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# Title: Determination of Selected Pesticides Collected on XAD-4 Resin by High Performance Liquid Chromatography Ion Trap Mass Spectrometry and Gas Chromatography Mass Spectrometry

1. Scope

This section method (SM) is for the analysis of the selected pesticides trapped in XAD-4 resin and extracted with ethyl acetate. These pesticides are azinphos-methyl, chlorothalonil, chlorpyrifos, cypermethrin, DEF, diazinon, dicofol, dimethoate, diuron, endosulfan, endosulfan sulfate, EPTC, malathion, metolachlor, molinate, DDVP, norflurazon, oryzalin, oxyfluorfen, permethrin, phosmet, propanil, propargite, simazine, thiobencarb, trifluralin, and the oxygen analogs of chlorpyrifos, diazinon, dimethoate and malathion. It is to be followed by all authorized section personnel. The reporting limits vary from 0.25 μg to 2.0 μg depending on the instrument sensitivity for individual compounds.

2. Principle:

Residues of the selected pesticides are extracted from XAD-4 resin using ethyl acetates. Nineteen compounds are determined by the injection of sample extract into an HPLC equipped with a C-18 column and a mass spectrometer (LC-MS). The remaining compounds, which cannot be confidently analyzed with LC-MS, 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 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:

On LC-MS it appears that the extract enhances the response of phosmet and azinphos methyl most of the time. On GC-MS it appears that the extract deteriorates the analytical column quickly and reduces the response of some compounds. The response and peak shape of some compounds in matrix extracts versus in plain

solvent shows great differences. To be consistent we have prepared standards in matrix extract to be used in GC-MS and LC-MS analysis.

5. Apparatus and Equipment:

5.1 Rotary evaporator (Büchi/Brinkman or equivalent)
5.2 Nitrogen evaporator (Meyer N-EVAP Organomation Model # 112 or equivalent)
5.3 Vortex-vibrating mixer
5.4 Separatory funnel, 250 mL
5.5 Conical tube with glass stopper, 15-mL graduated
5.6 Boiling flask, 500-mL
5.7 Funnel, 15 cm diameter
5.8 Disposable Pasteur pipettes, and other laboratory ware as needed
5.9 Liquid chromatograph (Waters Model 2695 HPLC) equipped with a Thermo Finnigan Ion Trap Mass detector.
5.10 Gas chromatograph (Agilent Model 6890) equipped with a mass spectrometer (Agilent model 5972)

6. Reagents and Supplies: (All reagents shall meet the minimum requirement in HPLC, residue and pesticide analysis)

6.1 Acetic acid,
6.2 Ammonium formate, (Aldrich, reagent grade or equivalent)
6.3 Ethyl acetate, (Fisher, reagent grade or equivalent)
6.4 Formic acid, HPLC grade (Fisher #A35-500 or equivalent)
6.3 Methanol, (Burdick &Jackson, MS grade, or equivalent)
6.4 Nitrogen, refrigerated liquid or nitrogen generator with capacity of delivering 20 liters per minute
6.5 Standards: The individual 1.0 mg/mL stock standards of each compound were obtained from the CDFA/CAC Standard Repository.

| | |
|---|---|
| Azinphos-methyl | CAS Number 86-50-0 |
| Chlorothalonil | CAS Number 1897-45-6 |
| Chlorpyrifos | CAS Number 2921-88-2 |
| Cypermethrin | CAS Number 52315-07-8 |
| DEF | CAS Number 78-48-8 |
| Diazinon | CAS Number 333-41-5 |
| Dicofol | CAS Number 115-32-2 |
| Dimethoate | CAS Number 60-51-5 |
| Diuron | CAS Number 330-54-1 |
| Endosulfan $\alpha$ | CAS Number 959-98-8 |

| | |
|---|---|
| Endosulfan β | CAS Number 332-13-65-9 |
| Endosulfan sulfate | CAS Number 1031-07-08 |
| EPTC | CAS Number 759-94-4 |
| Malathion | CAS Number 121-75-5 |
| Metolachlor | CAS Number 51218-45-2 |
| Molinate | CAS Number 2212-67-1 |
| DDVP | CAS Number 62-73-7 |
| Norflurazon | CAS Number 27314-13-2 |
| Oryzalin | CAS Number 19044-88-3 |
| Oxyfluorfen | CAS Number 42874-03-3 |
| Permethrin | CAS Number 52645-53-1 |
| Phosmet | CAS Number 732-11-6 |
| Propanil | CAS Number 709-98-8 |
| Propargite | CAS Number2312-35-8 |
| Simazine | CAS Number 122-34-9 |
| Thiobencarb | CAS Number 28249-77-6 |
| Trifluralin | CAS Number 1582-09-8 |
| Chlorpyrifos OA | CAS Number 0000-00-00 |
| Diazinon OA | CAS Number 962-58-3 |
| Dimethoate OA | CAS Number 1113-02-6 |
| Malathion OA | CAS Number 0000-00-00 |

6.6 Water, MS grade, Burdick & Jackson or equivalent

6.7 Analytical column: Waters SymmetryShield $RP_{18}$ 5 μm, 3.9 x 150 mm column (part number, 186000108) or equivalent

6.8 Guard column: Waters Symmetryshield RP 18 5 μm, 3.9 x 20 mm cartridge (part number,

6.9 Guard column cartridge holder: Waters Sentry guard holder universal (P/N wat064610)

7. Standards Preparation:

7.1 Dilute the 1.0 mg/mL standards, obtained from the CDFA/CAC Standards Repository, with methanol. The concentration of each individual standard is 20 ng/μL or 10 ng/μL.

7.2 The CDFA/CAC Standards Repository prepares the combination standards. One contains 26 compounds without the oxygen analogies (A). The other contains the 4 oxygen analogies (B). Each component of the combinations is 100 μg/mL prepared in methanol.

7.3 A combined stock solution is prepared by mixing equal amount of (A) and (B). This combined stock solution is for preparing working standards and QC spiking.

7.4 Working standards are prepared in sample matrix solution. The dilution ratios are:

| Concentration (ng/μL) | Amount of stock solution (μL) | Amount of matrix extract (μL) | Final volume (mL) |
|---|---|---|---|
| 0.10 | 4 | 1996 | 2.0 |
| 0.50 | 20 | 1980 | 2.0 |
| 1.0 | 40 | 1960 | 2.0 |
| 2.0 | 80 | 1920 | 2.0 |
| 5.0 | 200 | 1800 | 2.0 |

Working standards should be kept no longer than a week.

8. Sample Preservation and Storage:

All samples and sample extracts shall be stored in the refrigerator (0-5 $^{o}$C).

9. Test Sample Preparation:

9.1 Sample Preparation

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

9.1.2 Clip the sample tube on a laboratory rack in a hood, remove the stopper from the ends, put a 250 mL round flask under it, and place the bottom of the sample tube just inside the flask.

9.1.3 Set a 250 mL separatory funnel as a solvent reservoir on a ring and place the tip of the funnel just inside of the sample tube.

9.1.4 Pour 100 mL ethyl acetate into the separatory funnel. Open the stopcock and adjust the flow to a rate that the top of the resin bed maintains about 0.5 inch of solvent.

9.1.5 Allow the entire 100mLs of solvent to run through the sample tube.

9.1.6 Evaporate the solvent to about 10 mL on a rotary vacuum evaporator at 45°C and 24 inches vacuum.

9.1.7 Quantitatively transfer the solution to a 15 mL conical centrifuge tube and evaporate on a N-evap at 40°C to about 1 mL.

9.1.8 Perform solvent exchange by adding 4 mL methanol and evaporate to about 1 mL.

9.1.9 Adjust final volume to 2.0 mL with methanol. Vortex for 20 seconds and transfer to three auto-sampler vials, two with insert for analysis and one without insert for storage for in case of re-analysis.

10 Instrument Calibration:

10.1 The calibration standard curves consist of six levels. The lowest level must be at or below the corresponding reporting limits. (The current working standard levels are 0.02, 0.1, 0.5, 1.0, 2.0, and 5.0 ng/μL as prepared in 7.3.

10.2 The calibration curves for the LC-MS and GC-MS are generally obtained using linear regression. Quadratic fit may be used if the response of certain compounds exhibited quadratic behavior.

11 Analysis:

11.1 Injection Scheme

Both LC-MS and GC-MS may need to be conditioned with a matrix standard or a sample extract 2 to 5 runs before running the following sequence: A set of calibration standards in matrix, a matrix blank, a matrix spike, a set of up to 10 test samples, then a set of standards in matrix, etc.

11.2 HPLC-MS Instrumentation

11.2.1 Waters model 2695 HPLC and auto-sampler with column heater and remote control through Thermo Finnigan Xcalibur system.

11.2.2 Column: Waters SymmetryShield $RP_{18,}$ 5 μm, 3.9 x 150 mm column (part no. 186000108)

11.2.3 Guard column cartridge Holder and cartridge: Waters Sentry guard holder universal (P/N wat064610); Waters SymmetryShield RP 18 5μm, 3.9 x 20mm.

