Determination of 53 Pesticides in Groundwater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) and Gas Chromatography Tandem Mass Spectrometry (GC/MS/MS)

1. Scope:

This Section Method (SM) provides stepwise procedures for the analysis of 53 pesticides in well water. It is followed by all authorized Environmental Analysis Unit personnel.

2. Principle:

The pesticides are extracted from the well water sample with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated using a nitrogen evaporator and adjusted to a final volume of 2 mL. An aliquot of 1 mL is removed for analysis by gas chromatography tandem mass spectrometry (GC/MS/MS) and the remaining 1 mL is evaporated to dryness, reconstituted with 1 mL of methanol (MeOH) and then diluted with 1 mL of liquid chromatography/mass spectrometry (LC/MS) grade water (H_2O). This extract is then analyzed by liquid chromatography tandem mass spectrometry (LC/MS/MS).

The original extracted sample is acidified with hydrochloric acid (HCl) and re-extracted with methylene chloride. The extract is passed through sodium sulfate to remove residual H_2O. The anhydrous extract is evaporated to dryness using a nitrogen evaporator, reconstituted with 1 mL of MeOH and then diluted with 1 mL of LC/MS H_2O. This extract is then analyzed by LC/MS/MS for the pesticide, Bentazon.

3. Safety:

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

3.2 Methylene chloride is a regulated and controlled carcinogenic hazardous substance. It must be stored and handled in accordance with California Code of Regulations, Title 8, Subchapter 7, Group 16, Article 110, Section 5202.

3.3 Hydrochloric acid

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

4. Interferences:

There were no matrix interferences for the compounds at the time of method development.

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 Vortex mixer

5.5 High performance liquid chromatography (HPLC) coupled to a tandem quadrupole mass spectrometer

5.6 GC coupled to triple quadrupole mass spectrometer (MS)

6. Standards and Reagents and Supplies:

LC/MS/MS Standards:

6.1	Atrazine	CAS# 1912-24-9
6.2	Azinphos-methyl	CAS# 86-50-0
6.3	Azoxystrobin	CAS# 131860-33-8
6.4	Bensulide	CAS# 741-58-2
6.5	Bromacil	CAS# 314-40-9
6.6	Carbaryl	CAS# 63-25-2
6.7	Carbofuran	CAS# 1563-66-2
6.8	Diazinon	CAS# 333-41-5
6.9	Dimethenamide	CAS# 87674-68-8

6.10	Dimethoate	CAS# 60-51-5
6.11	Diuron	CAS# 330-54-1
6.12	Ethofumesate	CAS# 26225-79-6
6.13	Fenamiphos	CAS# 22224-92-6
6.14	Fludioxonil	CAS# 13141-86-1
6.15	Imidacloprid	CAS# 138261-41-3
6.16	Linuron	CAS# 330-55-2
6.17	Mefenoxam	CAS# 70630-17-0
6.18	Methiocarb	CAS# 2032-65-7
6.19	Metolachlor	CAS# 51218-45-2
6.20	Metribuzin	CAS# 21087-64-9
6.21	Napropamide	CAS# 15299-99-7
6.22	Norflurazon	CAS# 27314-13-2
6.23	Oryzalin	CAS# 19044-88-3
6.24	Prometon	CAS# 1610-18-0
6.25	Simazine	CAS# 175217-20-6
6.26	Tebuthiuron	CAS# 34014-18-1
6.27	Thiamethoxam	CAS# 153719-23-4
6.28	Thiobencarb	CAS# 28249-77-6
6.29	Uniconizole	CAS# 83657-17-4
6.30	Methoxyfenozide	CAS# 161050-58-4
6.31	Methomyl	CAS# 16752-77-5

6.32	Chlorantraniliprole	CAS# 500008-45-7
6.33	Isoxaben	CAS# 82558-50-7
6.34	Propiconazole	CAS# 60207-90-1
6.35	Pyraclostrobin	CAS# 175013-18-0
6.36	Cyprodinil	CAS#121552-61-2
6.37	Flutrifol	CAS# 76674-21-0
6.38	Alachlor	CAS# 15972-60-8
6.39	Bentazon	CAS# 25057-89-0

GC/MS/MS Standards:

