

2. Chromatograms/spectra

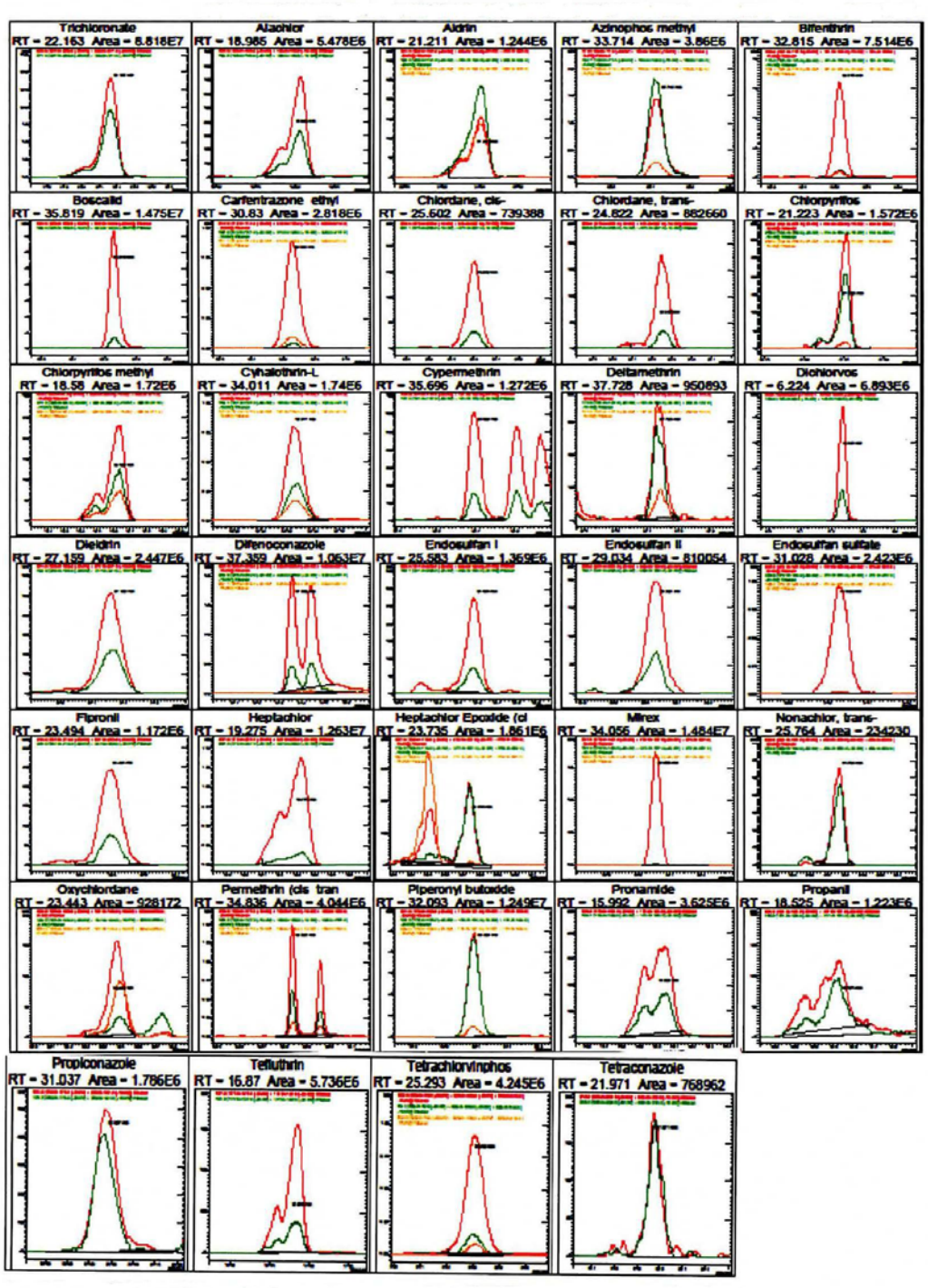
a. GC Negative Control



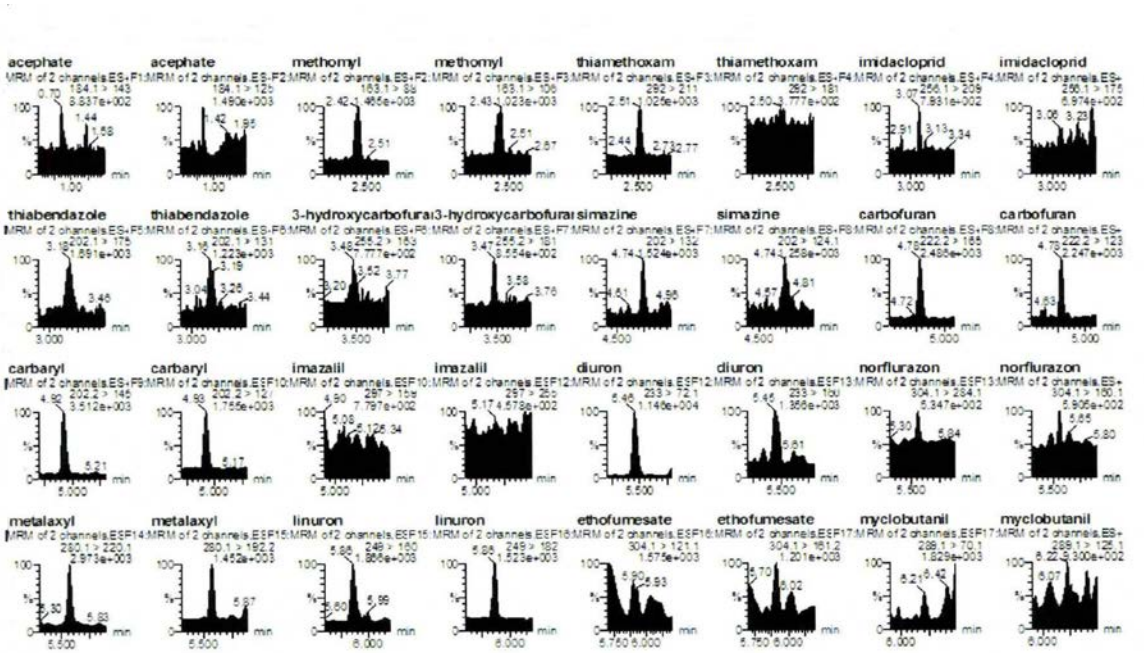
b. GC positive control



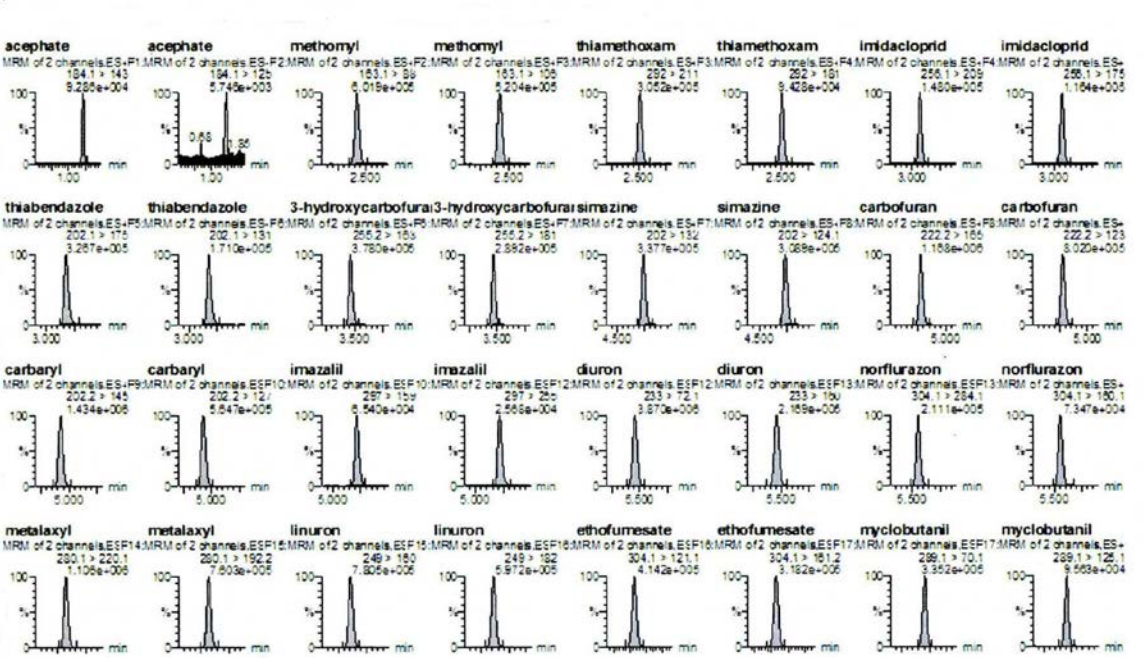
c. GC Solvent Standard



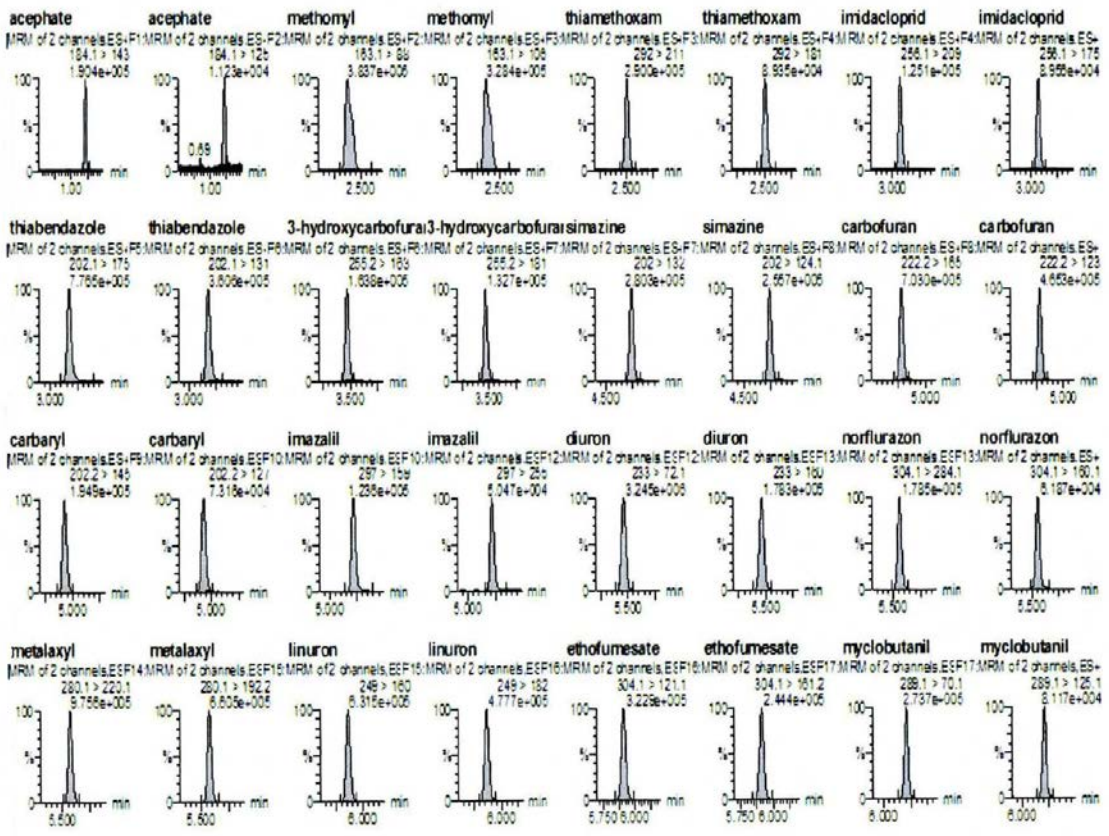
d. LC Negative Control



e. LC Positive Control



f. LC solvent standard



3. Possible fragmentation patterns

a. GC/MS/MS

	Ion (m/z)	Proposed fragment
Alachlor	269	[M]+
$C_{14}H_{20}ClNO_2$	188	[M - C_2H_6ClO]+
	160	[M - C_2H_6ClO - CO]+
	130	[M - C_2H_6ClO - C_2H_4NO]+
Aldrin	362	[M] +
$C_{12}H_8Cl_6$	293	[M + 1 - 2Cl]+
	263	[M + 2 - C_5H_6 - Cl]+
	257	[M + 1 - 3Cl]+
	193	[M + 2 - C_5H_6 - 3Cl] +
	191	[M - C_5H_6 - 3Cl] +
	186	[M + 1 - 5Cl]+
Azinphos methyl	317	[M]+