11.2.4 Column Temperature: 40 °C

11.2.5 Mobile Phase: Gradient

Solvent C: 3762 mL water, 200 mL methanol, 38 mL 1 M ammonium formate and 4.0 mL formic acid

Solvent D: 3600 mL methanol, 360 mL water, 36 mL 1.0 M ammonium formate, 4 mL formic acid

Flow rate: 0.75 mL/min

Gradient:

| Time(min) | Flow rate (mL/min) | A | B | C | D |
|---|---|---|---|---|---|
| 0 | 0.75 | 0 | 0 | 85 | 15 |
| 3 | 0.75 | 0 | 0 | 85 | 15 |
| 4 | 0.75 | 0 | 0 | 50 | 50 |
| 10 | 0.75 | 0 | 0 | 50 | 50 |
| 21 | 0.75 | 0 | 0 | 25 | 75 |
| 22 | 0.75 | 0 | 0 | 5 | 95 |
| 27 | 0.75 | 0 | 0 | 5 | 95 |
| 30 | 0.75 | 0 | 0 | 85 | 15 |
| 34 | 0.75 | 0 | 0 | 85 | 15 |

11.2.6 Injection Volume: 10 μL

11.2.8 Liquid Chromatograph Mass spectrometer (LC-MS) and Operating Parameters

| | |
|---|---|
| Model: | Finnigan Model DECA ion trap MS |
| Ion Source Type: | Atmospheric pressure Ionization (APCI) |
| Source Polarity: | Positive |
| APCI Vaporizer Temp: | 500°C |
| Capillary Temperature: | 200°C |
| Sheath Gas | 44 |
| Auxiliary Gas: | 3 |
| Mode of Operation: | MS/MS |

Retention time, molecular mass, ion filter range and product ions are listed below:

| Compound Name | Retention Time (min) | Molecular Masses | Ion Filter Range | Product Ions |
|---|---|---|---|---|
| Dimethoate OA | 3.16 | 213 | 214±1.5 | 183 |
| Dimethoate | 7.40 | 229 | 230±1.5 | 199 |
| Malathion OA | 10.04 | 314 | 315±1.5 | 126.9, 173, 268.8 |
| Simazine | 11.55 | 201, 203 | 203±1.5 | 124,132, 174 |
| Diazinon OA | 15.06 | 288 | 289±1.5 | 153, 261, 289 |
| Norflurazon | 16.23 | 303, 305 | 305±2 | 284, 286, 302, 304, 316, 317 |
| Diuron | 17.06 | 232, 234 | 235±2.5 | 72 |
| Phosmet | 17.40 | 317 | 318±1 | 160, 285.7 |
| Azinphos-methyl | 17.18 | 317 | 318±1 | 160, 171, 261 |
| Molinate | 18.05 | 187 | 188±1 | 126 |
| Malathion | 18.56 | 330 | 334±6 | 285 |
| Metolachlor | 19.59 | 283, 285 | 284±2 | 252 |
| Propanil | 19.63 | 217, 219 | 218±2.5 | 162 |
| Chlorpyrifos OA | 20.35 | 333, 335, 337 | 334±6 | 306, 308, 310 |
| EPTC | 20.55 | 189 | 190±1 | 128 |
| Oryzalin | 21.53 | 346 | 347±1 | 247, 288, 305 |
| Diazinon | 22.39 | 304 | 305±1.5 | 153, 169 |
| Thiobencarb | 24.43 | 257, 259 | 258±2.5 | 100, 125, 258 |
| DEF | 27.00 | 314 | 315±2.5 | 200.9, 257, 259 |

Note: The real retention times are expected within 30 seconds of that stated above when the column is new. The column conditions, temperature, mobile phase, etc. may slightly shift retention time.

11.2.9 Operating parameter detail and Tune method are listed in Appendix 1 and Appendix 2

11.3 GC-MSD Instrumentation:

11.3.1 Agilent GC-MSD model HP6890 with auto sampler. Operating software is Enviroquant ChemStation version G1701B.01.00
11.3.2 Column: HP-5MS 30m x 0.25mm x 0.25μm
11.3.3 Pre-column: not used
11.3.4 Temperature program

Injector Temperature: 250 °C
Oven Temperature:

| Oven Ramp | Program (°C/min) | Temperature (°C) | Hold (min) |
|---|---|---|---|
| initial | | 70 | 2 |
| Ramp 1 | 15 | 190 | 5 |
| Ramp 2 | 15 | 250 | 5 |
| Ramp 3 | 15 | 270 | 8 |

11.3.5 Retention times and ions selected for SIM acquisition:

| Compound name | Retention time | Selected ions | Starting time |
|---|---|---|---|
| DDVP | 7.25 | 109,145,185 | 5.0 |
| EPTC* | 8.35 | 128,189,86 | 8.10 |
| Molinate* | 10.01 | 126,187,98 | 9.80 |
| Trifluralin | 11.02 | 264, 306,264, 335 | 10.8 |
| Dimethoate* | 11.86 | 87, 125, 229 | 11.80 |
| Diazinon* | 12.58 | 179, 304, 137 | 12.50 |
| Chlorothalonil | 12.76 | 266, 229, 109 | 12.50 |
| Propanil* | 14.07 | 161,163,217 | 14.00 |
| Malathion* | 15.83 | 173, 125, 93 | 15.75 |
| Metolachlor* | 15.89 | 162, 238, 146 | 15.75 |
| Chlorpyrifos | 15.98 | 314, 197, 258 | 15.75 |
| Thiobencarb * | 16.04 | 100, 257, 125 | 15.75 |
| Dicofol p, p' | 16.46 | 139, 250, 111 | 16.28 |
| Endosulfan 1 | 18.02 | 195, 339, 241, 261 | 17.80 |
| DEF* | 18.61 | 202, 169, 147 | 18.50 |
| Oxyfluorfen | 18.68 | 252, 300, 361 | 18.50 |
| Endosulfan Sulfate | 20.04 | 272, 387, 229, 422 | 19.90 |
| Propargite | 20.5-20.6 | 135, 173, 350 | 20.45 |
| Phosmet | 21.31 | 160, 77, 93 | 20.60 |
| Azinphos Methyl | 22.56 | 160, 77, 132 | 20.60 |
| Permethrin | 24.8,25.09 | 183, 163, 127 | 24.80 |
| Cypermethrin | 26.41 | 163, 161,209 | 26.00 |

*Can be analyzed by LCMS confidently

12. Quality Control:

12.1 Each set of samples shall have a matrix blank and minimum of one matrix spike sample. Each set contains up to 12 samples.

12.2 The matrix blank shall be free of target compounds.

12.3 The recoveries of the matrix spike should be within the control limits.

12.4 The retention time shall be within ± 20 seconds of that of the standard.

12.5 To maintain the instrument performance, trim the front 10 inches off the GC column every 30 hours (about 50 injections). The response of the 0.02 ng/uL combination standards is a good measure of the instrument performance.

12.6 The sample extract shall be diluted if results fall outside the linear range of the standard curve.

12.7 Add additional levels if there is a need to extend the standard curve range.

12.8 Method Detection Limits (MDL)

The method detection limit refers to the lowest concentration of analyte that a method can detect reliably. To determine the MDL, 7 replicate XAD-4 sample tubes are spiked at 0.2 μg or 0.4 μg. The standard deviation from the spiked sample recoveries are used to calculate the MDL for each analyte using the follow 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 replicate used to determine the MDL, t=3.143.

12.9 Reporting limit (RL):

The reporting limit (RL) refers to the level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. In general, the RL is chosen in a range 1-5 times the MDL. The response reproducibility of each compound is also considered to determine the RL

MDL data and the RL are tabulated in Appendix 3 and 4.

12.10 Method Validation Recovery Data and Control Limits:

12.10.1 The method validation consisted of five sample sets. Each set included 4 levels of fortification (0.5, 1.0, 5.0 and 10.0 μg) and a method blank. All spikes, method blank and samples were processed through the entire analytical method.

12.10.2 Upper and Lower warning and control limits are set at ± 2 and ±3 standard deviations of the average % recovery, respectively.

12.10.3 Method validation results and control limits are tabulated in appendix 4.

13. Calculations:

13.1 The quantification is based on the sum of area counts of the product ion and the precursor of the compound analyzed. The calculation is based on external standard (ESTD).

13.2 The software LCQuan in the Xcalibur system and the software Enviroquant are used to establish the standard curve and to calculate the analytes in the samples. The correlation coefficient, slope, intercept of the linear regression line are calculated once the calibration standards are defined. The equation for calculating analytes is as follows:

$$y = mx + b$$

Where: y = peak response
m = slope
b = intercept
x = concentration of compound

When the unit and the dilution factor are entered correctly in the analysis sequence, the software will then correctly generate the results.

13.3 Results can be manually calculated by a single point standard. The unit is μg/sample. This calculation is to verify the results derived from the software

The general equation is as follows:

$$\mu g = \frac{(\text{sample peak area})\ (\text{std. conc. ng}/\mu L)\ (\text{std. vol. Injected}(\mu L))\ (\text{sample final vol., (mL)})}{(\text{std. peak area})\ (\text{sample vol. Injected }(\mu L))}$$

14. Reporting Procedure:

14.1 Perform Quantification with LCQuan:

14.1.1 Create a new Processing method
Open a raw file
Select calibration options
Identify components
Define calibration settings. Or

14.1.2 Open an existing quantification method and save to an appropriate sub-directory with a new name

14.1.3 Open the sequence and review the sequence. Or

14.1.4 Go to the appropriate sub-directory and select the raw files to be used as standards. Place the standard raw files to the appropriate calibration levels. Select the unknown raw files to be calculated.