6.40	Clomazone	CAS # 81777-89-1
6.41	Dichlobenil	CAS # 1194-65-6
6.42	Dichloran	CAS # 99-30-9
6.43	Disulfoton	CAS # 298-04-4
6.44	Ethoprophos	CAS # 13194-48-4
6.45	Fonofos	CAS # 944-22-9
6.46	Malathion	CAS # 121-75-5
6.47	Parathion Ethyl	CAS # 56-38-2
6.48	Parathion Methyl	CAS # 298-00-0
6.49	Phorate	CAS # 298-02-2
6.50	Piperonyl Butoxide	CAS # 51-03-6
6.51	Prometryn	CAS # 7287-19-6
6.52	Propanil	CAS # 709-98-8

6.53 Triallate CAS # 2303-17-5

Reagents and Supplies:

6.54 Methylene chloride, nanograde or equivalent pesticide grade

6.55 Water, MS grade, Burdick & Jackson or equivalent

6.56 Methanol, MS grade, Burdick & Jackson or equivalent

6.57 Formic acid, HPLC grade

6.58 Ammonium formate, reagent grade or equivalent

6.59 Separatory funnel, 2 L

6.60 Boiling flask, 500 mL

6.61 Sodium sulfate, ACS grade or equivalent

6.62 Funnels, long stem, 60°, 100 mm I.D.

6.63 Graduated conical tubes with glass stopper, 15 mL

6.64 Glass wool, Pyrex® fiber glass slivers 8 microns

6.65 Disposable Pasteur pipettes, and other laboratory ware as needed

6.66 Recommended HPLC analytical column:

- Ace Excel 2 C18-AR, 2.0 µm, 2.1 x 100 mm column or equivalent

6.67 LC/MS/MS 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.

6.68 LC/MS/MS 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.

6.69 Recommended GC Analytical Column:

- Restek Rxi-5Sil MS 30m X 0.025 mm ID, 0/025 µm df

7. Standards Preparation:

7.1 Stock mixes of 0.1 mg/mL are obtained from a commercial supplier (such as Restek).

LC/MS/MS Standards:

7.2 The stock mixes at 0.1 mg/mL are diluted to 10 µg/mL with methanol.

7.3 A combination of standards at 10 µg/mL are prepared from the individual 0.1 mg/mL standards in methanol. The combination standard at 10 µg/mL is serially diluted with methanol to produce the following concentrations: 0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5 and 1 µg/mL.

7.4 The above standards are diluted with an equal volume of H_2O to make the following concentrations: 0.00125, 0.0025, 0.005, 0.0125, 0.025, 0.05, 0.125, and 0.25 µg/mL. These standards are analyzed by LC/MS/MS to produce the calibration curve. Some pesticides had data points excluded from the lowest or highest standards due to weak or strong response.

GC/MS/MS Standards:

7.5 The stock mixes at 0.1 mg/mL are diluted to 10 µg/mL with acetone.

7.6 Two combinations of standards at 10 µg/mL are prepared from the individual 0.1 mg/mL standards in acetone and methylene chloride. The combination standard in methylene chloride at 10 µg/mL is serially diluted with methylene chloride to produce the following concentrations: 0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5 and 1 µg/mL. These standards are analyzed by GC/MS/MS to produce the calibration curve. Some pesticides had data points excluded from the lowest or highest standards due to weak or strong response.

7.7 A QC spike solution is prepared with all compounds at 1.0 µg/mL in Acetone.

7.8 Keep all standards in the designated refrigerator for storage.

7.9 The expiration date of each mixed working standard is from 6 to 24 months from the preparation date or same as the stock standard, if

sooner. The standards prepared with water are prepared fresh with each analysis.

7.10 A portion of the new standard is 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 is performed before the standard is 6 months old and documented along with comparison for that set of standards. There should be <20% 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 separate refrigerator (4 ± 3 °C).

9. Test Sample Preparation:

9.1 Background Preparation:

9.1.1 The Department of Pesticide Regulation (DPR) provides the background water for matrix blank and spikes.

9.2 Preparation of Matrix Blank and Matrix Spike Samples:

9.2.1 Matrix Blank: Weigh out 1000 g of background water and follow the test sample extraction procedure in 9.3.

9.2.2 Matrix Spike: Weigh out 1000 g of background water. Spike a client requested amount of pesticide (typically 0.2 µg/L) into the background water, mix well and let it stand for one minute. Follow the test sample extraction procedure in 9.3.