$C_{10}H_{12}N_3O_3PS_2$	160	[M - $C_2H_6O_2PS_2$]+
	132	[M - $C_2H_6O_2PS_2$ - CO]+
	104	[M - $C_2H_6O_2PS_2$ - CO - N_2]+
	77	[M - $C_2H_6O_2PS_2$ - CO - N_2 - NCH]+
Bifenthrin	422	[M]+
$C_{23}H_{22}ClF_3O_2$	181	[M - $C_9H_9ClF_3O_2$]+
	166	[M - $C_9H_9ClF_3O_2$ - CH_3]+
	165	[M - $C_{10}H_{13}ClF_3O_2$]+
	153	[M - $C_9H_9ClF_3O_2$ - C_2H_4]+
	115	[M - $C_{14}H_{15}$ ClF_3O_2]+
Boscalid	342	[M]+
$C_{18}H_{12}Cl_2N_2O$	205	[M + 2 - C_6H_2ClNO]+
	169	[M + 1 - $C_6H_2Cl_2NO$]+
	140	[M - $C_{12}H_9ClN$]+

Carfentrazone ethyl	411	[M]+
$C_{15}H_{14}Cl_2F_3N_3O_3$	340	[M - Cl - HCl]+
	312	[M -2Cl - C_2H_5]+
	195	[M - $C_4H_2Cl_2F_2N_3O$]+
	151	[M - $C_6H_6Cl_2F_2N_3O_2$]+
Chlordane cis	406	[M]+
$C_{10}H_6Cl_8$	375	[M + 4 - Cl]+
	266	[M - 4Cl]+
	337	[M + 1 - 2Cl]+
