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Determination of Selected Pesticides Collected on XAD-4 Resin by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) and Gas Chromatography Mass Spectrometry (GC/MS)

1. Scope:

This section method (SM) provides stepwise procedure for the analysis of 36 pesticides trapped in XAD-4 resin and extracted with ethyl acetate. It is followed by all authorized EA personnel. The reporting limits vary from 0.2 µg to 0.5 µg/sample.

2. Principle:

Residues of the selected pesticides are extracted from XAD-4 resin cartridge using ethyl acetate. The twenty compounds are determined by the injection of sample extract into an UPLC equipped with a HSS T3 column and a triple quadrupole mass spectrometer (LC-MS/MS). The other 16 compounds are determined by the injection of sample extract into a GC equipped with a mass selective detector (GC-MSD). The confirmation of compound identity on LC-MS/MS is achieved simultaneously with collision-induced dissociation to produce a product ion for each of the analytes. The confirmation of compound identity with GC-MSD is achieved by the ratio of selected ions.

3. Safety:

3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.

3.2 All solvents should be handled with care in a ventilated area.

4. Interferences:

The response and peak shape of some compounds in matrix extracts versus in solvent shows great differences. To be consistent, standards are prepared in matrix extract for both GC/MS and LC/MS/MS analysis.

5. Apparatus and Equipment:

5.1 Rotary Evaporator (Buchi/Brinkman or equivalent)

5.2 Nitrogen Evaporator (Meyer N-EVAP Organomation Model #112 or equivalent)
5.3 Balance (Mettler PC 4400 or equivalent)
5.4 Sonicator (Branson 5800 or equivalent)
5.5 Vortex-vibrating mixer
5.6 HPLC coupled to a tandem quadrupole mass spectrometer.
5.7 GC coupled to a quadrupole mass spectrometer.
5.8 Eppendorf pipettes 100µL and 1,000µL adjustable volume

6. Standards and Reagents and Supplies:

LC/MS/MS standards

6.1	Acephate	CAS# 30560-19-1
6.2	Bensulide	CAS# 741-58-2
6.3	Chlorpyrifos OA	CAS# 5598-15-2
6.4	DEF	CAS# 78-48-8
6.5	Diazinon	CAS# 333-41-5
6.6	Diazinon OA	CAS# 962-58-3
6.7	Dimethoate	CAS# 60-51-5
6.8	Dimethoate OA	CAS# 1113-02-6
6.9	Diuron	CAS# 330-54-1
6.10	Fenpyroximate	CAS# 134098-61-6
6.11	Malathion OA	CAS# 1634-78-2
6.12	Methidathion	CAS# 950-37-8
6.13	Methomyl	CAS# 16752-77-5
6.14	Metolachlor	CAS# 51218-45-2
6.15	Norflurazon	CAS# 27314-13-2
6.16	Oryzalin	CAS# 19044-88-3
6.17	Oxydemeton methyl	CAS# 301-12-2
6.18	Pendimethalin	CAS# 40487-42-1
6.19	Phosmet	CAS# 732-11-6
6.20	Simazine	CAS# 122-34-9

GC/MS/MS standards

6.21	Captan	CAS# 133-06-2
6.22	Chlorothalonil	CAS # 1897-45-6
6.23	Chlorpyrifos	CAS # 2921-88-2
6.24	Cypermethrin	CAS # 52315-07-8
6.25	Dacthal	CAS # 1861-32-1
6.26	DDVP	CAS # 62-73-7

6.27	Dicofol	CAS # 115-32-2
6.28	Endosulfan I	CAS # 959-98-8
6.29	Endosulfan sulfate	CAS # 1031-07-08
6.30	EPTC	CAS # 759-94-4
6.31	Iprodione	CAS # 36734-19-7
6.32	Malathion	CAS # 121-75-5
6.33	Oxyfluorfen	CAS # 42874-03-3
6.34	Permethrin	CAS # 52645-53-1
6.35	Propargite	CAS # 2312-35-8
6.36	Trifluralin	CAS # 1582-09-8

Reagents and Supplies

6.37 Ethyl Acetate, Burdick & Jackson or equivalent
6.38 Water, MS grade, Burdick & Jackson or equivalent
6.39 Methanol, MS grade, Burdick & Jackson or equivalent
6.40 Formic Acid, HPLC grade
6.41 Ammonium formate, reagent grade or equivalent
6.42 Mason Jars with lids
6.42 Boiling flask, 500 mL
6.43 Glass funnels
6.44 Graduated conical tubes with glass stopper, 15 mL
6.45 Glass wool, Pyrex® fiber glass slivers 8 microns
6.46 Disposable Pasteur pipettes, and other laboratory ware as needed
6.47 HPLC analytical column:
Ace Excel 2 C18-AR, 2.0 µm, 2.1 x 100 mm column or equivalent.
6:48 LCMS Aqueous Solution: For 500 mL, mix 470 ± 2mL H_2O, 25 ± 0.5 mL MeOH, 4.75 ± 0.25 mL 1 M ammonium formate and 0.5 ± 0.05 mL formic acid (FA).
6.49 LCMS Organic Solution: For 500 mL, mix 450 ± 2mL MeOH and 45 ± 0.5 mL H_2O with 4.50 ± 0.25 mL 1 M ammonium formate and 0.5 ± 0.05 mL formic acid.
6.50 Recommended GC analytical column:
Agilent DB5-MS UI 30m X 0.025mmID, 0.025µm film

7. Standards Preparation:

7.1 Combine and dilute each individual standard (at 1 mg/mL, except for Simazine which is at 0.25 mg/mL) from the CDFA/CAC Standards Repository with acetone to a final concentration of 20 µg/mL for each compound.

7.2 The working standards for GC/MS analysis are prepared as shown in the table below:

Working Standard Concentration	Air Network Std Soln Concentration	Volume Added	Final Vol. of Control Matrix
0.05 ug/mL	2.5 ug/mL	40 uL	2 mL
0.25 ug/mL	20 ug/mL	25 uL	2 mL
0.5 ug/mL	20 ug/mL	50 uL	2 mL
1.0 ug/mL	20 ug/mL	100 uL	2 mL
2.5 ug/mL	20 ug/mL	250 uL	2 mL

7.3 The working standards for LC/MS/MS analysis are prepared as shown in the table below:

Working Standard Concentration	Working Standard Concentration	Volume Added	Undiluted Blank Matrix	1:1 EtAc : MeOH Solution
0.0005 ug/mL	0.05 ug/mL	10 µL	30 µL	960 µL
0.001 ug/mL	0.05 ug/mL	20 µL	20 µL	960 µL
0.0025 ug/mL	0.25 ug/mL	10 µL	30 µL	960 µL
0.005 ug/mL	0.5 ug/mL	10 µL	30 µL	960 µL
0.01 ug/mL	1.0 ug/mL	10 µL	30 µL	960 µL
0.025 ug/mL	2.5 ug/mL	10 µL	30 µL	960 µL
0.1 ug/mL	1.0 ug/mL	100 µL	none	900 µL
0.25 ug/mL	2.5 ug/mL	100 µL	none	900 µL

7.4 The expiration date of each mixed working standard is from 12 to 24 months from the preparation date or same as the stock standard, if sooner.

7.5 A portion of the new standard will be vialed and set aside in the refrigerator. This will be used when doing the intermediate check and the check for a new set of standards. The intermediate check will be performed before the standard is 6 months old and be documented along with comparison for that set of standards. There should be <15% difference between the response of the new standard of the intermediate check standard and the response of the vialed standard.

8. Sample Preservation and Storage:

Store all samples waiting for extraction in a designated freezer. Extracts shall be stores in a designated freezer (-15 ± 14 °C).

9. Test Sample Preparation

9.1 Preparation of blank and spike

Matrix blank: Four grams XAD-4 resin in air sample tube.

Matrix spike: Four grams XAD-4 resin in air sampling tube spikes at 2.0 µg of each pesticide.

9.2 Sample Preparation

9.1.1 Remove samples from freezer and allow them to reach ambient temperature.

9.1.2 Add ~60 mL ethyl acetate into a Mason glass jar. Remove the cap from both ends of the sample tube then transfer the resin, screen, and polypropylene ring into glass jar.

9.1.3 Swirl the sample and verify that the components of the cartridge are submerged.

9.1.4 Place the jars in a sonicator and sonicate for 15 minutes at ambient temperature.

9.1.5 Decant the solvent through a funnel containing glass wool into a round bottom flask.

9.1.6 Add another ~60 mL ethyl acetate into the Mason jar. Repeat steps 9.1.3 and 9.1.4.

9.1.7 Pour the entire contents in the Mason jar into the funnel. Rinse the jar with ~50 mL of ethyl acetate and wash the contents of the cartridge through the funnel into the round bottom flask.

9.1.8 Evaporate the solvent in the round bottom flask to about 10 mL on a rotary vacuum evaporator at 40-45°C and ~24 inches of vacuum.

9.1.9 Quantitatively transfer the solution to a 15 mL conical centrifuge tube and evaporate on a Nitrogen-evaporator at 40°C to ~1 mL.

9.1.10 Adjust final volume to 2.0 mL with ethyl acetate. Mix sample extract for 10-20 seconds using a vortex.

9.1.11 For GC/MS analysis, transfer ~300 µL of the sample extract into two autosampler vials containing a glass insert.

9.1.12 For LC/MS/MS analysis, transfer 40 µL of the sample extract to an autosampler vial containing 960 µL of 1:1 ethyl acetate: methanol. Mix the diluted extract for 5-10 seconds using a vortex.

9.1.13 Transfer the remaining extract to an autosampler vial and store in a -20°C freezer.

10. Instrument Calibration:

10.1 The calibration standard curve consists of a minimum of five levels. The lowest level must be at or below the corresponding reporting limit.

10.2 Recommended working standard levels range from 0.025 to 0.5 ng/µL for GC/MS.

10.3 Recommended working standard levels range from 0.0005 to 0.25 µg/µL for the LC/MS/MS.

10.4 Some pesticides had data points excluded from the lowest or highest standards due to weak or strong response.

10.5 Calibration is obtained using a quadratic regression with the correlation coefficient (r) equal to or greater than 0.995, with all levels weighted 1/x.

11. Analysis:

11.1 Injection Scheme

The LC/MS/MS needs to be conditioned with standard or a sample extract 2 to 5 runs before running the following recommended sequence: A set of calibration standards, a solvent blank, a matrix blank, a matrix spike, a solvent blank, a set of up to 12 test samples, then a set of standards, etc.