14.1.5 Review the calibration

14.1.6 Review all calculated results

14.1.7 Create, review, and print peak integration report, calibration report, and summary report

14.2 Perform Quantification with EnviroQuant:

14.2.1 Load a standard data file
Integrate the data file
Edit compounds based on retention time and identity
Review the window range of each compound and adjust it as needed.
Reintegrate the data file based on the new method
Update levels
View the calibration curves
Save as a new method

14.2.2 Load a sample data file
Do quantification with this new method with new calibration curves
Review each compound and do integration correction
Save this reviewed file
Print this reviewed data file

14.3 Acceptance Criteria:

14.3.1 Peak retention time between standards, QC spikes and unknowns shall be within 20 seconds. If there is a known reason for retention time shifting, an explanation memo shall be included.

14.3.2 Peak response shall be within the calibration range

14.3.3 The $R^2$ of calibration curve or overlay calibration curves shall be 0.990 or better.

14.3.4 Recoveries of spike QC shall be within the established control range, otherwise a rerun of the entire set shall be performed. If problems remain, an explanation memo shall be included.

14.3.5 The ratio of product ion and precursor ion between standard and unknown shall be consistent and the variation of the ratio between standard and unknown shall be within ±20 %.

14.3.6 Manual single point calculation result is acceptable with explanation

14.4 Reporting:

14.4.1 Sample results are reported out according to the client's analytical laboratory specification sheet.
14.4.2 Fill out COC, QC sheet, and control chart.
14.4.3 Prepare data package. Peer review. Report.

## 15 Discussion

15.1 It was a challenging task to analyze chlorothalonil by GC. Since the beginning of this project, we were able to analyze it by GC for a period of 8 months. The

sensitivity was getting better gradually. Later, we injected air sample extracts of the quartz and glass fiber filters. Immediately after this event, the response of chlorothalonil was getting worse. Eventually we were unable to meet the method reporting limit. A lot of attempts failed to restore the response of chlorothalonil by GC-MS method. Finally, a LC-MS method on negative mode was developed. The chlorothalonil molecular mass is 264 (266, 268, etc). During the infusion of chlorothalonil into the LC-MS we observed the ions $245^-$, $247^-$, and $249^-$. It appears the chlorothalonil molecule fragmented to ions $245^-$, $247^-$, and $249^-$. Loss of 19 is likely due to a chlorine on the aromatic ring being replaced by a hydroxyl group. Since we have this method we successfully reanalyzed all those samples that did not meet the reporting limit.

15.2 The GC column maintenance: About every 80-100 injections we trim off 15 inches of column from the front end. To compensate the retention time change due to a shorter column we add 10-15 seconds to the initial temperature holding time. Then check the retention time for each compound and make necessary changes.

15.3 Excluding ammonium salt from the mobile phase greatly increase the response of propanil by LC-MS

16. References:

## APPENDIX I Operating parameters

Creator: PAUL LEE

MS Run Time (min): 35.00

Divert Valve: in use during run

| Divert Time (min) | Valve State |
|---|---|
| 0.00 | To Waste |
| 1.99 | To Source |
| 32.41 | To Waste |

Contact Closure: not used during run

MS Detector Settings:

Acquisition Start Delay (min): 2.00
Real-time modifications to method disabled

Segment 1 Information

Duration (min): 10.76
Number of Scan Events: 3
Tune Method: oryzalin

Scan Event Details:
1: Pos ·(230.0)->o(60.0-250.0)
MS/MS: Amp. 22.0% Q 0.250 Time 30.000 IsoW 3.0

2: Pos ·(214.0)->o(55.0-250.0)
MS/MS: Amp. 25.0% Q 0.250 Time 30.000 IsoW 3.0

3: Pos ·(315.0)->o(85.0-350.0)
MS/MS: Amp. 23.0% Q 0.250 Time 30.000 IsoW 3.0

Segment 2 Information

Duration (min): 2.26
Number of Scan Events: 1
Tune Method: oryzalin

Scan Event Details:
1: Pos ·(203.0)->o(55.0-250.0)
MS/MS: Amp. 36.0% Q 0.250 Time 30.000 IsoW 3.0

Segment 3 Information

Duration (min): 3.18
Number of Scan Events: 2
Tune Method: oryzalin

Scan Event Details:
1: Pos ·(305.0)->o(80.0-350.0)
MS/MS: Amp. 36.0% Q 0.250 Time 30.000 IsoW 4.0

2: Pos ·(289.0)->o(75.0-350.0)
MS/MS: Amp. 30.0% Q 0.250 Time 30.000 IsoW 3.0

Segment 4 Information

Duration (min): 1.77
Number of Scan Events: 4
Tune Method: oryzalin

Scan Event Details:
1: Pos ·(305.0)->o(80.0-350.0)
MS/MS: Amp. 36.0% Q 0.250 Time 30.000 IsoW 4.0

2: Pos ·(235.0)->o(60.0-300.0)
MS/MS: Amp. 35.0% Q 0.250 Time 30.000 IsoW 5.0

3: Pos ·(318.0)->o(85.0-350.0)
MS/MS: Amp. 20.0% Q 0.250 Time 30.000 IsoW 2.0

4: Pos ·(188.0)->o(50.0-250.0)
MS/MS: Amp. 27.0% Q 0.250 Time 30.000 IsoW 2.0

Segment 5 Information

Duration (min): 0.94
Number of Scan Events: 3
Tune Method: oryzalin

Scan Event Details:
1: Pos ·(188.0)->o(50.0-250.0)
MS/MS: Amp. 27.0% Q 0.250 Time 30.000 IsoW 2.0

2: Pos ·(334.0)->o(90.0-400.0)
MS/MS: Amp. 25.0% Q 0.250 Time 30.000 IsoW 12.0

3: Pos ·(318.0)->o(85.0-350.0)

MS/MS: Amp. 20.0% Q 0.250 Time 30.000 IsoW 2.0

Segment 6 Information

Duration (min): 1.55
Number of Scan Events: 4
Tune Method: oryzalin

Scan Event Details:
1: Pos ·(284.0)->o(75.0-350.0)
MS/MS: Amp. 36.0% Q 0.250 Time 30.000 IsoW 4.0

2: Pos ·(218.0)->o(60.0-250.0)
MS/MS: Amp. 35.0% Q 0.250 Time 30.000 IsoW 5.0

3: Pos ·(334.0)->o(90.0-400.0)
MS/MS: Amp. 25.0% Q 0.250 Time 30.000 IsoW 12.0

4: Pos ·(190.0)->o(50.0-250.0)
MS/MS: Amp. 27.0% Q 0.250 Time 30.000 IsoW 2.0

Segment 7 Information

Duration (min): 2.77
Number of Scan Events: 4
Tune Method: oryzalin

Scan Event Details:
1: Pos ·(347.0)->o(95.0-400.0)
MS/MS: Amp. 30.0% Q 0.250 Time 30.000 IsoW 2.0

2: Pos ·(305.0)->o(80.0-350.0)
MS/MS: Amp. 30.0% Q 0.250 Time 30.000 IsoW 3.0

3: Pos ·(190.0)->o(50.0-250.0)
MS/MS: Amp. 27.0% Q 0.250 Time 30.000 IsoW 2.0

4: Pos ·(334.0)->o(90.0-400.0)
MS/MS: Amp. 25.0% Q 0.250 Time 30.000 IsoW 12.0

Segment 8 Information

Duration (min): 1.57
Number of Scan Events: 1
Tune Method: oryzalin

Scan Event Details:
1: Pos ·(258.0)->o(70.0-300.0)
MS/MS: Amp. 28.0% Q 0.250 Time 30.000 IsoW 5.0

Segment 9 Information

Duration (min): 1.60
Number of Scan Events: 4
Tune Method: oryzalin

Scan Event Details:
1: Neg ·(332.0)->o(90.0-400.0)
MS/MS: Amp. 32.0% Q 0.250 Time 30.000 IsoW 4.0

2: Pos ·(350.0)->o(95.0-400.0)
MS/MS: Amp. 28.0% Q 0.250 Time 30.000 IsoW 5.0

3: Neg ·(360.0)->o(95.0-380.0)
MS/MS: Amp. 38.0% Q 0.250 Time 30.000 IsoW 4.0

4: Pos ·(335.0)->o(90.0-400.0)
MS/MS: Amp. 35.0% Q 0.250 Time 30.000 IsoW 3.0

Segment 10 Information

Duration (min): 3.79
Number of Scan Events: 2
Tune Method: oryzalin

Scan Event Details:
1: Pos ·(315.0)->o(85.0-400.0)
MS/MS: Amp. 32.0% Q 0.250 Time 30.000 IsoW 3.0

2: Pos ·(350.0)->o(95.0-400.0)
MS/MS: Amp. 28.0% Q 0.250 Time 30.000 IsoW 5.0

Segment 11 Information

Duration (min): 4.81
Number of Scan Events: 1
Tune Method: oryzalin

Scan Event Details:
1: Pos ·(350.0)->o(95.0-400.0)
MS/MS: Amp. 28.0% Q 0.250 Time 30.000 IsoW 5.0