9.3 Test Sample Extraction:

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

9.3.2 Record the weight of water samples to 0.1 g by subtracting the weight of the sample container before and after water has been transferred into a separatory funnel.

9.3.3 Shake with 100 ± 5 mL of methylene chloride for 2 minutes. Vent frequently to relieve pressure.

9.3.4 After phases have separated, drain the lower methylene chloride layer through 25 ± 4 g of anhydrous sodium sulfate and glass wool into a 500 mL boiling flask.

9.3.5 Repeat steps 9.3.3 & 9.3.4 two more times using 80 ± 5 mL of methylene chloride and shake for 1 minute each time. Combine the extracts in the same boiling flask.

9.3.6 After draining the final extraction, rinse the sodium sulfate with 25 ± 5 mL of methylene chloride.

9.3.7 Evaporate the sample extract to 2 - 4 mL on a rotary evaporator using a water bath at 35 ± 2 °C and 15 – 20 inches of Hg vacuum. Transfer the extract to a calibrated 15 mL graduated test tube.

9.3.8 Rinse flask 3 more times with 2 - 4 mL of methylene chloride and transfer each rinse to the same test tube.

9.3.9 Evaporate the sample extract in the calibrated 15 mL graduated test tube to ~1.5 mL in a water bath at 40 ± 2 °C under a gentle stream of nitrogen. Then bring the final volume to 2 mL and transfer 1 mL of the extract to an auto sampler vial for GC/MS/MS analysis.

9.3.10 The remaining 1 mL of extract is evaporated to dryness in a water bath at 40 ± 2 °C under a gentle stream of nitrogen. Reconstitute the dried extract with 1 mL of methanol. Add 1.0 mL of water to the extract and mix well, for a final volume of 2 mL. Transfer the final extract into two separate auto sampler vials. Submit extract vials for LC/MS/MS analysis.

For the analyte, Bentazon continue with the following procedure below. If Bentazon is not requested, the extraction process is completed.

9.3.11 Place the used glass funnel with sodium sulfate in a clean 500 mL boiling flask. To the original sample in the separatory funnel, add 4 mL of concentrated hydrochloric acid (~12 M). Using pH paper, verify the pH of the sample is less than 2. If the pH is not below 2, add another 1 mL of concentrated hydrochloric acid. Continue adding concentrated hydrochloric acid until the pH of the sample is ≤ 2, then document the additional hydrochloric acid volume on the extraction sheet.

9.3.12 Shake with 80 ± 5 mL of methylene chloride for 1 minute. Vent frequently to relieve pressure.

9.3.13 After phases have separated, drain the lower methylene chloride layer through 25 ± 4 g of anhydrous sodium sulfate and glass wool into a clean 500 mL boiling flask.

9.3.14 Repeat steps 9.3.12 & 9.3.13 two more times using 80 ± 5 mL of methylene chloride and shake for 1 minute each time. Combine the extracts in the same boiling flask.

9.3.15 After draining the final extraction, rinse the sodium sulfate with 25 ± 5 mL of methylene chloride.

9.3.16 Evaporate the sample extract to 2 - 4 mL on a rotary evaporator using a water bath at 35 ± 2 °C and 15 – 20 inches Hg vacuum. Rinse flask 3 more times with 2 - 4 mL of methylene chloride and transfer each rinse to the same test tube.

9.3.17 Evaporate the sample extract to dryness in a water bath at 40 ± 2 °C under a gentle stream of nitrogen. Reconstitute the dried extract with 1 mL of methanol. Add 1.0 mL of water to the extract and mix well, for a final volume of 2 mL. Transfer the final extract into two new auto sampler vials. Submit extract vials for LC/MS/MS analysis.

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 The current working standard levels range from 0.00125 to 0.25 µg/µL for the LC/MS/MS.

10.3 The current working standard levels range from 0.025 to 0.5 ng/µL for GC/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. Instrumental Analysis:

LC/MS/MS:

11.1 Injection Scheme:

11.1.1 The LC/MS/MS needs to be conditioned with standard or a sample extract 2 to 5 runs before running the following sequence:

- A set of calibration standards
- Matrix blank
- Matrix spike
- A set of up to 12 test samples
- A set of standards, etc.