11.2 Recommended LC/MS/MS Conditions

11.2.1 HPLC Chromatography Conditions: Shimadzu LC30

Column: Ace Excel 2 C18-AR, 2.0 µm, 2.1 x 100 mm column
Column Temperature: 40 °C
Mobile Phase A (MP-A): Aqueous Solution
Mobile Phase B (MP-B): Organic Solution
Gradient:

Time(min)	Flow rate (mL/min)	MP-A	MP-B
Initial	0.4	100	0
0.5	0.4	100	0
2.0	0.4	50	50
10.0	0.4	5	95
14.0	0.4	5	95
16.0	0.4	100	0

Injection Volume: Typically, 3.0 µL, but can vary due to instrument sensitivity

11.2.2 Mass Spectrometer and Operating Parameters

Model:	ABSciex QTRAP 5500
Ionization:	Electrospray Ionization (ESI)
Polarity:	Positive
Curtain Gas:	30
Ion Spray Voltage:	4000
Source Temp:	500°C
Ion Source Gas 1	60
Ion Source Gas 2	60
Entrance Potential	10 V
Collision Gas:	9
Electron Multiplier:	2750 V
Dwell Time per Transition	10 msec

Compound	RT (min)	Precursor Ion	Product Ion	Declustering Potential (DP)	Collision Energy (CE)	Exit Potential (CXP)
Acephate	2.1	184.1	**143.1**	60	25	18
		184.1	95.0	60	30	9
Bensulide	8.7	398.1	**313.9**	80	16	18
		398.1	158.1	80	30	16
Chlorpyrifos OA	8.4	334.0	**278.0**	80	24	18
		334.0	198.0	80	43	18
DEF	11.5	315.0	**169.0**	80	21	15
		315.0	113.0	80	30	15
Diazinon	8.80	305.2	**153.0**	80	28	13
		305.2	169.1	80	27	14
Diazinon OA	6.00	289.1	**233.1**	80	26	17
		289.1	93.0	80	42	15
Dimethoate	3.50	230.0	**199.0**	60	13	18
		230.0	125.1	60	28	10
Dimethoate OA	2.30	214.1	**183.0**	70	15	14
		214.1	125.0	70	28	9
Diuron	5.80	233.1	**71.9**	60	36	12
		233.1	45.9	60	37	12
Fenpyroximate	11.7	422.2	**366.1**	50	24	14
		422.2	135.0	50	43	15
Malathion OA	5	315.2	**99.1**	80	30	11
		315.2	127.0	80	17.5	14
Methomyl	2.4	163.1	**88.0**	35	13	14
		163.1	105.9	35	13	15
Methidathion	7	303.0	**144.9**	100	13	13
		303.0	84.9	100	31	17
Metolachlor	7.9	284.1	**252.2**	70	21	13
		284.1	176.2	70	35	14
Norflurazon	6.4	304.0	**284.1**	90	34	13
		304.0	140.0	90	47	16

Oryzalin	8.3	347.3	**288.1**	30	24	15
		347.3	305.1	30	18.5	15
Oxydemeton methyl	2.4	247.1	**169.0**	90	19	15
		247.1	109.0	90	37	12
Pendimethalin	11.2	282.1	**212.1**	40	16	15
		282.1	194.1	40	25	17
Phosmet	7.4	318.0	**160.0**	80	21	14
		318.0	133.0	80	50	16
Simazine	4.5	202.0	**124.2**	60	25	15
		202.0	132.1	60	26	11

Quantitation transition is in bold.

11.3 Recommended GC/MS Conditions:

11.3.1 GC Chromatography Conditions: Agilent 7890 GC
Column: Agilent DB5-MS UI, 30m x 0.25mmID x 0.25 µm df
Carrier Gas: Helium at constant pressure, ~60 psi
Flow Rate: 1.3 mL/minute
Injection-Type: Splitless Injection, 10.39 psi
Injector Temperature: 230 °C
Injection Volume: 2.0 µL

Gradient:

Recommended GC Instrument parameters:
Oven temperature 50 °C, hold 2 min., ramp 20 °C/min. to 200 °C, hold 1 min., ramp 5 °C/min to 275°C, hold 8 minutes

11.3.2 Recommended Mass Spectrometer and Operating Parameters:

Model: Agilent Technologies Mass Detector Model 5975C MSD
Ionization: Electron Impact (EI)
Polarity: Positive
Transfer Line Heater: 270°C
MS Source Temperature: 230
MS Quad Temperature: 150
Dwell Time: 50 ms

Selected Ions: See Table below

Compound Name	Retention Time (Min)	Selected Ions	Group Number	Group Start Time(Min)
EPTC	8.97	**189**, 128, 86	1	6.00
DDVP	8.04	**185** 109, 145	1	6.00
Trifluralin	11.37	**306**, 264, 335	2	10.00
Chlorothalonil	12.96	**266**, 229, 264	2	10.00
Dacthal	15.24	**301**, 303, 332	3	13.50
Chlorpyrifos	15.1	**314**, 197, 258	3	13.50
p,p-Dicofol	15.59	**250**, 139, 111	3	13.50
Malathion	14.38	**173**, 125, 93	3	13.50
Endosulfan I	17.54	**339**, 195, 241, 261	4	17.00
Endosulfan sulfate	20.66	**272**, 422, 229	5	19.50
Oxyfluorfen	18.25	**361**, 300, 252	4	17.00
Propargite	21.33	**135**, 173, 350	5	19.50
Iprodione	22.11	**314**, 316, 187	5	19.50
Permethrin	26.24	**183**, 163, 127	6	23.00
Cypermethrin	28.28	**181**, 163, 209	7	27.00
Captan	16.65	**79**, 107, 117	3	10.00

Quantitation transition is in bold.

12. Quality Control:

12.1 Method Detection Limits (MDL)

Method Detection Limit (MDL) refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, 7 XAD-4 resin cartridge samples are spiked at 0.2 µg for each analyte and processed through the entire method along with a blank. The standard deviation derived from the spiked sample recoveries was used to calculate the MDL using the following equation:

MDL = tS

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicates used to determine the MDL, t=3.143.

The results for the standard deviations (SD) and MDL from the LC/MS/MS and GC/MS analysis are shown in Appendix 1 and 3, respectively.

12.2 Reporting Limit (RL)

Reporting limit (RL) refers to a level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. The RL is chosen in a range 1-5 times the MDL. The reporting limit for this method is 0.2 - 0.5 µg for all compounds. The RL are listed in Appendix 1 and 3.

12.3 Method Validation

The method validation consisted of five sample sets. Each set included five levels of fortification and a method blank. All spikes and method blanks were processed through the entire analytical method. Spike levels and recoveries for the analytes are shown in Appendix 2 and 4.

12.4 Control Charts and Limits

A control chart was generated using the data from the method validation. The upper and lower control limits are set at ± 3 standard deviations of the percent recovery.

12.5 Acceptance Criteria

12.5.1 Each set of samples will have a matrix blank and a spiked matrix sample.

12.5.2 The retention time should be within ± 0.1 minute of that of the standards.

12.5.3 The recoveries of the matrix spikes shall be within the control limits.

12.5.3.1 When spike recoveries fall outside the control limits, the chemist must investigate the cause. The entire extraction set of samples is re-analyzed. If the spike recoveries fall within the limit, then the results from the re-analyzed samples shall be reported.

12.5.3.2 If the spike recoveries still fall outside the control limits, the client will be notified.

12.5.4 If the calibration curve does not meet the acceptance criteria, the samples shall be re-analyzed. If the calibration criteria are met, the sample results will be reported. If the calibration criteria are still not met, a method deviation will be prepared and approved by the supervisor of designee. The client will be notified of the deviation and a copy of the method deviation detailing what was changed and why it was changed will be included with the samples results and the data will be flagged to let the data user know of the deviation.

12.5.5 The sample shall be diluted if results fall above the calibration curve.

12.5.6 Bracketing standard curves should have a percent change less than 20%.

12.5.7 Relative abundance of qualifier ions to be within ± 30 %.

13. Calculations:

Quantitation is based on an external standard (ESTD) calculation using either the peak area or height. The Tandem Quadruple LC/MS/MS software used a quadratic curve fit, with all levels weighted 1/x. Alternatively, at the chemist's discretion, sample results may be calculated using the response factor for the standard.

$$ppb = \frac{(\text{sample peak area or ht}) \times (\text{std conc.}) \times (\text{std vol. Injected}) \times (\text{final vol. of sample})(1000\ \mu L/mL)}{(\text{std peak area or ht}) \times (\text{sample vol. injected}) \times (\text{sample wt (g)})}$$

14. Reporting Procedure:

Sample results are reported out according to the client's analytical laboratory specification sheets.

15. Trapping Efficiency Study:

A trapping efficiency study was performed with this validation. The experiment consisted of fortifying XAD-4 columns (N=3) with at three levels, 0.2, 1 and 5 µg of each analyte. A fortified column at each level and a blank column was placed on a pump and air was passed through the columns for at least 24 hours. The columns were then stored in a freezer until analysis. The results of the study are shown in Appendix V and VI.

16. Storage Stability Study:

A storage stability study was also performed with this validation. The experiment consisted of fortifying XAD-4 columns (N=27) with 1 µg of each analyte. Twenty-four of the fortified columns and 8 blank columns were stored in a freezer until analysis. A blank and the three remaining fortified columns were extracted. These samples were the Day 0 analysis. The stored columns were analyzed on Days 3, 7, 14, 21, 29, 50 and 66. One additional storage stability experiment will be performed in the future. The results of the storage stability study (through Day 29 only) are shown in Appendix VII and VIII.

17. Discussion and References:

17.1 The extraction was modified from dripping ethyl acetate through the XAD-4 resin sample tube to placing the XAD-4 resin into a Mason jar and sonicating for 15 minutes twice resulting in a more robust extraction.

18. References:

18.1 Schwarz, Timo; Snow, Timothy A.; Santee, Christopher J.; Mulligan, Christopher C.; Class, Thomas; Wadsley, Michael P.; and Nanita, Sergio C., "QuEChERS Multiresidue Method Validation and Mass Spectrometric Assessment for the Novel Anthranilic Diamide Insecticides Chlorantraniliprole and Cyantraniliprole", J. Agric. Food Chem. 2011, 59, 814-821

18.2 "Crop Protection Handbook, 2010", MeisterPro Executive Office 27722 Euclid Ave., Willoughby, OH.