Custom Dependent Data Settings:
Not enabled

## APPENDIX 2 Tune Method

| | |
|---|---|
| Capillary Temp (C): | 200 |
| APCI Vaporizer Temp (C): | 500 |
| Ion Time (ms): | 5 |
| Sheath Gas Flow (): | 44 |
| Aux Gas Flow (): | 3 |
| Source Type: | APCI |
| Injection Waveforms: | Off |
| AGC: | On |
| | |
| POSITIVE POLARITY | |
| Source Voltage (kV): | 6 |
| Source Current (uA): | 5 |
| Capillary Voltage (V): | 3 |
| Tube Lens Offset (V): | 15 |
| Octapole RF Amplifier (Vp-p): | 290 |
| Octapole 1 Offset (V): | -7.75 |
| Octapole 2 Offset (V): | -10 |
| Entrance Lens (V): | -26 |
| InterOctapole Lens Voltage (V): | -50 |
| Trap DC Offset Voltage (V): | -10 |
| Zoom Micro Scans: | 5 |
| Zoom AGC Target: | 20000000 |
| Zoom Max Ion Time (ms): | 50 |
| Full Micro Scans: | 3 |
| Full AGC Target: | 50000000 |
| Full Max Ion Time (ms): | 300 |
| SIM Micro Scans: | 3 |
| SIM AGC Target: | 20000000 |
| SIM Max Ion Time (ms): | 100 |
| MSn Micro Scans: | 2 |
| MSn AGC Target: | 20000000 |
| MSn Max Ion Time (ms): | 1000 |
| | |
| NEGATIVE POLARITY | |
| Source Voltage (kV): | 5 |
| Source Current (uA): | 80 |
| Capillary Voltage (V): | -47 |
| Tube Lens Offset (V): | -35 |
| Octapole RF Amplifier (Vp-p): | 120 |

| | |
|---|---|
| Octapole 1 Offset (V): | 6.25 |
| Octapole 2 Offset (V): | 12 |
| InterOctapole Lens Voltage (V): | 68 |
| Entrance Lens (V): | 52 |
| Trap DC Offset Voltage (V): | 10 |
| Zoom Micro Scans: | 5 |
| Zoom AGC Target: | 20000000 |
| Zoom Max Ion Time (ms): | 0 |
| Full Micro Scans: | 3 |
| Full AGC Target: | 50000000 |
| Full Max Ion Time (ms): | 200 |
| SIM Micro Scans: | 5 |
| SIM AGC Target: | 20000000 |
| SIM Max Ion Time (ms): | 200 |
| MSn Micro Scans: | 2 |
| MSn AGC Target: | 20000000 |
| MSn Max Ion Time (ms): | 800 |

## Appendix 3

Method Detection Limit (MDL) data

| | | Replicates | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Spiked (ug) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | Average | Stdev | MDL=STDEV* 3.143 | RL (suggest) |
| | | | | | | | | | | | | |
| DimethoateOA | 0.2 | 0.195 | 0.192 | 0.209 | 0.191 | 0.203 | 0.214 | 0.213 | 0.199 | 0.013 | 0.042 | 0.250 |
| Dimethoate | 0.2 | 0.160 | 0.173 | 0.208 | 0.192 | 0.200 | 0.175 | 0.189 | 0.186 | 0.016 | 0.050 | 0.250 |
| Malathion OA | 0.2 | 0.185 | 0.186 | 0.191 | 0.186 | 0.192 | 0.179 | 0.183 | 0.189 | 0.009 | 0.028 | 0.250 |
| Simazine | 0.2 | 0.181 | 0.177 | 0.179 | 0.190 | 0.182 | 0.183 | 0.199 | 0.186 | 0.008 | 0.026 | 0.250 |
| Diazinon OA | 0.2 | 0.213 | 0.190 | 0.219 | 0.227 | 0.229 | 0.233 | 0.225 | 0.218 | 0.014 | 0.045 | 0.250 |
| Norflurazon | 0.2 | 0.184 | 0.175 | 0.144 | 0.213 | 0.211 | 0.178 | 0.218 | 0.187 | 0.026 | 0.081 | 0.250 |
| Diuron | 0.2 | 0.175 | 0.203 | 0.132 | 0.205 | 0.178 | 0.137 | 0.223 | 0.184 | 0.035 | 0.111 | 0.250 |
| Phosmet | 0.4 | NO Data | | | | | | | | | | |
| Azinphos Methyl | 0.4 | 0.377 | 0.364 | 0.278 | 0.372 | 0.349 | 0.257 | 0.412 | 0.345 | 0.052 | 0.164 | 1.000 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Molinate | 0.2 | 0.151 | 0.167 | 0.179 | 0.171 | 0.148 | 0.176 | 0.150 | 0.163 | 0.012 | 0.039 | 0.250 |
| Malathion | 0.2 | 0.152 | 0.141 | 0.131 | 0.118 | 0.130 | 0.157 | 0.155 | 0.141 | 0.015 | 0.047 | 0.250 |
| Metolachlor | 0.2 | 0.166 | 0.177 | 0.204 | 0.184 | 0.173 | 0.175 | 0.176 | 0.184 | 0.019 | 0.059 | 0.250 |
| Propanil | 0.2 | 0.178 | 0.182 | 0.158 | 0.209 | 0.189 | 0.186 | 0.199 | 0.184 | 0.016 | 0.050 | 0.250 |
| Chlorpyrifos OA | 0.2 | 0.199 | 0.225 | 0.198 | 0.174 | 0.171 | 0.182 | 0.171 | 0.189 | 0.020 | 0.063 | 0.250 |
| EPTC | 0.2 | 0.162 | 0.157 | 0.176 | 0.177 | 0.167 | 0.143 | 0.173 | 0.165 | 0.011 | 0.036 | 0.250 |
| Oryzalin | 0.2 | 0.216 | 0.229 | 0.228 | 0.232 | 0.227 | 0.220 | 0.220 | 0.227 | 0.010 | 0.030 | 0.250 |
| Diazinon | 0.2 | 0.185 | 0.176 | 0.196 | 0.192 | 0.191 | 0.189 | 0.185 | 0.190 | 0.008 | 0.025 | 0.250 |
| Thioben carb | 0.2 | 0.229 | 0.162 | 0.269 | 0.198 | 0.181 | 0.156 | 0.226 | 0.200 | 0.038 | 0.121 | 0.500 |
| DEF | 0.2 | 0.191 | 0.190 | 0.190 | 0.204 | 0.193 | 0.199 | 0.226 | 0.198 | 0.012 | 0.038 | 0.250 |

| | Spiked (ug) | MDL-1 | MDL-2 | MDL-3 | MDL-4 | MDL-5 | MDL-6 | MDL-7 | Average | STDEV | MDL =3.143 x stdev | RL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Dichlorvos | 0.2 | 0.19 | 0.2 | 0.18 | 0.2 | 0.23 | 0.21 | 0.16 | 0.196 | 0.022 | 0.070 | 1.0 |
| Trifluralin | 0.2 | 0.26 | 0.26 | 0.26 | 0.26 | 0.29 | 0.26 | 0.26 | 0.264 | 0.011 | 0.036 | 0.5 |
| Chlorothalonil | 0.4 | 0.544 | 0.624 | 0.504 | 0.63 | 0.674 | 0.4 | 0.514 | 0.556 | 0.094 | 0.295 | 2.0 |
| Chlorpyrfos | 0.2 | 0.136 | 0.201 | 0.175 | 0.193 | 0.252 | 0.201 | 0.194 | 0.193 | 0.035 | 0.109 | 1.0 |
| Dicifol | 0.2 | 0.192 | 0.214 | 0.205 | 0.205 | 0.239 | 0.208 | 0.2199 | 0.212 | 0.015 | 0.046 | 1.0 |
| Endosulfan | 0.2 | 0.172 | 0.209 | 0.199 | 0.187 | 0.241 | 0.204 | 0.185 | 0.200 | 0.022 | 0.070 | 1.0 |
| Oxyfluorfen | 0.4 | 0.354 | 0.408 | 0.357 | 0.394 | 0.477 | 0.367 | 0.424 | 0.397 | 0.044 | 0.138 | 1.0 |
| Endosulfan sulfate | 0.2 | 0.216 | 0.242 | 0.185 | 0.186 | 0.256 | 0.172 | 0.191 | 0.207 | 0.032 | 0.100 | 1.0 |
| Propargite | 0.4 | 0.36 | 0.41 | 0.35 | 0.36 | 0.4 | 0.34 | 0.36 | 0.369 | 0.026 | 0.082 | 1.0 |
| Permethrin | 0.4 | 0.402 | 0.472 | 0.431 | 0.463 | 0.555 | 0.434 | 0.489 | 0.464 | 0.050 | 0.156 | 1.0 |
| Cypermethrin | 0.4 | 0.45 | 0.49 | 0.5 | 0.51 | 0.53 | 0.44 | 0.49 | 0.487 | 0.032 | 0.101 | 1.0 |