11.2 LC/MS/MS Conditions

11.2.1 Column: Ace Excel 2 C18-AR, 2.0 µm, 2.1 x 100 mm column

11.2.2 Column Temperature: 40 °C

11.2.3 Mobile Phase A (MP-A): Aqueous Solution

11.2.4 Mobile Phase B (MP-B): Organic Solution

11.2.5 Gradient: See Table 1

Table 1 – LC/MS/MS Mobile Phase Gradient Flow Rate

Flow Rate			
Time (min)	**Flow Rate (mL/min)**	**MP-A**	**MP-B**
Initial	0.4	95.0	5.0
1.0	0.4	95.0	5.0
12.0	0.4	5.0	95.0
15.0	0.4	5.0	95.0
16.0	0.4	95.0	5.0

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

11.2.7 Recommended Mass Spectrometer and Operating Parameters:

11.2.7.1 Model: ABSciex QTRAP 6500

11.2.7.2 Ionization: Electrospray Ionization (ESI)

11.2.7.3 Polarity: Positive and Negative

11.2.7.4 Curtain Gas: 30

11.2.7.5 Ion Spray Voltage: 4500 / -4500

11.2.7.6 Source Temp: 350 °C

11.2.7.7 Ion Source Gas 1: 50

11.2.7.8 Ion Source Gas 2: 50

11.2.7.9 Collision Gas: Medium

11.2.7.10 Electron Multiplier: 2600 V for positive / 2700 V for negative

11.2.7.11 Scheduled MRM: Yes

11.2.7.12 MRM Detection Window: 60 sec.

11.2.7.13 Target Scan Time: 1.0 sec.

Table 2 – LC/MS/MS Instrument Conditions

Compound	RT	Precursor Ion [1]	Product Ion [1]	De-Clustering Potential	Collision Energy	Entrance Potential	Exit Potential
Atrazine	10.1	**216.0**	**173.9**	41	23	10	18
		216.0	96.0	41	31	10	10
Azinphos-methyl	12.0	**317.9**	**131.9**	16	19	10	12
		317.9	77.0	16	45	10	10
Azoxystrobin	12.1	**404.0**	**372.0**	50	19	10	12
		404.0	329.0	50	41	10	10
Bensulide	12.9	**398.0**	**313.8**	36	15	10	10
		398.0	157.9	36	31	10	14

Compound	RT	Precursor Ion [1]	Product Ion [1]	De-Clustering Potential	Collision Energy	Entrance Potential	Exit Potential
Bromacil	9.20	**262.9**	**206.9**	26	19	10	18
		262.9	190.0	26	39	10	16
Carbaryl	9.80	**202.2**	**145.0**	25	13	10	10
		202.2	127.0	25	38	10	16
Carbofuran	9.40	**222.0**	**123.1**	41	29	10	0
		222.0	165.1	41	17	10	46
Diazinon	13.0	**305.0**	**169.1**	20	28	10	9
		305.0	153.0	20	26	10	5
Dimethenamide	11.6	**276.0**	**244.0**	36	19	10	10
		276.0	168.0	36	33	10	10
Dimethoate	7.20	**229.9**	**199.0**	16	13	10	18
		229.9	124.8	16	27	10	16
Diuron	10.6	**234.9**	**72.0**	46	21	10	10
		234.9	46.1	46	35	10	6
Ethofumesate NH4	11.7	**287.0**	**121.0**	1	20	10	10
		287.0	161.0	1	20	10	10
Fenamiphos	12.4	**304.0**	**217.0**	61	31	10	18
		304.0	202.0	61	45	10	16
Fludioxonil NH4	11.6	**266.0**	**229.0**	15	15	10	18
		266.0	158.0	15	47	10	10
Imidacloprid	7.30	**256.0**	**208.9**	30	21	10	26
		256.0	175.1	30	25	10	16
Linuron	11.4	**249.0**	**159.9**	26	23	10	16
		249.0	182.0	26	21	10	20
Mefenoxam	10.7	**280.0**	**220.1**	36	19	10	18
		280.0	192.2	36	25	10	16
Methiocarb	11.6	**226.0**	**169.0**	36	15	10	16
		226.0	121.0	36	25	10	12
Metolachlor	12.4	**284.0**	**252.0**	35	19	10	24
		284.0	176.2	35	35	10	16