Appendix I

Results from MDL Experiment (Fortify at 0.2 µg), LC/MS/MS Analysis

All LC/MS/MS compounds have a reporting limit of 0.2 µg/sample

Compound Name	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	SD	MDL
Acephate	0.172	0.176	0.160	0.134	0.130	0.182	0.161	0.0202	0.0634
Bensulide	0.171	0.203	0.157	0.138	0.139	0.174	0.150	0.0230	0.0722
Chlorpyrifos OA	0.163	0.172	0.160	0.136	0.136	0.159	0.157	0.0137	0.0430
DEF	0.166	0.172	0.161	0.139	0.135	0.163	0.154	0.0139	0.0436
Diazinon	0.165	0.173	0.162	0.136	0.134	0.157	0.155	0.0146	0.0458
Diazinon OA	0.164	0.171	0.164	0.138	0.136	0.159	0.156	0.0134	0.0421
Dimethoate	0.169	0.177	0.162	0.137	0.134	0.159	0.156	0.0158	0.0496
Dimethoate OA	0.169	0.181	0.157	0.135	0.132	0.180	0.166	0.0199	0.0625
Diuron	0.165	0.178	0.165	0.139	0.134	0.157	0.154	0.0154	0.0484
Fenpyroximate	0.164	0.172	0.160	0.136	0.133	0.165	0.153	0.0150	0.0471
Malathion OA	0.165	0.169	0.162	0.137	0.136	0.159	0.155	0.0132	0.0414
Methomyl	0.161	0.174	0.156	0.133	0.129	0.173	0.158	0.0178	0.0559
Methidathion	0.152	0.188	0.164	0.146	0.142	0.177	0.135	0.0194	0.0609
Metolachlor	0.162	0.171	0.162	0.135	0.132	0.156	0.153	0.0145	0.0455
Norflurazon	0.163	0.170	0.162	0.138	0.133	0.154	0.153	0.0135	0.0424
Oryzalin	0.146	0.160	0.189	0.151	0.138	0.166	0.169	0.0169	0.0531
Oxydemeton methyl	0.165	0.165	0.152	0.131	0.129	0.171	0.159	0.0169	0.0531
Pendimethalin	0.176	0.182	0.174	0.140	0.145	0.167	0.165	0.0159	0.0499
Phosmet	0.154	0.166	0.156	0.136	0.136	0.164	0.162	0.0126	0.0396
Simazine	0.167	0.173	0.167	0.139	0.141	0.160	0.157	0.0132	0.0414

Appendix II

Results (% Recovery) from Method Validation, LC/MS/MS Analysis

Compound	MV Run	Blank	Spike Level 0.2 µg	0.5 µg	1 µg	2 µg	5 µg	Control Limits %	
Acephate	1	ND	89.5	87.2	90.3	95.5	87.2	**Mean:**	**92.5**
	2	ND	89.0	90.4	88.6	95.0	92.6	**SD:**	**7.50**
	3	ND	75.5	88.8	93.0	88.0	86.0	**UCL:**	**115**
	4	ND	86.0	84.6	96.4	114	96.2	**uwl:**	**108**
	5	ND	102	99.0	96.2	101	99.8	**lwl:**	**77.5**
								LCL:	**70.0**
Bensulide	1	ND	96.5	83.8	85.3	92.0	92.8	**Mean:**	**90.8**
	2	ND	90.0	89.4	83.6	93.0	97.2	**SD:**	**8.36**
	3	ND	78.0	92.2	91.2	79.0	82.6	**UCL:**	**116**
	4	ND	83.0	75.6	86.4	94.5	90.6	**uwl:**	**108**
	5	ND	98.5	102	101	110	101	**lwl:**	**74.1**
								LCL:	**65.7**
Chlorpyrifos OA	1	ND	89.0	83.2	86.3	91.5	89.2	**Mean:**	**88.9**
	2	ND	85.5	85.8	85.3	87.5	92.6	**SD:**	**6.29**
	3	ND	74.0	88.2	91.7	90.0	88.2	**UCL:**	**108**
	4	ND	80.5	79.4	86.1	102	87.8	**uwl:**	**101**
	5	ND	95.0	96.0	91.1	98.5	98.6	**lwl:**	**76.3**
								LCL:	**70.0**
DEF	1	ND	86.5	83.8	87.8	91.0	86.2	**Mean:**	**89.3**
	2	ND	86.0	85.4	86.5	88.0	92.6	**SD:**	**6.47**
	3	ND	75.5	88.6	90.6	91.0	89.6	**UCL:**	**109**
	4	ND	81.0	79.6	86.2	103	88.6	**uwl:**	**102**
	5	ND	97.0	96.0	90.9	101	99.6	**lwl:**	**76.4**
								LCL:	**69.9**
Diazinon	1	ND	92.0	83.4	88.1	90.0	87.6	**Mean:**	**88.5**
	2	ND	87.0	85.6	85.2	86.5	91.2	**SD:**	**6.11**
	3	ND	74.0	89.6	89.6	88.0	87.4	**UCL:**	**107**
	4	ND	80.0	79.0	83.9	102	88.0	**uwl:**	**101**
	5	ND	94.0	94.6	89.0	98.0	97.6	**lwl:**	**76.3**
								LCL:	**70.2**

Results (% Recovery) from Method Validation, LC/MS/MS Analysis

			Spike Level					Control Limits	
Compound	**MV Run**	**Blank**	**0.2 µg**	**0.5 µg**	**1 µg**	**2 µg**	**5 µg**	**%**	
Diazinon OA	1	ND	88.5	84.6	88.0	91.5	90.2	**Mean:**	**89.4**
	2	ND	86.5	86.2	84.4	87.5	91.8	**SD:**	**6.46**
	3	ND	73.5	88.2	90.9	92.5	88.8	**UCL:**	**109**
	4	ND	81.0	79.4	86.8	103	89.0	**uwl:**	**102**
	5	ND	94.5	96.6	92.2	100	99.0	**lwl:**	**76.5**
								LCL:	**70.0**
Dimethoate	1	ND	88.0	85.4	88.2	92.5	88.4	**Mean:**	**90.0**
	2	ND	87.0	86.6	86.4	87.5	94.8	**SD:**	**6.87**
	3	ND	74.5	89.0	92.8	89.5	88.8	**UCL:**	**111**
	4	ND	80.5	80.2	87.2	104	89.0	**uwl:**	**104**
	5	ND	96.5	97.2	92.7	102	102	**lwl:**	**76.3**
								LCL:	**69.4**
Dimethoate OA	1	ND	90.5	91.0	90.8	96.5	90.4	**Mean:**	**93.6**
	2	ND	89.0	89.8	89.1	90.0	91.2	**SD:**	**8.03**
	3	ND	77.5	88.2	91.6	90.0	85.6	**UCL:**	**118**
	4	ND	90.0	88.0	100	120	99.6	**uwl:**	**110**
	5	ND	101	99.0	97.4	101	103	**lwl:**	**77.5**
								LCL:	**69.5**
Diuron	1	ND	87.5	82.4	84.9	91.0	87.8	**Mean:**	**88.9**
	2	ND	87.0	86.4	85.3	87.0	91.2	**SD:**	**6.08**
	3	ND	76.0	89.2	91.8	89.5	89.6	**UCL:**	**107**
	4	ND	81.0	80.2	86.1	103	88.4	**uwl:**	**101**
	5	ND	94.5	96.4	90.0	98.0	98.8	**lwl:**	**76.7**
								LCL:	**70.7**
Fenpyroximate	1	ND	87.5	84.0	87.6	90.0	85.8	**Mean:**	**89.2**
	2	ND	86.0	87.8	87.3	89.0	91.4	**SD:**	**6.07**
	3	ND	74.5	88.2	90.6	91.0	88.4	**UCL:**	**107**
	4	ND	81.0	81.2	86.0	102	88.2	**uwl:**	**101**
	5	ND	95.0	96.0	92.3	100	98.4	**lwl:**	**77.1**
								LCL:	**71.0**

Results (% Recovery) from Method Validation, LC/MS/MS Analysis

Compound	MV Run	Blank	Spike Level 0.2 µg	0.5 µg	1 µg	2 µg	5 µg	Control Limits %	
Malathion OA	1	ND	88.5	82.6	86.2	93.5	87.6	**Mean:**	**88.5**
	2	ND	84.0	85.0	84.3	87.0	92.0	**SD:**	**6.02**
	3	ND	75.0	88.0	91.5	90.0	88.2	**UCL:**	**107**
	4	ND	82.0	81.2	86.3	104	90.6	**uwl:**	**101**
	5	ND	90.0	91.6	87.9	97.0	99.2	**lwl:**	**76.5**
								LCL:	**70.4**
Methomyl	1	ND	91.0	90.2	89.2	94.5	90.8	**Mean:**	**91.1**
	2	ND	82.0	86.6	86.2	87.0	89.2	**SD:**	**7.94**
	3	ND	72.5	88.6	92.9	88.0	87.8	**UCL:**	**115**
	4	ND	84.5	83.4	91.7	113	93.2	**uwl:**	**107**
	5	ND	103	98.2	94.7	97.5	103	**lwl:**	**75.2**
								LCL:	**67.3**
Methidathion	1	ND	88.5	87.0	87.3	96.0	89.6	**Mean:**	**90.7**
	2	ND	91.5	75.4	85.2	90.0	89.8	**SD:**	**8.82**
	3	ND	73.5	93.4	94.1	86.5	92.4	**UCL:**	**117**
	4	ND	77.5	86.0	88.5	98.5	84.8	**uwl:**	**108**
	5	ND	104	102	92.0	101	113	**lwl:**	**73.1**
								LCL:	**64.2**
Metolachlor	1	ND	86.0	83.0	84.4	89.5	86.8	**Mean:**	**88.3**
	2	ND	85.0	84.8	84.8	87.0	91.0	**SD:**	**6.45**
	3	ND	74.0	87.2	90.9	90.0	89.0	**UCL:**	**108**
	4	ND	79.0	79.4	85.3	102	89.2	**uwl:**	**101**
	5	ND	96.0	94.2	91.4	98.5	99.0	**lwl:**	**75.4**
								LCL:	**69.0**
Norflurazon	1	ND	88.0	82.4	86.6	90.5	88.4	**Mean:**	**88.8**
	2	ND	87.0	85.6	84.9	86.5	91.4	**SD:**	**6.23**
	3	ND	75.0	87.8	90.5	90.5	89.2	**UCL:**	**107**
	4	ND	80.0	80.2	86.0	103	88.6	**uwl:**	**101**
	5	ND	95.5	94.6	91.0	99.0	98.6	**lwl:**	**76.3**
								LCL:	**70.1**