## Appendix 4
## Method Validation Data

| | | Set 1 | | Set 2 | | Set 3 | | Set 4 | | Set 5 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Spike Level** | **Result** | **Recovery** | **Result** | **Recovery** | **Result** | **Recovery** | **Result** | **Recovery** | **Result** | **Recovery** |
| | (µg) | (µg) | (%) | (µg) | (%) | (µg) | **(%)** | (µg) | **(%)** | (µg) | (%) |
| DimethoateOA | 0.5 | 0.599 | 120 | 0.53 | 106 | 0.524 | 105 | 0.445 | 89 | 0.469 | 94 |
| | 1 | 1.11 | 111 | 1.13 | 113 | 0.993 | 99 | 0.921 | 92 | 0.924 | 92 |
| | 5 | 5.26 | 105 | 5.33 | 107 | 4.73 | 95 | 4.15 | 83 | 4.63 | 93 |
| | 10 | 10.33 | 103 | 10.78 | 108 | 9.62 | 96 | 9.75 | 97 | 9.47 | 95 |
| Dimethoate | 0.5 | 0.411 | 82 | 0.505 | 101 | 0.498 | 100 | 0.51 | 102 | 0.415 | 83 |
| | 1 | 0.914 | 91 | 0.864 | 86 | 0.959 | 96 | 1.15 | 115 | 0.792 | 79 |
| | 5 | 4.02 | 80 | 4.47 | 89 | 5.00 | 100 | 4.21 | 84 | 4.6 | 92 |
| | 10 | 8.71 | 87 | 9.81 | 98 | 9.03 | 90 | 10.7 | 107 | 8.7 | 87 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Malathion OA | 0.5 | 0.546 | 109 | 0.603 | 121 | 0.521 | 104 | 0.44 | 88 | 0.477 | 95 |
| | 1 | 1.14 | 114 | 1.03 | 103 | 1.06 | 106 | 0.947 | 95 | 1.03 | 103 |
| | 5 | 5.09 | 102 | 5.02 | 100 | 5.46 | 109 | 4.85 | 97 | 4.73 | 95 |
| | 10 | 10.57 | 106 | 10.23 | 102 | 10.0 | 100 | 9.39 | 94 | 10.6 | 106 |
| Simazine | 0.5 | 0.463 | 93 | 0.506 | 101 | 0.439 | 88 | 0.538 | 108 | 0.442 | 88 |
| | 1 | 1.06 | 106 | 0.963 | 96 | 0.815 | 82 | 1.09 | 109 | 0.917 | 92 |
| | 5 | 4.51 | 90 | 4.66 | 93 | 4.61 | 92 | 5.06 | 101 | 4.61 | 92 |
| | 10 | 9.49 | 95 | 9.88 | 99 | 8.66 | 87 | 11.1 | 111 | 9.01 | 90 |
| Diazinon OA | 0.5 | 0.516 | 103 | 0.651 | 130 | 0.509 | 102 | 0.28 | 94 | 0.494 | 99 |
| | 1 | 1.05 | 105 | 1.18 | 118 | 0.948 | 95 | 0.576 | 97 | 0.992 | 99 |
| | 5 | 5.03 | 101 | 5.75 | 115 | 4.96 | 99 | 2.73 | 92 | 4.01 | 80 |
| | 10 | 10.07 | 101 | 11.09 | 111 | 9.66 | 97 | 6.21 | 105 | 10.3 | 103 |
| Norflurazon | 0.5 | 0.45 | 90 | 0.563 | 113 | 0.349 | 70 | 0.503 | 101 | 0.554 | 111 |
| | 1 | 1.06 | 106 | 1.1 | 110 | 0.864 | 86 | 1.06 | 106 | 0.837 | 84 |
| | 5 | 4.85 | 97 | 5.3 | 106 | 4.25 | 85 | 5.12 | 102 | 4.1 | 82 |
| | 10 | 9.59 | 96 | 9.44 | 94 | 8.08 | 81 | 10.9 | 109 | 8.71 | 87 |
| Diuron | 0.5 | 0.493 | 99 | 0.424 | 85 | 0.438 | 88 | 0.499 | 100 | 0.61 | 122 |
| | 1 | 1.1 | 110 | 1.05 | 105 | 0.915 | 91 | 1.09 | 109 | 1.15 | 115 |
| | 5 | 5.87 | 117 | 4.8 | 96 | 5.06 | 101 | 4.56 | 91 | 4.07 | 81 |
| | 10 | 9.76 | 98 | 11.37 | 114 | 9.75 | 98 | 10.1 | 101 | 7.26 | 73 |
| Phosmet | 1.0/0.5 | 1.48 | 148 | 1.235 | 123 | 1.30 | 130 | 0.392 | 78.4 | 0.437 | 87 |
| | 2.0/1.0 | 3.64 | 182 | 2 | 100 | 2.73 | 136 | 0.884 | 88.4 | 1.02 | 102 |
| | 10/5.0 | 14.4 | 144 | 10.1 | 101 | 11.58 | 116 | 0.460 | 92 | 5.28 | 106 |
| | 20/10. | 33.13 | 166 | 15.88 | 79 | 20.6 | 103 | 1.09 | 109 | 11.8 | 118 |
| Azinphos Methyl | 1.0/0.5 | 0.553 | 55 | 0.691 | 69 | 0.713 | 71 | 0.476 | 95 | 0.297 | 59 |
| | 2.0/1.0 | 1.79 | 89 | 1.73 | 86 | 2.11 | 105 | 1.00 | 100 | 0.647 | 65 |
| | 10/5.0 | 8.08 | 81 | 8.15 | 81 | 9.63 | 96 | 4.85 | 97 | 3.55 | 71 |
| | 20.0/10.0 | 16.55 | 83 | 15.88 | 79 | 19.2 | 96 | 11.3 | 113 | 8.34 | 83 |
| Molinate | 0.5 | 0.304 | 61 | 0.328 | 66 | 0.390 | 78 | 0.448 | 90 | 0.389 | 78 |
| | 1 | 0.636 | 64 | 0.62 | 62 | 0.774 | 77 | 0.907 | 91 | 0.821 | 82 |
| | 5 | 2.98 | 60 | 3.35 | 67 | 5.01 | 100 | 4.54 | 91 | 4.28 | 86 |
| | 10 | 7.84 | 78 | 8.32 | 83 | 9.48 | 95 | 10.2 | 102 | 9.34 | 93 |
| Malathion | 0.5 | 0.369 | 74 | 0.496 | 99 | 0.342 | 68 | 0.577 | 115 | 0.335 | 67 |
| | 1 | 0.835 | 84 | 0.84 | 84 | 0.928 | 93 | 1.08 | 108 | 0.68 | 68 |
| | 5 | 4.01 | 80 | 4.02 | 80 | 5.29 | 106 | 6.15 | 123 | 4.19 | 84 |
| | 10 | 8.2 | 82 | 7.57 | 76 | 8.53 | 85 | 11.9 | 119 | 8.82 | 88 |
| Metolachlor | 0.5 | 0.391 | 78 | 0.451 | 90 | 0.354 | 71 | 0.556 | 111 | 0.449 | 90 |
| | 1 | 0.938 | 94 | 0.938 | 94 | 0.935 | 93 | 1.09 | 109 | 0.887 | 89 |
| | 5 | 4.02 | 80 | 3.96 | 79 | 4.97 | 99 | 5.77 | 115 | 5.13 | 103 |
| | 10 | 9.07 | 91 | 8.5 | 85 | 6.69 | 67 | 10.9 | 109 | 10.6 | 106 |
| Propanil | 0.5 | 0.407 | 81 | 0.504 | 101 | 0.488 | 98 | 0.484 | 97 | 0.53 | 106 |
| | 1 | 0.841 | 84 | 1.02 | 102 | 0.865 | 86 | 0.969 | 97 | 0.904 | 90 |
| | 5 | 3.5 | 70 | 4.44 | 89 | 4.76 | 95 | 4.75 | 95 | 4.87 | 97 |
| | 10 | 7.91 | 79 | 9.63 | 96 | 9.52 | 95 | 10.6 | 106 | 11 | 110 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Chlorpyrifos OA | 0.5 | 0.546 | 109 | 0.577 | 115 | 0.474 | 95 | 0.723 | 145 | 0.46 | 92 |
| | 1 | 1.25 | 125 | 1.09 | 109 | 1.02 | 102 | 1.3 | 130 | 0.969 | 97 |
| | 5 | 4.17 | 83 | 4.56 | 91 | 4.90 | 98 | 4.94 | 99 | 5.24 | 105 |
| | 10 | 9.83 | 98 | 9.3 | 93 | 6.48 | 65 | 10.2 | 102 | 10.9 | 109 |
| EPTC | 0.5 | 0.27 | 54 | 0.343 | 69 | 0.415 | 83 | 0.446 | 89 | 0.394 | 79 |
| | 1 | 0.344 | 34 | 0.689 | 69 | 0.676 | 68 | 0.928 | 93 | 0.773 | 77 |
| | 5 | 2.2 | 44 | 3.04 | 61 | 4.08 | 82 | 4.68 | 94 | 4.08 | 82 |
| | 10 | 7.42 | 74 | 8.12 | 81 | 8.12 | 81 | 10.4 | 104 | 8.58 | 86 |
| Oryzalin | 0.5 | 0.544 | 109 | 0.519 | 104 | 0.439 | 88 | 0.605 | 121 | 0.554 | 111 |
| | 1 | 0.989 | 99 | 0.949 | 95 | 0.955 | 95 | 1.08 | 108 | 1.02 | 102 |
| | 5 | 4.49 | 90 | 3.76 | 75 | 4.80 | 96 | 5.73 | 115 | 5.26 | 105 |
| | 10 | 10.99 | 110 | 8.32 | 83 | 8.45 | 84 | 11.1 | 111 | 11.6 | 116 |
| Diazinon | 0.5 | 0.418 | 84 | 0.407 | 81 | 0.387 | 77 | 0.401 | 80 | 0.474 | 95 |
| | 1 | 0.884 | 88 | 0.772 | 77 | 0.938 | 94 | 0.899 | 90 | 0.959 | 96 |
| | 5 | 3.97 | 79 | 3.72 | 74 | 5.07 | 101 | 5.05 | 101 | 4.66 | 93 |
| | 10 | 8.47 | 85 | 8.13 | 81 | 8.82 | 88 | 11.4 | 114 | 9.86 | 99 |
| Thioben carb | 0.5 | 0.435 | 87 | 0.517 | 103 | 0.511 | 102 | 0.427 | 85 | 0.463 | 93 |
| | 1 | 0.947 | 95 | 0.815 | 81 | 0.879 | 88 | 0.926 | 93 | 0.943 | 94 |
| | 5 | 4.31 | 86 | 4.00 | 80 | 5.22 | 104 | 4.8 | 96 | 4.79 | 96 |
| | 10 | 8.41 | 84 | 8.83 | 88 | 10.1 | 101 | 9.69 | 97 | 9.87 | 99 |
| DEF | 0.5 | 0.434 | 87 | 0.463 | 93 | 0.496 | 99 | 0.488 | 98 | 0.478 | 96 |
| | 1 | 0.915 | 91 | 0.922 | 92 | 0.951 | 95 | 0.991 | 99 | 0.948 | 95 |
| | 5 | 4.01 | 80 | 4.38 | 88 | 5.06 | 101 | 4.98 | 100 | 4.8 | 96 |
| | 10 | 9.11 | 91 | 9.03 | 90 | 9.30 | 93 | 10.8 | 108 | 9.97 | 100 |