Chlordane trans	406	[M]+
$C_{10}H_6Cl_8$	375	[M + 4 - Cl]+
	337	[M - 4Cl]+
	266	[M + 1 - 2Cl]+
Chlorpyrifos	349	[M]+
$C_9H_{11}Cl_3NO_3PS$	314	[M - Cl]+
	286	[M - Cl - C_2H_4]+
	260	[M + 2 - Cl - C_4H_8]+
	258	[M - Cl - C_4H_8]+
Chlorpyrifos methyl	321	[M]+
$C_7H_7Cl_3NO_3PS$	286	[M - Cl]+
	271	[M - Cl - CH_3]+
	208	[M - Cl - C_2H_5OS]+
	93	[M - CH_2OPS]+
Cyhalothrin	449	[M]+
$C_{23}H_{19}ClF_3NO_3$	197	[M - $C_{15}H_{10}NO_3$]+
	181	[M - $C_{10}H_{10}ClF_3NO_2$]+
	152	[M - $C_{10}H_{10}ClF_3NO_2$ - CHO]+
	141	[M - $C_{15}H_{10}NO_3$ - C_3H_4O]+
	127	[M - $C_{10}H_{16}ClF_3NO_2$ - C_5H_7O]+

Cypermethrin	415	[M]+
$C_{22}H_{19}ClNO_3$	181	[M - $C_9H_{10}Cl_2NO_2$]+
	152	[M - $C_{10}H_{11}Cl_2NO_3$]+
	127	[M - $C_9H_{10}Cl_2NO_2$ - C_4H_6]+