Results (% Recovery) from Method Validation, LC/MS/MS Analysi

Compound	MV Run	Blank	Spike Level 0.2 µg	0.5 µg	1 µg	2 µg	5 µg	Control Limits %	
Oryzalin	1	ND	81.5	78.4	87.0	91.0	87.4	**Mean:**	**91.2**
	2	ND	95.0	87.4	86.0	89.0	90.4	**SD:**	**7.86**
	3	ND	80.0	89.4	91.0	93.5	90.0	**UCL:**	**115**
	4	ND	80.5	84.6	91.5	106	90.0	**uwl:**	**107**
	5	ND	105	102	96.7	104	102	**lwl:**	**75.5**
								LCL:	**67.6**
Oxydemeton-methyl	1	ND	91.5	89.6	89.9	99.0	88.4	**Mean:**	**91.4**
	2	ND	83.0	84.6	83.2	89.0	93.4	**SD:**	**8.64**
	3	ND	71.0	86.0	89.9	88.0	87.8	**UCL:**	**117**
	4	ND	87.5	84.0	95.3	118	95.6	**uwl:**	**109**
	5	ND	97.5	96.4	96.1	99.5	101	**lwl:**	**74.1**
								LCL:	**65.5**
Pendimethalin	1	ND	96.0	83.6	92.2	93.0	86.8	**Mean:**	**91.6**
	2	ND	93.5	90.4	88.0	89.5	90.0	**SD:**	**6.05**
	3	ND	80.5	94.2	97.3	92.0	90.6	**UCL:**	**110**
	4	ND	82.0	81.0	89.4	101	87.2	**uwl:**	**104**
	5	ND	102	97.2	93.5	99.5	99.2	**lwl:**	**79.5**
								LCL:	**73.5**
Phosmet	1	ND	92.5	86.4	87.8	91.5	87.2	**Mean:**	**88.0**
	2	ND	82.0	81.6	81.4	81.5	85.6	**SD:**	**6.32**
	3	ND	76.5	84.8	87.9	88.0	86.4	**UCL:**	**107**
	4	ND	84.5	81.2	85.1	104	89.2	**uwl:**	**101**
	5	ND	95.0	94.4	88.8	98.5	97.2	**lwl:**	**75.4**
								LCL:	**69.0**
Simazine	1	ND	89.0	86.0	86.9	90.5	86.8	**Mean:**	**89.7**
	2	ND	86.5	87.2	86.1	87.0	92.0	**SD:**	**6.08**
	3	ND	74.5	87.6	90.5	91.0	88.8	**UCL:**	**108**
	4	ND	84.5	81.8	87.1	102	89.6	**uwl:**	**102**
	5	ND	99.0	96.4	92.4	99.5	99.4	**lwl:**	**77.5**
								LCL:	**71.5**

Appendix III

Results from MDL Experiment (Fortify at 0.2 µg), GC/MS/MS Analysis

Compound Name	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	SD	MDL
EPTC	0.155	0.168	0.159	0.131	0.131	0.144	0.146	0.01395	0.0438
DDVP	0.150	0.165	0.159	0.133	0.132	0.142	0.143	0.01249	0.0392
Trifluralin	0.137	0.151	0.150	0.122	0.123	0.136	0.135	0.01146	0.0360
Chlorothalonil	0.147	0.167	0.156	0.126	0.125	0.147	0.144	0.01513	0.0475
Dacthal	0.161	0.178	0.168	0.139	0.139	0.158	0.156	0.01431	0.0449
Chlorpyrifos	0.154	0.171	0.163	0.133	0.135	0.151	0.151	0.01374	0.0431
pp-Dicofol	0.160	0.178	0.197	0.176	0.180	0.170	0.181	0.01128	0.0354
Malathion	0.155	0.173	0.173	0.146	0.141	0.158	0.158	0.01219	0.0383
Endosulfan 1	0.162	0.177	0.173	0.140	0.142	0.158	0.155	0.01409	0.0442
Endosulfan Sulfate	0.157	0.174	0.163	0.136	0.133	0.161	0.157	0.01479	0.0464
Oxyfluorfen	0.125	0.139	0.135	0.109	0.112	0.135	0.129	0.01173	0.0368
Propargite	0.136	0.158	0.137	0.114	0.113	0.157	0.136	0.01798	0.0565
Iprodione	0.168	0.187	0.168	0.137	0.135	0.165	0.166	0.01856	0.0583
Permethrin	0.177	0.190	0.175	0.145	0.145	0.178	0.175	0.01737	0.0545
Cypermethrin	0.174	0.202	0.171	0.145	0.136	0.188	0.185	0.02364	0.0742
Captain	0.168	0.195	0.165	0.137	0.133	0.155	0.157	0.02078	0.0652

All GC/MS compounds have a reporting limit of 0.50 µg/sample except for EPTC, Dacthal, Malathion and Iprodione which have a reporting limit of 0.2 µg/sample.

Appendix IV

Results (% Recovery) from Method Validation, GC/MS

Compound	MV Run	Blank	Spike Level 0.2 µg	0.5 µg	1 µg	2 µg	5 µg	Control Limits %	
EPTC	1	ND	91.5	85.2	85.0	88.5	88.6	**Mean:**	**84.2**
	2	ND	86.0	85.4	81.4	81.5	83.2	**SD:**	**5.24**
	3	ND	73.5	86.8	89.6	86.5	81.0	**UCL:**	**100**
	4	ND	76.0	75.6	80.9	88.0	73.4	**uwl:**	**95**
	5	ND	89.5	89.6	85.7	90.0	82.4	**lwl:**	**73.7**
								LCL:	**68.5**
DDVP	1	ND	93.5	86.4	86.9	89.5	89.6	**Mean:**	**84.4**
	2	ND	82.5	82.0	79.8	81.0	85.2	**SD:**	**5.72**
	3	ND	73.0	87.6	89.9	87.5	83.2	**UCL:**	**102**
	4	ND	74.0	75.0	80.3	88.5	75.6	**uwl:**	**96**
	5	ND	88.0	89.2	85.7	92.5	82.6	**lwl:**	**73.0**
								LCL:	**67.2**
Trifluralin	1	ND	80.0	82.0	87.9	95.5	94.6	**Mean:**	**85.1**
	2	ND	73.5	77.8	80.6	85.0	90.4	**SD:**	**8.90**
	3	ND	66.5	85.2	92.3	93.0	88.8	**UCL:**	**112**
	4	ND	69.0	74.6	83.7	96.0	82.4	**uwl:**	**103**
	5	ND	84.5	91.8	92.7	102	77.2	**lwl:**	**67.3**
								LCL:	**58.4**
Chlorothalonil	1	ND	88.0	80.0	86.3	97.0	89.6	**Mean:**	**85.8**
	2	ND	85.5	80.0	81.2	86.0	85.4	**SD:**	**6.18**
	3	ND	71.5	87.0	90.2	89.0	86.0	**UCL:**	**104**
	4	ND	75.5	81.0	84.4	92.5	79.4	**uwl:**	**98**
	5	ND	87.0	89.6	90.9	99.0	82.2	**lwl:**	**73.4**
								LCL:	**67.3**
Dacthal	1	ND	96.0	89.8	90.4	94.5	92.4	**Mean:**	**89.9**
	2	ND	89.5	86.2	84.4	85.0	89.2	**SD:**	**5.72**
	3	ND	78.0	91.6	94.7	91.5	87.4	**UCL:**	**107**
	4	ND	82.0	83.2	86.9	95.5	81.4	**uwl:**	**101**
	5	ND	96.5	97.4	95.0	101	87.2	**lwl:**	**78.5**
								LCL:	**72.7**

Results (% Recovery) from Method Validation, GC/MS

Compound	MV Run	Blank	Spike Level 0.2 µg	0.5 µg	1 µg	2 µg	5 µg	Control Limits %	
Chlorpyrifos	1	ND	91.5	88.2	90.0	95.5	94.0	**Mean:**	**88.8**
	2	ND	85.5	84.4	84.3	86.0	89.2	**SD:**	**6.20**
	3	ND	75.5	89.6	94.4	91.5	88.0	**UCL:**	**107**
	4	ND	77.5	81.6	86.5	96.0	81.8	**uwl:**	**101**
	5	ND	93.5	95.6	94.6	101	83.4	**lwl:**	**76.4**
								LCL:	**70.2**
pp-Dicofol	1	ND	95.5	91.6	94.0	97.0	104	**Mean:**	**92.3**
	2	ND	87.5	83.4	84.8	87.0	90.2	**SD:**	**7.14**
	3	ND	88.0	100	112	98.0	94.4	**UCL:**	**114**
	4	ND	84.0	84.6	89.4	103	84.2	**uwl:**	**107**
	5	ND	92.5	94.0	88.0	91.5	88.4	**lwl:**	**78.0**
								LCL:	**70.9**
Malathion	1	ND	94.0	89.6	92.9	101	94.4	**Mean:**	**90.6**
	2	ND	83.5	85.2	86.7	88.0	90.6	**SD:**	**6.72**
	3	ND	83.5	92.4	97.0	93.5	89.4	**UCL:**	**111**
	4	ND	81.5	84.2	88.7	98.0	83.2	**uwl:**	**104**
	5	ND	97.0	96.6	97.6	102	75.0	**lwl:**	**77.2**
								LCL:	**70.4**
Endosulfan 1	1	ND	96.0	89.8	90.5	94.5	92.2	**Mean:**	**89.0**
	2	ND	88.5	85.6	84.4	84.5	88.2	**SD:**	**5.19**
	3	ND	78.5	90.0	93.4	90.5	87.6	**UCL:**	**105**
	4	ND	81.0	82.4	85.8	95.5	81.0	**uwl:**	**99**
	5	ND	94.0	94.4	92.7	97.0	86.0	**lwl:**	**78.6**
								LCL:	**73.4**
Endosulfan Sulfate	1	ND	101	86.4	91.9	102	93.8	**Mean:**	**89.3**
	2	ND	90.0	80.4	84.9	87.5	86.2	**SD:**	**6.92**
	3	ND	74.5	85.8	92.0	90.5	87.8	**UCL:**	**110**
	4	ND	81.5	84.2	88.7	97.5	83.0	**uwl:**	**103**
	5	ND	90.5	93.2	92.9	103	82.2	**lwl:**	**75.5**
								LCL:	**68.5**
Oxyfluorfen	1	ND	79.5	80.0	91.6	102	96.2	**Mean:**	**83.9**
	2	ND	71.0	69.8	80.2	90.0	91.6	**SD:**	**13.35**
	3	ND	59.0	76.2	92.3	96.0	90.0	**UCL:**	**124**
	4	ND	63.0	72.2	86.3	104	85.8	**uwl:**	**111**
	5	ND	73.0	86.0	93.5	108	61.2	**lwl:**	**57.2**
								LCL:	**43.9**