| | | SET 1 | | SET 2 | | SET 3 | | SET 4 | | SET 5 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Analyte** | **Spike Level** | Result | Recovery | Result | Recovery | Result | Recovery | Result | Recovery | Result | Recovery |
| | **(ug)** | **(ug)** | **(%)** | **(ug)** | **(%)** | **(ug)** | **(%)** | (ug) | (%) | (ug) | (%) |
| 1) DICHLORVOS | 0.5 | 0.227 | 45 | 0.576 | 115 | 0.550 | 0.5 | 0.570 | 114 | 0.680 | 136 |
| | 1.0 | 0.499 | 50 | 1.04 | 104 | 0.960 | 96 | 1.09 | 109 | 1.01 | 101 |
| | 5 | 3.36 | 67 | 3.34 | 67 | 4.68 | 94 | 4.09 | 82 | 5.24 | 105 |
| | 10 | 6.58 | 66 | 9.70 | 97 | 12.6 | 126 | 10.8 | 108 | 9.48 | 95 |
| 2) TRIFLURALIN | 0.5 | 0.486 | 97 | 0.506 | 101 | 0.530 | 106 | 0.600 | 120 | 0.630 | 126 |
| | 1.0 | 0.955 | 96 | 1.05 | 105 | 0.840 | 84 | 1.08 | 108 | 0.970 | 97 |
| | 5.0 | 4.78 | 96 | 4.25 | 85 | 4.68 | 94 | 4.23 | 85 | 5.15 | 103 |
| | 10 | 9.86 | 99 | 9.42 | 94 | 11.8 | 118 | 12.4 | 124 | 11.0 | 110 |
| 3) CHLOROTHALONIL | 1.0/0.5 | 1.20 | 120 | 1.17 | 117 | 1.45 | 145 | 0.749 | 150 | 1.31 | 262 |
| | 2.0/1.0 | 1.91 | 95 | 2.14 | 107 | 2.08 | 104 | 1.03 | 103 | 1.49 | 149 |
| | 10/5.0 | 8.62 | 86 | 9.26 | 93 | 9.59 | 96 | 4.64 | 93 | 5.38 | 108 |
| | 20.0/10.0 | 23.6 | 118 | 9.55 | 48 | 23.4 | 117 | 15.8 | 158 | 12.2 | 122 |
| 4) | 0.5 | 0.470 | 94 | 0.459 | 92 | 0.640 | 128 | 0.510 | 102 | 0.530 | 106 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CHLORPYRIFOS | | | | | | | | | | | |
| | 1.0 | 0.877 | 88 | 1.05 | 105 | 0.920 | 92 | 1.19 | 119 | 0.900 | 90 |
| | 5 | 4.73 | 95 | 4.10 | 82 | 2.88 | 58 | 5.29 | 106 | 5.34 | 107 |
| | 10.0 | 7.80 | 78 | 9.36 | 94 | 10.4 | 104 | 12.4 | 124 | 9.92 | 99 |
| 5) DICOFOL p,p' | 0.5 | 0.498 | 100 | 0.484 | 97 | 0.500 | 100 | 0.380 | 76 | 0.430 | 86 |
| | 1.0 | 0.941 | 94 | 1.05 | 105 | 0.850 | 85 | 1.02 | 102 | 0.830 | 83 |
| | 5.0 | 5.09 | 102 | 4.20 | 84 | 4.29 | 86 | 4.78 | 96 | 5.23 | 105 |
| | 10 | 8.32 | 83 | 9.72 | 97 | 11.3 | 113 | 9.94 | 99 | 11.2 | 112 |
| 6) ENDOSULFAN (Thiodan 1) | 0.5 | 0.516 | 103 | 0.419 | 84 | 0.440 | 88 | 0.650 | 130 | 0.53 | 106 |
| | 1.0 | 1.05 | 105 | 1.17 | 117 | 0.800 | 80 | 1.08 | 108 | 0.91 | 91 |
| | 5.0 | 5.08 | 102 | 4.84 | 97 | 4.78 | 96 | 4.67 | 93 | 5.55 | 111 |
| | 10 | 10.8 | 108 | 9.7 | 97 | 12.0 | 120 | 10.7 | 107 | 10.6 | 106 |
| 7) OXYFLUORFEN | 1.0/0.5 | 1.03 | 103 | 1.03 | 103 | 1.13 | 113.0 | 0.440 | 88 | 0.78 | 156 |
| | 2.0/1.0 | 1.84 | 92 | 2.03 | 102 | 1.88 | 94 | 1.06 | 106 | 1.06 | 106 |
| | 10/5.0 | 9.70 | 97 | 8.93 | 89 | 9.94 | 99 | 4.78 | 96 | 5.52 | 110 |
| | 20.0/10.0 | 18.9 | 95 | 19.8 | 99 | 23.2 | 116 | 10.5 | 105 | 11.1 | 111 |
| 8) ENDOSULFAN SULFATE | 0.5 | 0.534 | 107 | 0.555 | 111 | 0.670 | 134 | 0.510 | 102 | 0.620 | 124 |
| | 1.0 | 0.882 | 88 | 0.966 | 97 | 1.05 | 105 | 1.11 | 111 | 0.930 | 93 |
| | 5 | 4.49 | 90 | 4.88 | 98 | 5.23 | 105 | 4.93 | 99 | 5.46 | 109 |
| | 10.0 | 12.0 | 120 | 9.00 | 90 | 12.3 | 123 | 11.4 | 114 | 11.0 | 110 |
| 9) PROPARGITE | 1.0/0.5 | 0.972 | 97 | 0.801 | 80 | 1.36 | 136 | 0.390 | 78 | 0.550 | 110 |
| | 2.0/1.0 | 2.13 | 107 | 2.11 | 106 | 2.03 | 102 | 1.11 | 111 | 1.10 | 110 |
| | 10/5.0 | 12.3 | 123 | 8.41 | 84 | 8.65 | 87 | 3.83 | 77 | 4.97 | 99 |
| | 20.0/10.0 | 18.9 | 95 | 16.8 | 84 | 21.4 | 107 | 8.65 | 87 | 9.36 | 94 |
| 10) PERMETHRIN | 1.0/0.5 | 0.960 | 96 | 1.00 | 100 | 1.10 | 110.0 | 0.470 | 94 | 0.500 | 100 |
| | 2.0/1.0 | 1.93 | 97 | 2.25 | 112 | 1.90 | 95 | 1.02 | 102 | 0.870 | 87 |
| | 10/5.0 | 9.44 | 94 | 9.60 | 96 | 10.6 | 106 | 5.00 | 100 | 5.52 | 110 |
| | 20.0/10.0 | 19.0 | 95 | 19.7 | 99 | 24.9 | 124 | 10.5 | 105 | 11.2 | 112 |
| 11) CYPERMETHRIN | 1.0/0.5 | 0.974 | 97 | 1.03 | 103 | 1.33 | 133 | 0.650 | 130 | 0.540 | 108 |
| | 2.0/1.0 | 1.77 | 89 | 2.11 | 106 | 2.06 | 103 | 1.20 | 120 | 0.900 | 90 |
| | 10.0/5.0 | 9.20 | 92 | 9.34 | 93 | 10.0 | 100 | 4.36 | 87 | 5.29 | 106 |
| | 20.0/10.0 | 19.6 | 98 | 16.5 | 83 | 24.0 | 120 | 11.5 | 115 | 11.5 | 115 |