Deltamethrin	503	[M]+
$C_{22}H_{19}Br_2NO_3$	253	[M + 2 - $C_{15}H_{10}NO_3$]+
	181	[M - $C_9H_{10}NO_2Br_2$]+
	172	[M - $C_{15}H_{10}NO_3$ - Br]+
	152	[M - $C_{10}H_{11}NO_3Br_2$]+
	127	[M - $C_9H_{10}NO_2Br_2$ - C_4H_6]+
Dichlorvos (DDVP)	220	[M]+
$C_4H_7Cl_2O_4P$	185	[M - Cl]+
	109	[M - C_2HOCl_2]+
	93	[M - $C_2HO_2Cl_2$]+
Dieldrin	378	[M]+
$C_{12}H_8Cl_6O$	345	[M + 2 - Cl]+
	277	[M -2Cl - CHO]+
	263	[M + 2 - C_5H_6ClO]+
	241	[M - 3Cl - CHO]+
	193	[M + 2 - C_5H_6ClO - 2Cl]+
Difenoconazole	405	[M]+
$C_{19}H_{17}Cl_2N_3O_3$	323	[M - $C_3H_4N_3$]+
	267	[M + 2 - $C_3H_4N_3$ - C_3H_6O]+
	265	[M - $C_3H_4N_3$ - C_3H_6O]+
	202	[M - $C_3H_4N_3$ - COCl]+
Endosulfan I	404	[M]+
$C_9H_6Cl_6O_3S$	339	[M + 2 - O_2Cl]+
	241	[M - C_4ClO_3S]+
	206	[M - $C_4Cl_2O_3S$]+