Results (% Recovery) from Method Validation, GC/MS

Compound	MV Run	Blank	Spike Level 0.2 µg	0.5 µg	1 µg	2 µg	5 µg	Control Limits %	
Propargite	1	ND	90.5	83.0	95.0	112	97.6	**Mean:**	**87.2**
	2	ND	77.0	76.8	82.7	92.0	91.4	**SD:**	**11.85**
	3	ND	62.5	77.4	90.0	94.5	91.2	**UCL:**	**123**
	4	ND	68.0	76.6	87.6	104	86.6	**uwl:**	**111**
	5	ND	72.5	84.8	93.0	109	85.2	**lwl:**	**63.5**
								LCL:	**51.7**
Iprodione	1	ND	98.0	86.0	93.1	104	97.2	**Mean:**	**91.1**
	2	ND	96.0	84.2	89.9	93.0	89.0	**SD:**	**7.29**
	3	ND	74.0	86.4	95.1	92.0	89.2	**UCL:**	**113**
	4	ND	85.5	88.0	92.3	101	84.8	**uwl:**	**106**
	5	ND	91.0	93.6	94.0	104	76.4	**lwl:**	**76.5**
								LCL:	**69.2**
Permethrin	1	ND	101	89.8	96.8	103	96.6	**Mean:**	**92.0**
	2	ND	97.0	86.2	89.0	93.5	86.8	**SD:**	**6.61**
	3	ND	77.5	90.2	96.9	91.5	89.4	**UCL:**	**112**
	4	ND	88.5	90.2	94.2	100	85.8	**uwl:**	**105**
	5	ND	92.5	92.4	91.2	102	76.8	**lwl:**	**78.8**
								LCL:	**72.2**
Cypermethrin	1	ND	96.5	82.4	94.2	109	98.4	**Mean:**	**91.5**
	2	ND	98.5	81.8	87.8	94.5	89.8	**SD:**	**8.83**
	3	ND	73.5	82.0	93.8	91.5	90.8	**UCL:**	**118**
	4	ND	93.0	91.6	96.1	104	88.2	**uwl:**	**109**
	5	ND	90.5	89.8	93.0	105	70.6	**lwl:**	**73.8**
								LCL:	**65.0**
Captain	1	ND	104	88.6	87.9	103	89.8	**Mean:**	**88.2**
	2	ND	99.0	81.2	81.5	83.0	86.2	**SD:**	**10.17**
	3	ND	76.0	82.8	90.3	89.0	86.6	**UCL:**	**119**
	4	ND	79.0	82.0	85.8	97.0	82.4	**uwl:**	**109**
	5	ND	94.0	93.0	95.7	108	59.2	**lwl:**	**67.9**
								LCL:	**57.7**

Appendix V

Results from Trapping Efficiency Study (Fortify at 0.2, 1 and 5 µg), LC/MS/MS Analysis

Result: % Recovery

Compound	Sample Name	Blank	Spike Level 2 µg	0.2 µg	1 µg	5 µg			Validation Control Limits (%)	
Acephate	Controls	ND	94.5							
	Group A	ND		85.0	86.2	82.2	**Mean:**	**82.8**	**Mean:**	**92.5**
	Group B	ND		83.5	79.6	83.2	**SD:**	**3.45**	**UCL:**	**115**
	Group C	ND		77.0	80.6	88.2	**% CV**	**4.17**	**LCL:**	**70.0**
Bensulide	Controls	ND	86.5							
	Group A	ND		94.0	92.9	92.6	**Mean:**	**89.1**	**Mean:**	**90.8**
	Group B	ND		85.5	85.9	84.6	**SD:**	**5.20**	**UCL:**	**116**
	Group C	ND		81.0	88.9	96.6	**% CV**	**5.84**	**LCL:**	**65.7**
Chlorpyrifos OA	Controls	ND	93.0							
	Group A	ND		85.5	85.2	91.4	**Mean:**	**86.0**	**Mean:**	**88.9**
	Group B	ND		88.5	81.6	88.2	**SD:**	**4.25**	**UCL:**	**108**
	Group C	ND		80.5	81.3	91.6	**% CV**	**4.94**	**LCL:**	**70.0**
DEF	Controls	ND	94.0							
	Group A	ND		85.0	84.0	87.8	**Mean:**	**84.3**	**Mean:**	**89.3**
	Group B	ND		87.5	80.6	87.8	**SD:**	**4.59**	**UCL:**	**109**
	Group C	ND		76.5	79.2	90.0	**% CV**	**5.44**	**LCL:**	**69.9**
Diazinon	Controls	ND	93.0							
	Group A	ND		87.0	84.2	86.2	**Mean:**	**84.6**	**Mean:**	**88.5**
	Group B	ND		87.5	81.0	86.4	**SD:**	**3.82**	**UCL:**	**107**
	Group C	ND		79.0	80.0	90.2	**% CV**	**4.52**	**LCL:**	**70.2**

Results from Trapping Efficiency Study (Fortify at 0.2, 1 and 5 µg), LC/MS/MS Analysis

Compound	Sample Name	Blank	Spike Level 2 µg	0.2 µg	1 µg	5 µg			Validation Control Limits (%)	
Diazinon OA	Controls	ND	93.0							
	Group A	ND		85.5	84.3	89.8	**Mean:**	**84.9**	**Mean:**	**89.4**
	Group B	ND		86.5	81.4	88.2	**SD:**	**4.51**	**UCL:**	**109**
	Group C	ND		77.5	80.1	90.8	**% CV**	**5.31**	**LCL:**	**70.0**
Dimethoate	Controls	ND	93.0							
	Group A	ND		83.0	82.0	83.4	**Mean:**	**81.8**	**Mean:**	**90.0**
	Group B	ND		85.0	78.0	83.8	**SD:**	**3.58**	**UCL:**	**111**
	Group C	ND		76.0	78.2	86.6	**% CV**	**4.38**	**LCL:**	**69.4**
Dimethoate OA	Controls	ND	88.5							
	Group A	ND		84.0	81.1	82.0	**Mean:**	**81.0**	**Mean:**	**93.6**
	Group B	ND		85.0	75.6	84.0	**SD:**	**3.44**	**UCL:**	**118**
	Group C	ND		77.5	77.2	83.0	**% CV**	**4.25**	**LCL:**	**69.5**
Diuron	Controls	ND	93.5							
	Group A	ND		84.0	82.9	86.8	**Mean:**	**84.0**	**Mean:**	**88.9**
	Group B	ND		88.0	79.6	87.4	**SD:**	**4.68**	**UCL:**	**107**
	Group C	ND		77.5	78.7	91.0	**% CV**	**5.57**	**LCL:**	**70.7**
Fenpyroximate	Controls	ND	93.5							
	Group A	ND		84.0	83.9	88.4	**Mean:**	**84.0**	**Mean:**	**89.2**
	Group B	ND		85.5	80.9	87.6	**SD:**	**4.65**	**UCL:**	**107**
	Group C	ND		77.0	78.2	90.8	**% CV**	**5.54**	**LCL:**	**71.0**

Results from Trapping Efficiency Study (Fortify at 0.2, 1 and 5 µg), LC/MS/MS Analysis

Compound	Sample Name	Spike Level						Validation Control Limits (%)	
		Blank	2 µg	0.2 µg	1 µg	5 µg			
Malathion OA	Controls	ND	94.0						
	Group A	ND		84.0	83.4	89.4	**Mean: 85.2**	**Mean:**	**88.5**
	Group B	ND		90.0	80.5	89.8	**SD: 5.12**	**UCL:**	**107**
	Group C	ND		78.0	80.1	91.8	**% CV 6.01**	**LCL:**	**70.4**
Methomyl	Controls	ND	92.0						
	Group A	ND		81.0	79.5	79.4	**Mean: 79.3**	**Mean:**	**91.1**
	Group B	ND		82.5	74.4	79.4	**SD: 2.46**	**UCL:**	**115**
	Group C	ND		79.5	76.7	81.4	**% CV 3.10**	**LCL:**	**67.3**
Methidathion	Controls	ND	91.5						
	Group A	ND		89.0	85.3	84.4	**Mean: 88.3**	**Mean:**	**90.7**
	Group B	ND		106	86.3	85.0	**SD: 7.28**	**UCL:**	**117**
	Group C	ND		83.0	83.2	92.4	**% CV 8.24**	**LCL:**	**64.2**
Metolachlor	Controls	ND	93.5						
	Group A	ND		84.5	84.9	87.8	**Mean: 84.6**	**Mean:**	**88.3**
	Group B	ND		87.5	80.6	88.0	**SD: 4.28**	**UCL:**	**108**
	Group C	ND		78.0	79.8	90.4	**% CV 5.06**	**LCL:**	**69.0**
Norflurazon	Controls	ND	93.0						
	Group A	ND		86.0	83.7	89.0	**Mean: 85.3**	**Mean:**	**88.8**
	Group B	ND		88.0	81.8	88.4	**SD: 4.49**	**UCL:**	**107**
	Group C	ND		79.0	80.0	92.2	**% CV 5.26**	**LCL:**	**70.1**

Results from Trapping Efficiency Study (Fortify at 0.2, 1 and 5 µg), LC/MS/MS Analysis

Compound	Sample Name	Spike Level						Validation Control Limits (%)	
		Blank	2 µg	0.2 µg	1 µg	5 µg			
Oryzalin	Controls	ND	90.5						
	Group A	ND		85.5	79.4	84.6	**Mean: 82.3**	**Mean:**	**91.2**
	Group B	ND		88.0	77.5	87.0	**SD: 5.43**	**UCL:**	**115**
	Group C	ND		76.0	74.4	88.0	**% CV 6.60**	**LCL:**	**67.6**
Oxydemeton-methyl	Controls	ND	88.5						
	Group A	ND		80.5	76.1	75.4	**Mean: 76.3**	**Mean:**	**91.4**
	Group B	ND		79.0	71.5	75.8	**SD: 3.20**	**UCL:**	**117**
	Group C	ND		74.0	73.6	80.8	**% CV 4.19**	**LCL:**	**65.5**
Pendimethalin	Controls	ND	94.5						
	Group A	ND		86.5	85.9	86.0	**Mean: 85.7**	**Mean:**	**91.6**
	Group B	ND		88.0	83.5	88.2	**SD: 2.95**	**UCL:**	**110**
	Group C	ND		83.5	80.0	89.6	**% CV 3.44**	**LCL:**	**73.5**
Phosmet	Controls	ND	99.0						
	Group A	ND		93.5	91.8	98.0	**Mean: 93.4**	**Mean:**	**88.0**
	Group B	ND		94.5	88.0	99.2	**SD: 6.31**	**UCL:**	**107**
	Group C	ND		84.5	87.1	104	**% CV 6.76**	**LCL:**	**69.0**
Simazine	Controls	ND	94.0						
	Group A	ND		82.5	82.7	87.4	**Mean: 83.4**	**Mean:**	**89.7**
	Group B	ND		86.5	80.6	86.0	**SD: 3.99**	**UCL:**	**108**
	Group C	ND		77.0	79.4	88.8	**% CV 4.78**	**LCL:**	**71.5**