# Appendix 5
# Sample Storage Data

**Storage Recovery LC-MS**

| | | | Sample 1 | | Sample 2 | | Sample 3 | |
|---|---|---|---|---|---|---|---|---|
| | | Spiked (µg) | Found(µg) | Recovery (%) | Found (µg) | Recovery (%) | Found (µg)) | Recovery (%) |
| DimethoateOA | Day 0 | none | 0.415 | | trace | | 0.398 | |
| | Day 7 | none | trace | | 0.39 | | 0.403 | |
| | Day14 | none | 0.513 | | 0.481 | | 0.578 | |
| | Day 28 | none | trace | | trace | | trace | |
| Dimethoate | Day 0 | 10.0 | 10.4 | 104 | 8.55 | 86 | 9.78 | 98 |
| | Day 7 | 10.0 | 9.56 | 96 | 9.54 | 95 | 9.33 | 93 |
| | Day14 | 10.0 | 9.68 | 97 | 10.5 | 105 | 8.04 | 80 |
| | Day 28 | 10.0 | 10.7 | 107 | 9.86 | 99 | 9.75 | 97 |
| Malathion OA | Day 0 | none | 0.194 | | trace | | 0.217 | |
| | Day 7 | none | trace | | trace | | 0.209 | |
| | Day14 | none | 0.270 | | 0.271 | | 0.301 | |
| | Day 28 | none | 0.051 | | trace | | trace | |
| Simazine | Day 0 | 10.0 | 9.99 | 100 | 9.52 | 95 | 10.3 | 103 |
| | Day 7 | 10.0 | 9.63 | 96 | 9.503 | 95 | 10.7 | 107 |
| | Day14 | 10.0 | 9.78 | 98 | 10.3 | 103 | 10.1 | 101 |
| | Day 28 | 10.0 | 10.6 | 106 | 10.0 | 100 | 10.5 | 105 |
| Diazinon OA | Day 0 | none | 0.405 | | trace | | 0.423 | |
| | Day 7 | none | trace | | 0.458 | | 0.435 | |
| | Day14 | none | 0.548 | | 0.519 | | 0.649 | |
| | Day 28 | none | trace | | trace | | trace | |
| Norflurazon | Day 0 | 10.0 | 10.4 | 104 | 9.38 | 94 | 10.6 | 106 |
| | Day 7 | 10.0 | 9.28 | 93 | 9.341 | 93 | 9.84 | 98 |
| | Day14 | 10.0 | 10.4 | 104 | 10.4 | 104 | 10.7 | 107 |
| | Day 28 | 10.0 | 11.2 | 112 | 10.5 | 105 | 10.2 | 102 |
| Diuron | Day 0 | 10.0 | 8.91 | 89 | 9.26 | 93 | 9.99 | 100 |
| | Day 7 | 10.0 | 11.3 | 113 | 10.1 | 101 | 9.49 | 95 |
| | Day14 | 10.0 | 11.5 | 115 | 10.7 | 107 | 10.4 | 104 |
| | Day 28 | 10.0 | 9.54 | 95 | 10.0 | 100 | 8.98 | 90 |
| Phosmet | Day 0 | 10.0 | 10.8 | 108 | 10.3 | 103 | 9.10 | 91 |
| | Day 7 | 10.0 | 12.0 | 120 | 13.9 | 139 | 11.5 | 115 |
| | Day14 | 10.0 | 16.6 | 166 | 18.1 | 181 | 16.4* | 164 |
| | Day 28 | 10.0 | 12.4* | 124 | 11.5 | 115 | 11.7 | 117 |
| Azinphos Methyl | Day 0 | 10.0 | 10.1 | 101 | 9.98 | 100 | 11.0 | 110 |
| | Day 7 | 10.0 | 11.5 | 115 | 11.460 | 115 | 11.466 | 115 |
| | Day14 | 10.0 | 9.23 | 92 | 10.8 | 108 | 9.30 | 93 |
| | Day 28 | 10.0 | 10.6 | 106 | 9.99 | 100 | 9.59 | 96 |
| Molinate | Day 0 | 10.0 | 8.29 | 83 | 8.77 | 88 | 7.62 | 76 |
| | Day 7 | 10.0 | 8.90 | 89 | 8.212 | 82 | 7.702 | 77 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Day14 | 10.0 | 8.49 | 85 | 8.40 | 84 | 7.91 | 79 |
| | Day 28 | 10.0 | 10.5 | 105 | 9.41 | 94 | 9.70 | 97 |
| Malathion | Day 0 | 10.0 | 8.49 | 85 | 8.03 | 80 | 7.36 | 74 |
| | Day 7 | 10.0 | 7.80 | 78 | 7.748 | 77 | 7.320 | 73 |
| | Day14 | 10.0 | 10.2 | 102 | 9.23 | 92 | 7.42 | 74 |
| | Day 28 | 10.0 | 10.4 | 104 | 9.91 | 99 | 9.72 | 97 |
| Metolachlor | Day 0 | 10.0 | 11.3 | 113 | 9.62 | 96 | 11.7 | 117 |
| | Day 7 | 10.0 | 9.95 | 100 | 9.274 | 93 | 9.484 | 95 |
| | Day14 | 10.0 | 9.14 | 91 | 10.1 | 101 | 9.62 | 96 |
| | Day 28 | 10.0 | 10.2 | 102 | 9.81 | 98 | 9.90 | 99 |
| Propanil | Day 0 | 10.0 | 10.9 | 109 | 9.75 | 97 | 10.8 | 108 |
| | Day 7 | 10.0 | 9.43 | 94 | 10.181 | 102 | 10.563 | 106 |
| | Day14 | 10.0 | 9.47 | 95 | 10.8 | 108 | 10.0 | 100 |
| | Day 28 | 10.0 | 9.14 | 91 | 9.00 | 90 | 8.93 | 89 |
| Chlorpyrifos OA | Day 0 | none | 0.403 | | 0.36 | | 0.398 | |
| | Day 7 | none | 0.273 | | 0.315 | | 0.300 | |
| | Day14 | none | trace | | trace | | trace | |
| | Day 28 | none | 0.303 | | 0.322 | | ND | |
| EPTC | Day 0 | 10.0 | 8.18 | 82 | 9.13 | 91 | 7.82 | 78 |
| | Day 7 | 10.0 | 8.54 | 85 | 7.836 | 78 | 7.625 | 76 |
| | Day14 | 10.0 | 7.40 | 74 | 7.60 | 76 | 7.38 | 74 |
| | Day 28 | 10.0 | 9.48 | 95 | 9.57 | 96 | 8.69 | 87 |
| Oryzalin | Day 0 | 10.0 | 9.83 | 98 | 8.71 | 87 | 9.76 | 98 |
| | Day 7 | 10.0 | 10.8 | 108 | 10.4 | 104 | 10.1 | 101 |
| | Day14 | 10.0 | 10.4 | 104 | 10.6 | 106 | 10.5 | 105 |
| | Day 28 | 10.0 | 11.9 | 119 | 11.7 | 117 | 11.3 | 113 |
| Diazinon | Day 0 | 10.0 | 9.25 | 92 | 9.89 | 99 | 9.15 | 91 |
| | Day 7 | 10.0 | 9.93 | 99 | 9.87 | 99 | 9.22 | 92 |
| | Day14 | 10.0 | 9.18 | 92 | 9.86 | 99 | 9.77 | 98 |
| | Day 28 | 10.0 | 11.6 | 116 | 10.8 | 108 | 10.8 | 108 |
| Thioben carb | Day 0 | 10.0 | 8.72 | 87 | 9.02 | 90 | 9.41 | 94 |
| | Day 7 | 10.0 | 9.94 | 99 | 10.1 | 101 | 9.66 | 97 |
| | Day14 | 10.0 | 10.2 | 102 | 11.1 | 111 | 9.32 | 93 |
| | Day 28 | 10.0 | 9.77 | 98 | 9.90 | 99 | 9.97 | 100 |
| DEF | Day 0 | 10.0 | 9.84 | 98 | 9.51 | 95 | 10.3 | 103 |
| | Day 7 | 10.0 | 9.84 | 98 | 9.93 | 99 | 10.31 | 103 |
| | Day14 | 10.0 | 10.5 | 105 | 11.1 | 111 | 10.3 | 103 |
| | Day 28 | 10.0 | 10.3 | 103 | 9.65 | 97 | 9.63 | 96 |