	160	$[M - C_{2C}l_4O_3S]+$
Endosulfan II	404	[M]+
$C_9H_6Cl_6O_3S$	241	$[M + 2 - O_2Cl]+$
	337	$[M - C_4ClO_3S]+$
	206	$[M - C_4Cl_2O_3S]+$
	160	$[M - C_2Cl_4O_3S]+$
Endosulfan sulfate	420	[M]+
$C_9H_6Cl_6O_4S$	272	$[M + 2 - C_4H_6SO_4]+$
	237	$[M + 2 - C_4H_6SO_4 - Cl]+$
	235	$[M - C_4H_6SO_4 - Cl]+$
	143	$[M - C_6H_4Cl_3O_4S]+$
Fipronil	436	[M]+
$C_{12}H_4Cl_2F_6N_4OS$	367	$[M - CF_3]+$
	255	$[M - C_4H_2F_3N_2OS]+$
	213	$[M - C_5F_3H_2N_4OS]+$
Heptachlor	370	[M]+
$C_{16}H_5Cl_7$	337	$[M + 2 - Cl]+$
	272	$[M + 2 - C_5H_5Cl]+$
	266	$[M + 2 - HCl - 2Cl]+$
	237	$[M + 2 - C_5H_5Cl - Cl]+$
Heptachlor epoxide (cis & trans)	386	[M]+
$C_{16}H_{15}Cl_7O$	353	$[M + 2 - Cl]+$
	317	$[M + 2 - 2Cl]+$
	272	$[M + 2 - C_5H_5ClO]+$
	237	$[M + 2 - C_5H_5ClO - Cl]+$
	183	$[M - C_5Cl_4]+$
	119	$[M + 2 - C_5Cl_6]+$

Mirex	540	[M]+
$C_{10}Cl_{12}$	272	[M + 2 - C_5Cl_6]+
	237	[M + 2 - C_5Cl_6 - Cl]+
	140	[M + 1 - C_5Cl_6 - C_2Cl_2 - Cl]+
	167	[M + 2 - C_5Cl_6 - 3Cl]+
Nonachlor trans	440	[M]+
$C_{10}H_5Cl_9$	409	[M + 4 - Cl]+
	302	[M + 2 - 4Cl]+
	263	[M + 2 - $C_3H_3Cl_3$ - Cl]+
	109	[M - $C_7H_2Cl_6$ - Cl]+
Oxychlordane	420	[M]+
$C_{16}H_4Cl_8O$	389	[M + 4 - Cl]+
	335	[M + 2 - Cl - HClO]+
	187	[M + 2 - C_5Cl_5]+
	185	[M - C_5Cl_5]+
	149	[M - C_5Cl_5 - HCl]+
	123	[M - $C_7H_3Cl_6O$]+
Permethrin (cis & trans)	390	[M]+
$C_{21}H_{20}Cl_2O_3$	183	[M - $C_8H_9O_2Cl_2$]+
	165	[M + 2 - $C_{14}H_{11}O_3$]+
	152	[M - $C_8H_9O_2Cl_2$ - CH_3O]+
	127	[M - $C_8H_9O_2C_{l2}$ - C_3H_4O]+
Piperonyl butoxide	338	[M]+
$C_{19}H_{30}O_5$	176	[M - $C_8H_{18}O_3$]+
	149	[M - $C_8H_{18}O_3$ - C_2H_5O]+
	131	[M - $C_8H_{18}O_3$ - C_4H_7O]+
	103	[M - $C_8H_{18}O_3$ - C_2H_3]+
Pronamide	255	[M]+
$C_{12}H_{11}Cl_2NO$	173	[M - C_5H_8N]+