Appendix VI

Results from Trapping Efficiency Study (Fortify at 0.2, 1 and 5 µg), GC/MS Analysis

Result: % Recovery

Compound		Spike Level Blank	0.2 µg	1 µg	5 µg	Quality Control %	
EPTC	A	ND	85.0	85.3	76.2	**Mean:**	**80.6**
	B	ND	84.0	77.7	76.6	**SD:**	**3.50**
	C	ND	79.0	81.3	80.2	**% CV**	**4.34**
DDVP	A	ND	84.0	88.0	78.2	**Mean:**	**82.5**
	B	ND	85.5	80.7	78.6	**SD:**	**3.20**
	C	ND	82.0	84.1	81.8	**% CV**	**3.88**
Trifluralin	A	ND	93.5	103	84.8	**Mean:**	**93.8**
	B	ND	98.5	97.0	86.4	**SD:**	**6.50**
	C	ND	94.0	100	87.0	**% CV**	**6.93**
Chlorothalonil	A	ND	94.5	100	86.8	**Mean:**	**93.4**
	B	ND	96.0	93.6	91.4	**SD:**	**3.80**
	C	ND	92.0	96.3	90.4	**% CV**	**4.07**
Dacthal	A	ND	86.0	90.1	82.4	**Mean:**	**85.8**
	B	ND	89.0	84.0	84.8	**SD:**	**2.40**
	C	ND	85.0	86.1	84.8	**% CV**	**2.80**
Chlorpyrifos	A	ND	85.5	90.7	82.2	**Mean:**	**86.2**
	B	ND	89.0	85.2	85.0	**SD:**	**2.60**
	C	ND	84.5	88.4	85.2	**% CV**	**3.02**
pp-Dicofol	A	ND	59.0	56.8	68.2	**Mean:**	**61.0**
	B	ND	61.0	52.8	61.4	**SD:**	**4.80**
	C	ND	61.5	61.1	67.6	**% CV**	**7.87**

Results from Trapping Efficiency Study (Fortify at 0.2, 1 and 5 µg), GC/MS Analysis

Malathion	A	ND	91.5	97.1	79.4	**Mean:**	**90.1**
	B	ND	95.5	92.4	82.4	**SD:**	**6.50**
	C	ND	93.0	95.8	83.6	**% CV**	**7.21**
Endosulfan 1	A	ND	86.0	90.7	82.0	**Mean:**	**85.9**
	B	ND	90.5	84.1	84.6	**SD:**	**3.00**
	C	ND	85.5	86.2	83.6	**% CV**	**3.49**
Endosulfan Sulfate	A	ND	92.5	95.1	82.8	**Mean:**	**90.0**
	B	ND	95.0	89.5	87.0	**SD:**	**4.40**
	C	ND	91.0	92.7	84.6	**% CV**	**4.89**
Oxyfluorfen	A	ND	85.5	106	78.0	**Mean:**	**89.7**
	B	ND	89.0	100	81.8	**SD:**	**10.4**
	C	ND	84.5	102	80.2	**% CV**	**11.6**
Propargite	A	ND	117	95.9	76.8	**Mean:**	**97.1**
	B	ND	117	90.3	86.4	**SD:**	**16.0**
	C	ND	117	92.8	81.0	**% CV**	**16.5**
Iprodione	A	ND	104	107	82.8	**Mean:**	**97.3**
	B	ND	106	100	88.2	**SD:**	**9.9**
	C	ND	101	104	82.8	**% CV**	**10.2**
Permethrin	A	ND	99.0	99.6	80.0	**Mean:**	**91.6**
	B	ND	97.5	94.0	82.2	**SD:**	**9.1**
	C	ND	96.0	98.6	77.2	**% CV**	**9.9**
Cypermethrin	A	ND	119	107	84.0	**Mean:**	**102.9**
	B	ND	112	108	86.0	**SD:**	**15.4**
	C	ND	120	110	80.0	**% CV**	**15.0**
Captain	A	ND	89.0	112	84.0	**Mean:**	**97.6**
	B	ND	103	105	93.8	**SD:**	**9.9**
	C	ND	97.0	108	87.0	**% CV**	**10.1**

Appendix VII

Results from Storage Stability Experiment (Fortify at 1 µg), LC/MS/MS Analysis

Compound	Control Limits		Recovery (%) Day 0	Day 3	Day 7	Day 14	Day 21	Day 29
Acephate		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	85.5	107	97.5	93.5	94.5	100
		Spk 1 @ 1 ug	86.2	89.6	89.6	90.3	90.3	93.5
		Spk 2 @ 1 ug	82.6	94.2	90.3	85.5	94.5	90.3
		Spk 3 @ 1 ug	88.3	99.5	91.4	89.6	92.6	91.1
	Mean: 92.5	**Mean**	85.7	94.4	90.4	88.5	92.5	91.6
	UCL: 115	**SD**	2.88	4.95	0.907	2.59	2.10	1.67
	LCL: 70.0	**% CV**	3.36	5.24	1.00	2.93	2.27	1.82
Bensulide		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	86.5	115	91.0	86.0	86.5	90.0
		Spk 1 @ 1 ug	78.8	92.8	93.6	79.1	96.5	92.5
		Spk 2 @ 1 ug	93.7	101	84.6	86.1	103	93.6
		Spk 3 @ 1 ug	89.4	93.4	95.9	87.4	102	93.2
	Mean: 90.8	**Mean**	87.3	95.7	91.4	84.2	101	93.1
	UCL: 116	**SD**	7.67	4.57	5.97	4.46	3.50	0.557
	LCL: 65.7	**% CV**	8.79	4.78	6.53	5.30	3.47	0.598
Chlorpyrifos OA		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	85.0	99.0	93.0	89.0	93.0	91.5
		Spk 1 @ 1 ug	83.4	86.7	87.0	83.5	91.1	92.0
		Spk 2 @ 1 ug	82.8	88.5	85.0	84.0	94.3	88.4
		Spk 3 @ 1 ug	85.9	91.7	88.4	84.7	89.2	93.6
	Mean: 88.9	**Mean**	84.0	89.0	86.8	84.1	91.5	91.3
	UCL: 108	**SD**	1.64	2.53	1.71	0.603	2.58	2.66
	LCL: 70.0	**% CV**	1.95	2.84	1.97	0.495	2.82	2.91

Results from Storage Stability Experiment (Fortify at 1 µg), LC/MS/MS Analysis

Compound	Control Limits		Recovery (%) Day 0	Day 3	Day 7	Day 14	Day 21	Day 29
DEF		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	84.5	101	94.5	89.0	94.0	90.0
		Spk 1 @ 1 ug	83.4	87.8	89.4	83.1	90.4	93.5
		Spk 2 @ 1 ug	82.9	90.9	86.0	84.8	91.4	89.7
		Spk 3 @ 1 ug	87.1	93.0	89.8	85.6	87.0	95.4
	Mean: 89.3	**Mean**	84.5	90.6	88.4	84.5	89.6	92.9
	UCL: 109	**SD**	2.29	2.62	2.09	1.28	2.31	2.90
	LCL: 69.9	**% CV**	2.71	2.89	2.36	0.566	2.58	3.12
Diazinon		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	84.0	99.0	92.0	89.0	93.0	88.5
		Spk 1 @ 1 ug	82.3	85.8	86.5	83.3	90.3	93.7
		Spk 2 @ 1 ug	80.8	89.5	83.5	84.0	92.9	90.4
		Spk 3 @ 1 ug	85.5	89.3	89.2	85.8	87.1	93.8
	Mean: 88.5	**Mean**	82.9	88.2	86.4	84.4	90.1	92.6
	UCL: 107	**SD**	2.40	2.08	2.85	1.29	2.91	1.93
	LCL: 70.2	**% CV**	2.90	2.36	3.30	1.53	3.23	2.08
Diazinon OA		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	84.5	101	92.0	90.0	93.0	90.5
		Spk 1 @ 1 ug	82.7	85.4	88.9	84.3	90.8	92.4
		Spk 2 @ 1 ug	82.4	90.4	83.7	84.0	94.8	88.0
		Spk 3 @ 1 ug	86.4	91.0	89.1	84.0	88.5	92.3
	Mean: 89.4	**Mean**	83.8	88.9	87.2	84.1	91.4	90.9
	UCL: 109	**SD**	2.23	3.07	3.06	0.173	3.19	2.51
	LCL: 70.0	**% CV**	2.66	3.45	3.51	0.206	3.49	2.76

Results from Storage Stability Experiment (Fortify at 1 µg), LC/MS/MS Analysis

Compound	Control Limits		Recovery (%) Day 0	Day 3	Day 7	Day 14	Day 21	Day 29
Dimethoate OA		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	85.0	103	99.0	95.5	88.5	98.0
		Spk 1 @ 1 ug	84.3	90.5	91.6	90.1	89.7	94.6
		Spk 2 @ 1 ug	83.6	97.5	91.1	91.3	92.4	89.6
		Spk 3 @ 1 ug	89.9	97.0	97.9	88.4	88.3	93.3
	Mean: 93.6	**Mean**	85.9	95.0	93.5	89.9	90.1	92.5
	UCL: 118	**SD**	3.45	3.91	3.79	1.46	2.08	2.59
	LCL: 69.5	**% CV**	4.02	4.12	4.05	1.62	2.31	2.80
Diuron		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	85.0	101	93.5	89.0	93.5	89.5
		Spk 1 @ 1 ug	83.8	86.8	87.8	84.2	91.1	95.7
		Spk 2 @ 1 ug	82.6	91.3	84.9	84.1	94.2	91.4
		Spk 3 @ 1 ug	87.7	91.9	92.2	85.4	88.9	96.7
	Mean: 88.9	**Mean**	84.7	90.0	88.3	84.6	91.4	94.6
	UCL: 107	**SD**	2.67	2.79	3.68	0.723	2.66	2.82
	LCL: 70.7	**% CV**	3.15	3.10	4.17	0.855	2.91	2.98
Fenpyroximate		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	82.0	102	92.5	90.5	93.5	87.0
		Spk 1 @ 1 ug	83.5	85.5	88.8	85.2	90.6	91.9
		Spk 2 @ 1 ug	81.4	90.2	85.2	85.7	93.3	88.5
		Spk 3 @ 1 ug	87.1	91.1	89.6	86.5	87.3	94.8
	Mean: 89.2	**Mean**	84.0	88.9	87.9	85.8	90.4	91.7
	UCL: 107	**SD**	2.88	3.01	2.34	0.656	3.00	3.15
	LCL: 71.0	**% CV**	3.43	3.39	2.66	0.765	3.32	3.44