**Storage Recovery GC-MS**

| | | | Sample 1 | | Sample 2 | | Sample 3 | |
|---|---|---|---|---|---|---|---|---|
| | | Spiked (ug) | Found (ug) | % recovery | Found (ug) | % recovery | Found (ug) | % recovery |
| 1) DICHLORVOS | Day 0 | 10 | 10.8 | 108 | 11.4 | 114 | 10.1 | 101 |
| | Day 7 | 10 | 7.38 | 74 | 10.6 | 106 | 8.78 | 88 |
| | Day 14 | 10 | 11.7 | 117 | 8.1 | 81 | 12.6 | 126 |
| | DAy28 | 10 | 7.82 | 78 | 7.9 | 79 | 6.16 | 62 |
| 2) TRIFLURALIN | Day 0 | 10 | 10.5 | 105 | 11.6 | 116 | 10.2 | 102 |
| | Day 7 | 10 | 8.2 | 82 | 10.7 | 107 | 10.1 | 101 |
| | Day 14 | 10 | 11.0 | 110 | 8.3 | 83 | 11.8 | 118 |
| | DAy28 | 10 | 8.76 | 88 | 8.7 | 87 | 7.1 | 71 |
| 3) CHLOROTHALONIL | Day 0 | 10 | 13.0 | 130 | 13.9 | 139 | 11.7 | 117 |
| | Day 7 | 10 | 8.32 | 83 | 12.4 | 124 | 11.5 | 115 |
| | Day 14 | 10 | 12.2 | 122 | 8.8 | 88 | 13.5 | 135 |
| | DAy28 | 10 | 12.2 | 122 | 13.0 | 130 | 11.6 | 116 |
| 4) CHLORPYRIFOS | Day 0 | 10 | 10.4 | 104 | 12.1 | 121 | 10.0 | 100 |
| | Day 7 | 10 | 7.5 | 75 | 12.2 | 122 | 9.16 | 92 |
| | Day 14 | 10 | 11.7 | 117 | 7.4 | 74 | 11.4 | 114 |
| | DAy28 | 10 | 8.33 | 83 | 8.5 | 85 | 7.97 | 80 |
| 5) DICOFOL p,p' | Day 0 | 10 | 10.7 | 107 | 11.7 | 117 | 10.5 | 105 |
| | Day 7 | 10 | 9.36 | 94 | 12.3 | 123 | 12.1 | 121 |
| | Day 14 | 10 | 12.0 | 120 | 9.5 | 95 | 12.2 | 122 |
| | DAy28 | 10 | 8.82 | 88 | 9.1 | 91 | 7.58 | 76 |
| 6) Endosulfan | Day 0 | 10 | 10.2 | 102 | 12.6 | 126 | 10.1 | 101 |
| | Day 7 | 10 | 7.64 | 76 | 12.1 | 121 | 10.5 | 105 |
| | Day 14 | 10 | 11.5 | 115 | 8.2 | 82 | 12.1 | 121 |
| | DAy28 | 10 | 8.92 | 89 | 8.9 | 89 | 7.51 | 75 |
| 7) OXYFLUORFEN | Day 0 | 10 | 11.1 | 111 | 12.4 | 124 | 10.6 | 106 |
| | Day 7 | 10 | 7.84 | 78 | 12.6 | 126 | 10.7 | 107 |
| | Day 14 | 10 | 11.0 | 110 | 8.28 | 83 | 11.5 | 115 |
| | DAy28 | 10 | 8.63 | 86 | 8.76 | 88 | 7.41 | 74 |
| 8) ENDOSULFAN SULFATE | Day 0 | 10 | 11.1 | 111 | 12.3 | 123 | 9.20 | 92 |
| | Day 7 | 10 | 8.16 | 82 | 11.0 | 110 | 10.2 | 102 |
| | Day 14 | 10 | 10.8 | 108 | 7.04 | 70 | 11.6 | 116 |
| | DAy28 | 10 | 10.1 | 101 | 11.0 | 110 | 8.56 | 86 |
| 9) PROPARGITE | Day 0 | 10 | 7.28 | 73 | 7.92 | 79 | 9.26 | 93 |
| | Day 7 | 10 | 8.28 | 83 | 10.6 | 106 | 8.88 | 89 |
| | Day 14 | 10 | 11.6 | 116 | 7.9 | 79 | 10.2 | 102 |
| | DAy28 | 10 | 7.16 | 72 | 6.83 | 68 | 7.11 | 71 |
| 10) PERMETHRIN | Day 0 | 10 | 10.6 | 106 | 11.9 | 119 | 10.9 | 109 |
| | Day 7 | 10 | 8.54 | 85 | 11.5 | 115 | 11.4 | 114 |
| | Day 14 | 10 | 11.9 | 119 | 8.7 | 87 | 11.7 | 117 |
| | DAy28 | 10 | 9.62 | 96 | 9.97 | 100 | 7.37 | 74 |
| 11) CYPERMETHRIN | Day 0 | 10 | 10.9 | 109 | 13.2 | 132 | 11.1 | 111 |
| | Day 7 | 10 | 8.78 | 88 | 12.1 | 121 | 10.2 | 102 |
| | Day 14 | 10 | 11.4 | 114 | 8.26 | 83 | 11.8 | 118 |
| | DAy28 | 10 | 7.51 | 75 | 7.57 | 76 | 7.12 | 71 |

# Appendix 6
# Trapping Efficiency Data

**Trappimg Efficiency**

| Sample ID | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| Spiked (µg) | | 10.0 | 10.0 | 10.0 | 5.0 | 5.0 | 5.0 | 2.0 | 2.0 | 2.0 |
| DimethoateOA | No spike | 0.803 | 0.646 | 1.00 | 0.490 | 0.503 | 0.582 | 0.051 | 0.25 | trace |
| Dimethoate | | 8.39 | 8.95 | 7.60 | 4.30 | 4.01 | 4.21 | 1.53 | 1.75 | 2.05 |
| Malathion OA | No spike | 0.315 | 0.264 | 0.383 | 0.167 | 0.206 | 0.233 | trace | trace | trace |
| Simazine | | 11.1 | 10.2 | 11.3 | 5.23 | 5.28 | 4.93 | 2.18 | 2.27 | 2.29 |
| Diazinon OA | No spike | 0.552 | 0.507 | 0.677 | 0.311 | 0.376 | 0.399 | trace | trace | trace |
| Norflurazon | | 0.900 | 1.39 | 0.858 | 1.90 | 0.877 | 0.481 | 2.04 | 0.825 | 1.84 |
| Diuron | | 8.27 | 7.65 | 8.87 | 4.02 | 3.17 | 4.17 | 2.14 | 1.97 | 2.08 |
| Phosmet | | 10.6 | 9.79 | 10.5 | 3.89 | 4.66 | 4.51 | 2.36 | 1.76 | 2.24 |
| Azinphos Methyl | | 6.67 | 6.65 | 7.24 | 2.68 | 3.06 | 3.18 | 1.77 | 1.58 | 1.74 |
| Molinate | | 8.46 | 8.49 | 8.41 | 4.04 | 3.84 | 4.08 | 1.89 | 1.67 | 1.99 |
| | | | | | | | | | | |
| Malathion | | 6.89 | 8.73 | 10.4 | 3.80 | 3.56 | 4.45 | 2.26 | 1.84 | 1.93 |
| Metolachlor | | 8.37 | 6.40 | 7.71 | 4.81 | 3.80 | 4.11 | 1.94 | 1.75 | 1.83 |
| Propanil | | 10.5 | 9.32 | 10.2 | 5.08 | 5.01 | 4.58 | 1.68 | 1.91 | 2.31 |
| Chlorpyrifos OA | No spike | 0.47 | 0.45 | 0.496 | 0.434 | 0.437 | 0.456 | trace | 0.400 | trace |
| EPTC | | 9.05 | 8.87 | 8.81 | 4.11 | 4.02 | 3.74 | 1.86 | 1.69 | 1.84 |
| Oryzalin | | 1.25 | 1.73 | 1.34 | 2.26 | 0.95 | 0.53 | 1.74 | 0.473 | 1.65 |
| Diazinon | | 10.6 | 8.54 | 8.84 | 4.14 | 4.35 | 4.57 | 1.83 | 1.73 | 1.42 |
| Thioben carb | | 8.95 | 9.00 | 9.15 | 4.3 | 4.35 | 4.45 | 2.00 | 1.82 | 2.12 |
| DEF | | 9.85 | 9.09 | 10.1 | 4.59 | 4.6 | 4.81 | 1.9 | 1.81 | 2.06 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 1) DICHLORVOS | | 11.2 | 12.8 | 9.88 | 5.2 | 5.58 | 5.86 | 1.36 | 1.62 | 1.70 |
| 2) TRIFLURALIN | | 6.74 | 9.30 | 6.86 | 4.62 | 3.86 | 4.20 | 1.24 | 1.52 | 1.58 |
| 3) CHLOROTHALONIL | | 11.4 | 8.92 | 6.54 | 4.94 | 3.14 | 3.52 | 1.74 | 1.58 | 1.86 |
| 4) CHLORPYRIFOS | | 10.1 | 11.0 | 8.52 | 4.60 | 4.40 | 4.78 | 1.08 | 1.30 | 1.24 |
| 5) DICOFOL p,p' | | 10.3 | 11.4 | 9.9 | 5.14 | 5.22 | 4.98 | 1.24 | 1.84 | 1.58 |
| 6) Endosulfan | | 10.1 | 11.5 | 9.66 | 5.28 | 5.00 | 5.36 | 1.14 | 1.68 | 1.48 |
| 7) OXYFLUORFEN | | 1.98 | 2.82 | 1.96 | 3.04 | 1.70 | 1.54 | 1.38 | 1.10 | 1.60 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 8) ENDOSULFAN SULFATE | | 11.3 | 11.3 | 9.5 | 5.72 | 4.80 | 4.82 | 1.30 | 1.78 | 1.70 |
| 9) PROPARGITE | | 9.34 | 9.64 | 7.92 | 3.64 | 3.92 | 4.06 | 1.02 | 1.28 | 1.08 |
| 10) PERMETHRIN | | 8.70 | 10.1 | 9.24 | 5.36 | 4.90 | 4.72 | 1.18 | 1.88 | 1.62 |
| 11) CYPERMETHRIN | | 9.86 | 10.0 | 9.24 | 6.22 | 5.44 | 5.46 | 2.44 | 2.82 | 2.68 |

## Appendix 7

### Cleaning XAD-4 resin

1. Measure 1.6 kg XAD-4 resin (about 3.0-3.5 liters) to a 6 liters Teflon (or Glass) container.
2. Wet with 2 liters of residue grade methanol. Then add 2 liters of 0.25 N HCl. Stir occasionally with a glass or Teflon rod for about 30 minutes.
3. Transfer the content 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 out going water.
5. Transfer the water washed XAD-4 to the container of Soxhlet extractor. Drain the water through the stopcock. Add residue grade methanol to just cover the resin. Stir with a glass rod to help remove the air bubble.( Do not disturb the glass wool plug.). Drain the methanol through the stopcock.
6. Add about 4 liters methanol to the resin and allow the methanol to be siphoned to the solvent flask. The solvent flask should be 60% full.
7. Start the extraction and continue for at least 72 hours
8. Change extraction solvent to ethyl acetate and continue the process for at least 72 hours.
9. Dry the resin at 28 inches vacuum or higher and 40 °C for at least 72 hours until all traces of ethyl acetate is 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.

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

**Author**:

_____ _____
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**Approved By**:

_____ _____
Stephen Siegel Date
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**Reviewed By:**

_____ _____
Elaine Wong Date
Program Supervisor

## Revision Log:

| Date | What was Revised? Why? |
|---|---|
| 10/27/2008 | Added in section 15.1 |
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