	145	[M - C_5H_8N - CO]+
	109	[M - C_5H_8N - CO - HCl]+
Propanil	217	[M]+
$C_9H_9Cl_2NO$	161	[M + 1 - C_3H_5O]+
	126	[M + 1 - C_3H_5OCl]+
Propiconazole	341	[M]+
$C_{15}H_{17}Cl_2N_3O_2$	259	[M - $C_3H_4N_3$]+
	191	[M - $C_3H_4N_3$ - C_5H_8]+
	173	[M - $C_3H_4N_3$ - $C_5H_{10}O$]+
Tefluthrin	418	[M]+
$C_{17}H_{14}ClF_7O_2$	177	[M - $C_8H_9F_3Cl$ - CO_2]+
	137	[M - $C_{10}H_9O_2F_5Cl$]+
	127	[M - $C_9H_{10}O_2FCl$]+
Tetrachlorvinphos	364	[M]+
$C_{10}H_9Cl_4O_4P$	329	[M - Cl]+
	314	[M - CH_3Cl]+
	109	[M - $C_8H_3Cl_4O$]+
	79	[M - $C_9H_5Cl_4O_2$]
Tetraconazole	371	[M]+
$C_{13}H_{11}Cl_2F_4N_3O$	336	[M - Cl]+
	218	[M - $C_2H_2ClF_4O$]+
	204	[M - $C_3H_4ClF_4O$]+
Trichloronate	332	[M]+
$C_{10}H_{12}Cl_3O_2PS$	299	[M - Cl]+
	297	[M + 2 - Cl]+
	271	[M + 2 - C_2H_4 - Cl]+
	269	[M - C_2H_4 - Cl]+

b. LC/MS/MS

	Ion (m/z)	Fragment
3-HYDROXYCARBOFURAN		
$C_{12}H_{15}NO_4$	255.2	$[M + H + H_2O]+$
	181	$[M + H - C_2H_3NO]+$
	163	$[M + H - C_2H_5NO_2]+$
ACEPHATE		
$C_4H_{11}NO_3P$	184.1	$[M + H]+$
	143	$[M + H - C_2H_2O]+$
	125	$[M + H - C_2H_4O_2]+$
CARBARYL		
$C_{12}H_{11}NO_2$	202.2	$[M + H]+$
	145	$[M + H - C_2H_3NO]+$
	127	$[M + H - C_2H_5NO_2]+$
CARBOFURAN		
$C_{12}H_{15}NO_3$	222.2	$[M + H]+$
	165	$[M + H - C_2H_3NO]+$
	123	$[M + H - C_5H_9NO]+$
CLOFENTEZINE		
$C_{14}H_8Cl_2N_4$	303	$[M + H]+$
	138	$[M + H - C_7H_4N_3Cl]+$
	102.1	$[M + H - C_7H_5N_3Cl2]+$
DIFLUBENZURON		
$C_{14}H_9ClF_2N_2O_2$	311	$[M + H]+$
	158.2	$[M + H - C_7H_4NClO]+$
	141.1	$[M + H - C_7H_7N_2ClO]+$
DIURON		
$C_9H_{10}Cl_2N2O$	233	$[M + H]+$

	160	$[M + H - C_3H_7NO]+$
	72.1	$[M + H - C_6H_5NCl_2]+$
ETHOFUMESATE		
$C_{13}H_{18}O_5S$	304.1	$[M + NH_4]+$
	161.1	$[M + H - C_3H_{10}SO_3]+$
	121.1	$[M + H - C_{10}H_{14}O_2]+$
IMAZALIL		
$C_{14}H_{14}ClN_2O$	297	$[M + H]+$
	255	$[M + C_3H_6]+$
	159	$[M + C_5H_8Cl_2]+$
IMIDACLOPRID		
$C_9H_{10}ClN_5O_2$	256.1	$[M + H]+$
	209	$[M + H - HNO_2]+$
	175	$[M + H - NO_2Cl]+$
INDOXACARB		
$C_{22}H_{17}ClF_3N_3O_7$	528	$[M + H]+$
	203.2	$[M + H - C_{14}H_{14}ClN_2O_5]+$
	150.1	$[M + H - C_{15}H_{14}ClF_3N_2O_4]+$
LINURON		
$C_9H_{10}Cl_2N_2O_2$	249	$[M + H]+$
	183	$[M + H - CH_4OCl]+$
	160	$[M + H - C_3H_7NO_2]+$
METALAXYL		
$C_{15}H_{21}NO_4$	280.1	$[M + H]+$
	220.1	$[M + H - C_2H_4O_2]+$
	192.2	$[M + H - C_4H_8O_2]+$