Results from Storage Stability Experiment (Fortify at 1 µg), LC/MS/MS Analysis

Compound	Control Limits		Recovery (%) Day 0	Day 3	Day 7	Day 14	Day 21	Day 29
Malathion OA		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	84.0	97.0	90.0	89.5	94.0	92.0
		Spk 1 @ 1 ug	83.2	82.8	83.4	82.4	91.1	93.6
		Spk 2 @ 1 ug	82.0	87.5	81.4	84.5	94.2	88.4
		Spk 3 @ 1 ug	88.2	88.4	86.1	83.9	90.2	93.6
	Mean: 88.5	**Mean**	84.5	86.2	83.6	83.6	91.8	91.9
	UCL: 107	**SD**	3.29	3.01	2.36	1.08	2.10	3.00
	LCL: 70.4	**% CV**	3.89	3.49	2.82	1.29	2.29	3.26
Methomyl		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	84.0	105	97.5	92.0	92.0	97.5
		Spk 1 @ 1 ug	85.8	88.7	92.5	89.5	91.4	89.3
		Spk 2 @ 1 ug	83.4	93.1	88.2	89.6	92.5	85.7
		Spk 3 @ 1 ug	86.3	97.7	95.7	90.3	86.9	91.4
	Mean: 91.1	**Mean**	85.2	93.2	92.1	89.8	90.3	88.8
	UCL: 115	**SD**	1.55	4.50	3.76	0.436	2.97	2.88
	LCL: 67.3	**% CV**	1.82	4.83	4.08	0.486	3.29	3.24
Methidathion		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	80.0	94.0	85.5	82.5	91.5	90.5
		Spk 1 @ 1 ug	93.7	92.8	91.9	89.2	97.6	99.3
		Spk 2 @ 1 ug	87.9	93.1	89.2	89.9	99.5	89.1
		Spk 3 @ 1 ug	84.0	94.2	82.3	94.0	95.3	87.1
	Mean: 90.7	**Mean**	88.5	93.4	87.8	91.0	97.5	91.8
	UCL: 117	**SD**	4.88	0.737	4.95	2.59	2.10	6.54
	LCL: 64.2	**% CV**	5.51	0.778	5.64	2.85	2.15	7.12

Results from Storage Stability Experiment (Fortify at 1 µg), LC/MS/MS Analysis

Compound	Control Limits		Recovery (%) Day 0	Day 3	Day 7	Day 14	Day 21	Day 29
Metolachlor		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	82.5	100	92.0	89.5	93.5	92.0
		Spk 1 @ 1 ug	82.9	85.2	87.2	82.3	91.6	92.7
		Spk 2 @ 1 ug	82.3	90.7	84.8	83.7	93.8	89.0
		Spk 3 @ 1 ug	86.8	91.0	90.3	84.5	87.7	94.2
	Mean: 88.3	**Mean**	84.0	89.0	87.4	83.5	91.0	92.0
	UCL: 108	**SD**	2.44	3.27	2.76	1.11	3.09	2.68
	LCL: 69.0	**% CV**	2.90	3.67	3.16	1.33	3.40	2.91
Norflurazon		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	84.5	99.0	93.5	89.5	93.0	91.5
		Spk 1 @ 1 ug	83.1	83.9	87.4	84.9	92.1	93.2
		Spk 2 @ 1 ug	82.8	89.6	84.2	85.4	94.9	89.4
		Spk 3 @ 1 ug	86.6	91.4	91.5	85.7	89.5	93.8
	Mean: 88.8	**Mean**	84.2	88.3	87.7	85.3	92.2	92.1
	UCL: 107	**SD**	2.11	3.92	3.66	0.404	2.70	2.39
	LCL: 70.1	**% CV**	2.51	4.44	4.17	0.474	2.93	2.60
Oryzalin		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	85.0	101	97.5	93.5	90.5	90.0
		Spk 1 @ 1 ug	85.2	86.2	91.1	87.2	87.9	88.7
		Spk 2 @ 1 ug	81.8	89.1	87.5	88.6	88.5	85.0
		Spk 3 @ 1 ug	88.5	92.6	91.3	86.1	84.3	95.0
	Mean: 91.2	**Mean**	85.2	89.3	90.0	87.3	86.9	89.6
	UCL: 115	**SD**	3.35	3.20	2.14	1.25	2.27	5.06
	LCL: 67.6	**% CV**	3.93	3.58	2.38	1.43	2.61	5.65

Results from Storage Stability Experiment (Fortify at 1 µg), LC/MS/MS Analysis

Compound	Control Limits		Recovery (%) Day 0	Day 3	Day 7	Day 14	Day 21	Day 29
Oxydemeton-methyl		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	82.5	108	101	89.0	88.5	94.5
		Spk 1 @ 1 ug	81.2	87.5	92.0	87.5	89.3	89.7
		Spk 2 @ 1 ug	81.5	93.0	85.5	87.0	91.0	86.9
		Spk 3 @ 1 ug	85.0	95.9	93.5	86.3	87.1	91.4
	Mean: 91.4	**Mean**	82.6	92.1	90.3	86.9	89.1	89.3
	UCL: 117	**SD**	2.11	4.27	4.25	0.603	1.96	2.27
	LCL: 65.5	**% CV**	2.55	4.64	4.71	0.694	2.20	2.54
Pendimethalin		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	86.0	99.0	92.0	91.0	94.5	93.5
		Spk 1 @ 1 ug	89.0	85.4	89.1	85.2	89.6	99.9
		Spk 2 @ 1 ug	85.9	89.6	83.6	86.5	92.7	89.7
		Spk 3 @ 1 ug	88.9	91.0	89.4	85.9	85.2	98.8
	Mean: 91.6	**Mean**	87.9	88.7	87.4	85.9	89.2	96.1
	UCL: 110	**SD**	1.76	2.91	3.27	0.651	3.77	5.60
	LCL: 73.5	**% CV**	2.00	3.28	3.74	0.758	4.23	5.83

Results from Storage Stability Experiment (Fortify at 1 µg), LC/MS/MS Analysis

Compound	Control Limits		Recovery (%)					
			Day 0	Day 3	Day 7	Day 14	Day 21	Day 29
Phosmet		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	80.5	97.5	92.0	93.5	99.0	90.5
		Spk 1 @ 1 ug	80.4	82.4	85.3	87.5	90.9	105
		Spk 2 @ 1 ug	81.0	84.9	82.4	92.0	98.4	98.8
		Spk 3 @ 1 ug	86.5	87.2	86.2	90.7	90.7	106
	Mean: 88.0	**Mean**	82.6	84.8	84.6	90.1	93.3	103
	UCL: 107	**SD**	3.36	2.40	1.99	2.32	4.39	3.90
	LCL: 69.0	**% CV**	4.07	2.83	2.35	2.57	4.71	3.79
Simazine		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	83.5	99.0	92.0	89.5	94.0	91.5
		Spk 1 @ 1 ug	83.7	86.1	88.4	82.6	94.2	92.2
		Spk 2 @ 1 ug	83.2	89.4	84.5	83.8	95.8	88.5
		Spk 3 @ 1 ug	87.4	91.4	89.9	84.5	88.5	93.5
	Mean: 89.7	**Mean**	84.8	89.0	87.6	83.6	92.8	91.4
	UCL: 108	**SD**	2.29	2.68	2.79	0.961	3.84	2.59
	LCL: 71.5	**% CV**	2.70	3.01	3.18	1.15	4.14	2.83

Appendix VIII

Results from Storage Stability Experiment (Fortify at 1 µg), GC/MS Analysis

Analyte	Control Limits		% Recovery					
			Day 0	Day 3	Day 7	Day 14	Day 21	Day 29
EPTC		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	81.5	79.0	90.0	87.0	94.0	79.5
		Spk 1 @ 1 ug	81.8	73.8	83.5	79.6	93.7	85.6
		Spk 2 @ 1 ug	78.6	80.1	83.2	85.8	92.6	87.0
		Spk 3 @ 1 ug	77.8	79.3	88.7	79.7	88.2	94.8
	Mean: 84.2	**Mean**	79.4	77.7	85.1	81.7	91.5	89.1
	UCL: 100	**SD**	2.12	3.43	3.09	3.55	2.91	4.96
	LCL: 68.5	**% CV**	2.67	4.41	3.63	4.35	3.18	5.57
DDVP		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	83.5	79.0	91.5	89.0	96.0	80.0
		Spk 1 @ 1 ug	82.0	73.2	83.8	81.5	98.0	88.2
		Spk 2 @ 1 ug	79.7	80	83.1	87.6	97.1	90.9
		Spk 3 @ 1 ug	81.6	78.8	88.7	80.8	92.3	99.6
	Mean: 84	**Mean**	81.1	77.2	85.2	83.3	95.8	92.9
	UCL: 102	**SD**	1.23	3.52	3.05	3.74	3.06	5.96
	LCL: 67	**% CV**	1.52	4.56	3.58	4.49	3.19	6.42
Trifluralin		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	90.5	87.5	100	93.5	123	83.0
		Spk 1 @ 1 ug	88.2	77.5	88.9	85.2	120	96.0
		Spk 2 @ 1 ug	86.8	83.5	86.6	89.1	119	101
		Spk 3 @ 1 ug	87.9	84.0	92.1	84.0	114	112
	Mean: 85	**Mean**	87.6	81.7	89.2	86.1	118	103
	UCL: 112	**SD**	0.74	3.62	2.76	2.67	3.21	8.19
	LCL: 58.4	**% CV**	0.84	4.43	3.09	3.61	2.73	7.95