Compound	RT	Precursor Ion [1]	Product Ion [1]	De-Clustering Potential	Collision Energy	Entrance Potential	Exit Potential
Metribuzin	9.20	**215.1**	**187.0**	36	25	10	12
		215.1	84.0	36	31	10	10
Napropamide	12.5	**272.0**	**129.0**	34	23	10	14
		272.0	171.1	34	25	10	14
Norflurazon	11.1	**303.9**	**284.0**	106	31	10	26
		303.9	144.9	106	57	10	16
Oryzalin	12.6	**347.0**	**305.0**	31	19	10	10
		347.0	287.9	31	25	10	26
Prometon	10.0	**226.1**	**142.0**	56	31	10	16
		226.1	184.1	56	25	10	16
Simazine	9.00	**202.0**	**124.0**	61	25	10	6
		202.0	67.9	61	43	10	8
Tebuthiuron	9.40	**229.0**	**172.1**	41	23	10	16
		229.0	116.0	41	35	10	14
Thiamethoxam	6.20	**291.9**	**211.0**	16	19	10	20
		291.9	180.9	16	31	10	20
Thiobencarb	13.50	**258.0**	**124.9**	26	25	10	14
		258.0	89.0	26	63	10	14
Uniconazole-p	12.3	**292.0**	**70.0**	180	47	10	13
		294.0	70.0	180	47	10	13
Methoxyfenozide	11.80	**368.9**	**148.9**	35	22	10	16
		368.9	312.9	35	11	10	28
Methomyl	4.80	**162.9**	**87.8**	20	11	10	10
		162.9	105.8	20	12	10	12
Chlorantraniliprole	11.4	**483.9**	**285.7**	30	16	10	21
		483.9	452.9	30	22	10	13
Isoxaben	12.0	**332.8**	**165.0**	50	23	10	12
		332.8	106.8	50	74	10	12.5
Propiconazole	13.3	**341.8**	**158.9**	70	34	10	13
		341.8	204.9	70	24	10	16

Compound	RT	Precursor Ion [1]	Product Ion [1]	De-Clustering Potential	Collision Energy	Entrance Potential	Exit Potential
Pyraclostrobin	13.8	**387.9**	**194.0**	50	16	10	16
		387.9	163.0	50	31	10	16
Cyprodinil	12.7	**226.0**	**92.8**	85	39	10	8
		226.0	107.9	85	33	10	6
Flutriafol	10.6	**301.8**	**69.9**	45	20	10	10
		301.8	122.8	45	35	10	11
Alachlor	12.5	**270.0**	**238.1**	40	13	10	17
		270.0	147.0	40	39	10	12
Bentazon	8.40	**238.9**	**132.0**	-40	-34	-10	-14
		238.9	175.0	-40	-26	-10	-18

[1] Quantitation transition is in bold.

GC/MS/MS:

11.3 Recommended GC and Triple Quadrupole Mass Spectrometer and Operating Parameters:

11.3.1 Instrument Model: Agilent 7890GC 7010 Triple Quadrupole MS

11.3.2 Recommended Instrument Parameters:

11.3.2.1 Injector Temperature: 250 °C

11.3.2.2 MSD Transfer Line Heater: 280 °C

11.3.2.3 Oven temperature: 60 °C, hold 1 min., ramp 35 °C/min. to 180 °C, hold 0 min, ramp 8 °C/min to 220°C, hold 0 min, ramp 35 °C/min to 320 °C hold 2 min.

11.3.2.4 Injection volume: 2 µL.

Table 3 – G/MS/MS Instrument Conditions

Compound	Precursor Ion [1]	Product Ion [1]	Collision Energy
Clomazone	204.1	107.2	20
Clomazone	**204.1**	**78.2**	40

Compound	Precursor Ion [1]	Product Ion [1]	Collision Energy
Dichlobenil	**170.9**	**136**	15
Dichlobenil	170.9	110	15
Dichlobenil	170.9	100	25
Dichloran	205.9	176	10
Dichloran	205.9	148	25
Dichloran	**205.9**	**124**	30
Dichloran	176	148	15
Disulfoton	**274**	**88**	10
Disulfoton	274	60	25
Ethoprophos	157.9	114	5
Ethoprophos	157.9	97	20
Ethoprophos	**138.9**	**97**	5
Ethoprophos	125.9	65	10
Fonofos	246	137	10
Fonofos	**246**	**109.1**	15
Fonofos	246	81.1	30
Fonofos	109	80.9	5
Malathion	**173**	**127**	5
Malathion	173	117	13
Malathion	173	99	15
Parathion Ethyl	291	142	5
Parathion Ethyl	**291**	**109**	13
Parathion Ethyl	291	81	12
Parathion Ethyl	139	109	5