METHOMYL		
$C_5H_{10}N_2O_2S$	163.1	$[M + H]+$
	106	$[M + H - C_2H_3NO]+$
	88	$[M + H - C_3H_7S]+$
METHOXYFENOZIDE		
$C_{22}H_{28}N_2O_3$	369.1	$[M + H]+$
	149.2	$[M + H - C_{14}H_{22}NO]+$
	91.1	$[M + H - C_{15}H_{22}N_2O_3]+$
MYCLOBUTANIL		
$C_{15}H_{17}ClN_4$	289	$[M + H]+$
	125.1	$[M + H - C_8H_{12}N_4]+$
	70	$[M + H - C_{13}H_{14}ClN]+$
NORFLURAZONE		
$C_{12}H_{9C}lF_3N_3O$	304.1	$[M + H]+$
	284.1	$[M + H - HF]+$
	160	$[M + H - C_7H_3F_3]+$
ETHOPROPHOS		
$C_8H_{19}O_2PS_2$	243.1	$[M + H]+$
	173	$[M + H - C_5H_{10}]+$
PYRIDABEN		
$C_{19}H_{25}ClN_2OS$	365.2	$[M + H]+$
	309	$[M + H - C_4H_8]+$
	147	$[M + H - C_{10}H_{19}ClN_2O]+$
SIMAZINE		
$C_7H_{12}ClN_5$	202	$[M + H]+$
	132	$[M + H - C_4H_8N]+$

	124	$[M + H - C_3H_7Cl]+$
TEBUFENOZIDE		
$C_{22}H_{28}N_2O_2$	353.1	$[M + H]+$
	133	$[M + H - C_{13}H_{20}N_2O]+$
	105	$[M + H - C_{14}H_{20}N_2O2$
THIABENDAZOLE		
$C_{10}H_7N_3S$	202.1	$[M + H]+$
	175	$[M + H - CHN]+$
	131	$[M + H - C_2HNS]+$
THIAMETHOXAM		
$C_8H_{10}ClN_5O_3S$	292	$[M + H]+$
	211	$[M + H - ClNO_2]+$
	181	$[M + H - CH_2ClNO_3]+$

4. Minimum Level of Applicability (MLA)

Compound #	Name	Level (ppb)
1	Alachlor	10
2	Aldrin	25
3	Azinphos methyl	10
4	Bifenthrin	5
5	Boscalid	15
6	Carfentrazone ethyl	5
7	Chlordane cis	5
8	Chlordane trans	5
9	Chlorpyrifos	7.5
10	Chlorpyrifos methyl	5
11	L-Cyhalothrin	5
12	Cypermethrin	15
13	Deltamethrin	10
14	Dichlorvos (DDVP)	15

Compound #	Name	Level (ppb)
15	Dieldrin	25
16	Difenoconazole	15
17	Endosulfan I	22.5
18	Endosulfan II	22.5
19	Endosulfan sulfate	7.5
20	Fipronil	5
21	Heptachlor	25
22	Heptachlor epoxide, cis	25
23	Heptachlor epoxide, trans	25
24	Mirex	10
25	Nonachlor trans	5
26	Oxychlordane	10
27	Permethrin (cis & trans)	15
28	Piperonyl butoxide	22.5
29	Pronamide	5
30	Propanil	6
31	Propiconazole	15
32	Tefluthrin	5
33	Tetrachlorvinphos	10
34	Tetraconazole	5
35	3-Hydroxycarbofuran	20
36	Acephate	10
37	Carbaryl	25
38	Carbofuran	10
39	Clofentezine	25
40	Diflubenzuron	25
41	Diuron	80
42	Ethofumesate	20
43	Imazalil	5
44	Imidacloprid	25
45	Indoxacarb	50
46	Linuron	25
47	Metalaxyl	10

Compound #	Name	Level (ppb)
48	Methomyl	30
49	Methoxyfenozide	10
50	Myclobutanil	10
51	Norflurazon	10
52	Pyridaben	9
53	Simazine	10
54	Tebufenozide	40
55	Thiabendazole	15
56	Thiamethoxam	10

K. APPROVALS AND AUTHORITIES

1. Approvals on file.

2. Issuing Authority: Director, Laboratory Quality Assurance Division.