Results from Storage Stability Experiment (Fortify at 1 µg), GC/MS Analysis

Chlorothalonil		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	85.5	86.0	99.0	89.0	106	81.0
		Spk 1 @ 1 ug	83.2	79.6	89.1	88.3	112	105
		Spk 2 @ 1 ug	81.6	86.0	86.0	92.3	109	112
		Spk 3 @ 1 ug	84.6	86.8	93.0	87.0	106	126
	Mean: 86	**Mean**	83.1	84.1	89.4	89.2	109	114
	UCL: 104	**SD**	1.50	3.95	3.51	2.76	3.00	10.7
	LCL: 67	**% CV**	1.81	4.70	3.93	3.75	2.75	9.35
Dacthal		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	88.0	87.5	96.5	92.0	106	88.0
		Spk 1 @ 1 ug	88.4	80.5	90.4	88.3	103	91.0
		Spk 2 @ 1 ug	86.5	86.8	88.0	91.1	101	93.7
		Spk 3 @ 1 ug	89.9	87.4	93.8	86.7	97.7	104
	Mean: 90	**Mean**	88.3	84.9	90.7	88.7	101	96.2
	UCL: 107	**SD**	1.70	3.82	2.91	2.23	2.68	6.86
	LCL: 73	**% CV**	1.93	4.50	3.21	2.51	2.66	7.13
Chlorpyrifos		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	88.5	88.0	97.5	92.5	110	87.0
		Spk 1 @ 1 ug	88.8	80.0	89.8	87.8	107	90.6
		Spk 2 @ 1 ug	86.5	86.3	87.1	89.9	103	94.4
		Spk 3 @ 1 ug	89.4	86.9	93.0	85.7	100	105
	Mean: 89	**Mean**	88.2	84.4	90.0	87.8	103	96.7
	UCL: 107	**SD**	1.53	3.82	2.95	2.10	3.51	7.46
	LCL: 70.2	**% CV**	1.73	4.53	3.28	2.39	3.40	7.71
pp-Dicofol		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	99.5	89.0	89.5	87.5	97.0	92.5
		Spk 1 @ 1 ug	104	83.9	81.8	85.4	77.7	88.8
		Spk 2 @ 1 ug	95.5	88.4	78.6	82.6	73.7	86.8
		Spk 3 @ 1 ug	114	90.6	86.6	88.5	67.8	85.9
	Mean: 92.3	**Mean**	104.5	87.6	82.3	85.5	73.1	87.2
	UCL: 114	**SD**	9.26	3.42	4.03	2.95	4.98	1.48
	LCL: 71	**% CV**	8.86	3.90	4.90	3.45	6.81	1.70

Results from Storage Stability Experiment (Fortify at 1 µg), GC/MS Analysis

Malathion			**Blk**	ND	ND	ND	ND		
			QC Spk @ 2 ug	90.0	90.0	99.5	95.0	117	85.5
			Spk 1 @ 1 ug	93.3	82.2	90.9	91.8	114	96.5
			Spk 2 @ 1 ug	89.5	89.3	88.9	93.9	111	101
			Spk 3 @ 1 ug	90.6	87.6	95.2	88.5	107	111
	Mean:	**91**	**Mean**	91.1	86.4	91.7	91.4	111	103
	UCL:	**111**	**SD**	1.96	3.71	3.22	2.72	3.51	7.42
	LCL:	**70**	**% CV**	2.15	4.29	3.51	2.98	3.17	7.22
Endosulfan 1			**Blk**	ND	ND	ND	ND	ND	ND
			QC Spk @ 2 ug	88.5	88.0	96.0	90.5	104	86.5
			Spk 1 @ 1 ug	87.6	80.5	89.4	87.7	106	89.6
			Spk 2 @ 1 ug	85.4	86.4	86.5	90.4	98.0	93.2
			Spk 3 @ 1 ug	88.5	87.0	93.4	86.0	92.7	103
	Mean:	**###**	**Mean**	87.2	84.6	89.8	88.0	98.9	95.3
	UCL:	**105**	**SD**	1.59	3.59	3.46	2.22	6.70	6.93
	LCL:	**73**	**% CV**	1.82	4.24	3.85	2.52	6.77	7.27
Endosulfan Sulfate			**Blk**	ND	ND	ND	ND	ND	ND
			QC Spk @ 2 ug	86.5	93.5	98.5	90.5	107	88.0
			Spk 1 @ 1 ug	86.7	83.1	88.8	88.7	109	97.4
			Spk 2 @ 1 ug	83.7	90.8	84.7	92.8	107	102
			Spk 3 @ 1 ug	87.0	91.3	91.0	87.8	103	113
	Mean:	**89**	**Mean**	85.8	88.4	88.2	89.8	106	104
	UCL:	**110**	**SD**	1.82	4.60	3.20	2.67	3.06	8.02
	LCL:	**68.5**	**% CV**	2.12	5.20	3.63	2.97	2.88	7.70
Oxyfluorfen			**Blk**	ND	ND	ND	ND	ND	ND
			QC Spk @ 2 ug	93.0	97.5	105	96.5	133	85.5
			Spk 1 @ 1 ug	89.4	80.9	96.7	85.3	132	93.7
			Spk 2 @ 1 ug	87.0	89.2	84.2	91.5	131	103
			Spk 3 @ 1 ug	87.0	89.3	91.6	85.1	129	117
	Mean:	**84**	**Mean**	87.8	86.5	90.8	87.3	131	105
	UCL:	**124**	**SD**	1.39	4.82	6.29	3.64	1.53	11.73
	LCL:	**44**	**% CV**	1.58	5.57	6.93	4.17	1.17	11.21

Results from Storage Stability Experiment (Fortify at 1 µg), GC/MS Analysis

Propargite		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	90.5	98.5	104	93.0	99.0	88.0
		Spk 1 @ 1 ug	88.2	82.8	97.1	85.9	112	97.6
		Spk 2 @ 1 ug	85.7	91.1	81.9	93.2	110	102
		Spk 3 @ 1 ug	87.0	91.2	91.2	88.4	106	112
	Mean: 87	**Mean**	87.0	88.4	90.1	89.2	109	104
	UCL: 123	**SD**	1.25	4.82	7.66	3.71	3.06	7.38
	LCL: 52	**% CV**	1.44	5.45	8.50	4.16	2.80	7.10
Iprodione		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	88.5	100	99.5	89.5	123	84.0
		Spk 1 @ 1 ug	91.4	87.2	94.6	90.2	132	104
		Spk 2 @ 1 ug	86.7	96.0	86.0	94.8	131	110
		Spk 3 @ 1 ug	87.7	97.2	91.7	91.3	127	121
	Mean: 91	**Mean**	88.6	93.5	90.8	92.1	130	112
	UCL: 113	**SD**	2.48	5.46	4.38	2.40	2.65	8.62
	LCL: 69	**% CV**	2.80	0.849	4.82	2.61	2.04	7.72
Permethrin		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	88.5	102	97.5	86.5	118	87.0
		Spk 1 @ 1 ug	92.4	89.5	96.5	90.8	119	96.0
		Spk 2 @ 1 ug	88.3	97.3	84.7	94.5	117	101
		Spk 3 @ 1 ug	90.8	99.5	91.5	93.8	114	109
	Mean: 92.0	**Mean**	90.5	95.4	90.9	93.0	117	102
	UCL: 112	**SD**	2.07	5.25	5.92	1.97	2.52	6.56
	LCL: 72.2	**% CV**	2.29	5.50	6.51	2.12	2.16	6.43
Cypermethrin		**Blk**	ND	ND	ND	ND	ND	ND
		QC Spk @ 2 ug	88.5	104	99.5	87.0	129	86.0
		Spk 1 @ 1 ug	89.6	91.5	94.9	89.4	140	99.5
		Spk 2 @ 1 ug	85.9	99.0	82.2	95.8	133	110
		Spk 3 @ 1 ug	85.9	102	88.8	92.6	131	117
	Mean: 92	**Mean**	87.1	97.5	88.6	92.6	135	109
	UCL: 118	**SD**	2.14	5.41	6.35	3.20	4.73	8.81
	LCL: 65.0	**% CV**	2.46	5.55	7.17	3.46	3.51	8.10

Results from Storage Stability Experiment (Fortify at 1 µg), GC/MS Analysis

Captain									
			Blk	ND	ND	ND	ND	ND	ND
			QC Spk @ 2 ug	83.5	87.5	101	90.5	108	82.0
			Spk 1 @ 1 ug	79.8	78.2	88.0	88.5	120	109
			Spk 2 @ 1 ug	79.0	86.5	86.3	94.5	119	113
			Spk 3 @ 1 ug	82.1	85.5	93.5	86.7	113	141
	Mean:	**88**	**Mean**	80.3	83.4	89.3	89.9	117	121
	UCL:	**119**	**SD**	1.61	4.53	3.76	4.08	3.79	17.44
	LCL:	**58**	**% CV**	2.00	5.43	4.21	4.54	3.23	14.41

Appendix IX

Cleaning XAD-4 resin

1. Measure 600 mg of uncleaned XAD-4 resin into two 4-liter Teflon (or Glass) containers.
2. Wet each container with 1 liter of residue grade methanol and then add 1 liter of 0.25 N HCl to both. Stir occasionally with a glass or Teflon rod for about 30 minutes.
3. Transfer the contents to a glass cylinder (An open-end cylinder with rubber stopper tightly fit the bottom. A glass tube is inserted through the stopper and connected to a D.I. water faucet.). Cover the top with a fine screen.
4. Overfill the cylinder with D.I. water through the bottom at about 30 mL/min for at least 4 hours. The pH should be that of D.I. water, or no Cl^- reaction with a drop of 0.1 N $AgNO_3$ solution added to a 1 mL of outgoing water.
5. Transfer the water washed XAD-4 into a Büchner funnel/vacuum flask set-up and add acetone to the resin until it is fully covered. Turn on vacuum and allow the resin to dry for at least 6 hours (overnight is best).
6. Bring the dried resin to the continuous liquid/liquid extractor apparatus. Add a small amount of glass wood to the bottom of each extractor to prevent resin from flowing into the waste flask. Carefully add the resin to each needed extractor.
7. Before starting, add a single boiling chip to each boiling flask. Slowly poor enough methanol into the extractor until the round boiling flask at the bottom is 2/3 full. Stir with a glass rod to help remove air bubbles (Do not disturb the glass wool plug.). Attach the condensers to each extractor and set each heating dial to number "5" or "6". Start the chiller. Allow the solvent to run through the resin for at least 24 hrs. Drain solvent when finished.
8. For the second solvent, ethyl acetate, repeat part 7.
9. After the extraction phase, place the moist resin into a vacuum oven and dry it at 16-18mm Hg of vacuum and 40 °C for at least 72 hours or until all traces of ethyl acetate are gone. During the drying process allow dry air sweep through the oven at a flow rate that can just be felt by placing finger on the air inlet tube.
10. When dried, place cleaned resin into a desiccator for at least 40 minutes before filling jar.

Note: Use residue grade methanol and ethyl acetate to wash the resin

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Revision Log:

Date	What was revised? Why?
02/24/21	Changed to sonication extraction technique and added 4 new pesticides to the screen and validated the new method.