Compound	Precursor Ion [1]	Product Ion [1]	Collision Energy
Parathion Methyl	263	137	5
Parathion Methyl	**263**	**109**	13
Parathion Methyl	263	79	30
Phorate	260	231	5
Phorate	**260**	**75**	5
Piperonyl Butoxide	176	131	15
Piperonyl Butoxide	176	117	20
Piperonyl Butoxide	**176**	**103**	25
Prometryn	**241.1**	**184.2**	10
Prometryn	241.1	58.2	15
Propanil	161	126	30
Propanil	**161**	**99**	30
Propanil	161	90	30
Triallate	267.9	226.1	15
Triallate	**267.9**	**184.1**	20
Triallate	267.9	125	45

[1] Quantitation transition is in bold.

12. Quality Control:

12.1 Method Detection Limit

Method Detection Limit (MDL) refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, 7 well water samples are spiked at 0.02 ppb for LC/MS/MS analysis and 0.025 ppb for GC/MS/MS analysis 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 and MDL are in Appendix I and III.

12.2 Reporting Limit

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, as per client agreement. The reporting limit for this method is 0.02 – 0.05 ppb for all compounds. The RL's are listed in Appendix I and III.

12.3 Method Validation

The method validation consists of five sample sets. Each set includes 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 II and IV.

12.4 Control Charts and Limits

A control chart is generated using the data from the method validation. The upper and lower control limits are set at $\pm$ 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 $\pm$ 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. The backup samples will be re-extracted for analysis.

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 The relative abundance of qualifier ions shall be within ± 30%.

13. Calculations:

Quantitation is based on an external standard (ESTD) calculation using either the peak area or height. The LC/MS/MS quantitation software uses 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.

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

14. Reporting Procedure:

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

15. Discussion and References:

15.1 Acephate, dinotefuran, oxydemeton-methyl, and rimsulfuron were requested as part of the screen, but would not extract out of water using the current liquid/liquid extraction method. Aldicarb was also requested but was not very sensitive and had poor reproducibility so it was left out of the screen.

The water sample needs to be acidified in order to extract chlorothalonil so this compound was removed from the screen list. Iprodione is very unstable with recoveries ranging from 0% recovery for the lowest spike level up to 263% recovery on higher spike levels. Iprodione was also removed from the screen list.

References:

15.2 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

15.3 “Crop Protection Handbook, 2010”, MeisterPro Executive Office 27722 Euclid Ave., Willoughby, OH

Appendix I

MDL Determination (Fortified at 0.02 µg/L) by LC/MS/MS

Compound Name	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	SD	MDL	RL
Atrazine	0.0221	0.0202	0.0231	0.0215	0.0214	0.0212	0.0222	0.00091	0.00286	0.020
Azinphos-methyl	0.0186	0.0159	0.0191	0.0179	0.0177	0.0062	0.0131	0.00459	0.0144	0.050
Azoxystrobin	0.0280	0.0241	0.0246	0.0234	0.0239	0.0248	0.0277	0.00186	0.00584	0.020
Bensulide	0.0217	0.0182	0.0222	0.0195	0.0199	0.0172	0.0209	0.00182	0.00571	0.020
Bromacil	0.0214	0.0203	0.0217	0.0195	0.0190	0.0183	0.0194	0.00125	0.00393	0.020
Carbaryl	0.0221	0.0206	0.0234	0.0215	0.0205	0.0209	0.0210	0.00103	0.00323	0.020
Carbofuran	0.0235	0.0214	0.0223	0.0214	0.0207	0.0207	0.0196	0.00125	0.00393	0.020
Diazinon	0.0201	0.0189	0.0210	0.0189	0.0189	0.0206	0.0112	0.00334	0.0105	0.030
Dimethenamide	0.0197	0.0179	0.0194	0.0194	0.0194	0.0153	0.0183	0.00156	0.00490	0.020
Dimethoate	0.0221	0.0205	0.0226	0.0199	0.0199	0.0206	0.0206	0.00105	0.00330	0.020
Diuron	0.0218	0.0211	0.0240	0.0219	0.0219	0.0190	0.0228	0.00154	0.00484	0.020
Ethofumesate	0.0169	0.0152	0.0168	0.0166	0.0179	0.0102	0.0179	0.00269	0.00845	0.030
Fenamiphos	0.0167	0.0147	0.0206	0.0173	0.0185	0.00993	0.0180	0.00342	0.0107	0.030
Fludioxonil	0.0186	0.0162	0.0215	0.0192	0.0189	0.0125	0.0182	0.00284	0.00892	0.030
Imidacloprid	0.0226	0.0223	0.0226	0.0205	0.0201	0.0211	0.0211	0.00103	0.00323	0.020

Compound Name	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	SD	MDL	RL
Linuron	0.0217	0.0203	0.0226	0.0217	0.0214	0.0160	0.0218	0.00222	0.00697	0.020
Mefenoxam	0.0234	0.0225	0.0228	0.0214	0.0213	0.0209	0.0214	0.00094	0.00295	0.020
Methiocarb	0.0194	0.0182	0.0215	0.0189	0.0192	0.0142	0.0199	0.00226	0.00710	0.020
Metolachlor	0.0209	0.0194	0.0220	0.0210	0.0200	0.0138	0.0212	0.00276	0.00867	0.020
Metribuzin	0.0185	0.0173	0.0173	0.0158	0.0167	0.0153	0.0147	0.00132	0.00414	0.020
Napropamide	0.0212	0.0201	0.0229	0.0212	0.0213	0.0184	0.0223	0.00147	0.00462	0.020
Norflurazon	0.0221	0.0206	0.0249	0.0237	0.0237	0.0211	0.0249	0.00175	0.00550	0.020
Oryzalin	0.0198	0.0185	0.0222	0.0187	0.0187	0.0105	0.0168	0.00364	0.0114	0.050
Prometon	0.0231	0.0223	0.0234	0.0218	0.0212	0.0219	0.0218	0.00078	0.00245	0.020
Simazine	0.0221	0.0208	0.0229	0.0214	0.0203	0.0208	0.0217	0.00089	0.00279	0.020
Tebuthiuron	0.0256	0.0223	0.0240	0.0218	0.0215	0.0215	0.0210	0.00167	0.00524	0.020
Thiamethoxam	0.0207	0.0191	0.0209	0.0179	0.0178	0.0188	0.0189	0.00123	0.00386	0.020
Thiobencarb	0.0202	0.0207	0.0213	0.0205	0.0197	0.0190	0.0209	0.00078	0.00245	0.020
Uniconizole	0.0197	0.0187	0.0236	0.0215	0.0220	0.0104	0.0213	0.00435	0.0137	0.050
Methoxyfenozide	0.0208	0.0219	0.0172	0.0185	0.0164	0.0197	0.0205	0.00200	0.00628	0.030
Methomyl	0.0202	0.0184	0.0205	0.0181	0.0182	0.0191	0.0194	0.00096	0.00301	0.020
Chlorantraniliprole	0.0204	0.0201	0.0212	0.0201	0.0196	0.0178	0.0208	0.00110	0.00345	0.020

Compound Name	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	SD	MDL	RL
Isoxaben	0.0178	0.0149	0.0165	0.0154	0.0157	0.0130	0.0170	0.00157	0.00493	0.020
Propiconazole	0.0210	0.0194	0.0234	0.0203	0.0213	0.0224	0.0205	0.00135	0.00424	0.020
Pyraclostrobin	0.0222	0.0215	0.0231	0.0218	0.0216	0.0231	0.0225	0.00067	0.00210	0.020
Cyprodinil	0.0220	0.0202	0.0243	0.0220	0.0237	0.0216	0.0223	0.00136	0.00427	0.020
Flutriafol	0.0225	0.0211	0.0215	0.0209	0.0204	0.0194	0.0210	0.00095	0.00298	0.020
Alachlor	0.0205	0.0191	0.0207	0.0203	0.0201	0.0126	0.0206	0.00293	0.00920	0.030
Bentazon	0.0214	0.0193	0.0208	0.0207	0.0203	0.0221	0.0203	0.00089	0.00279	0.020

Appendix II

Method Validation Data for LC/MS/MS Compounds

Compound	Spike Level							Control Limits	
	MV Run	Blank	0.02 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb	%	
Atrazine	1	ND	95.5	105	115	102	118	**Mean:**	**113**
	2	ND	101	106	109	106	114	**SD:**	**8.24**
	3	ND	107	124	120	111	117	**UCL:**	**138**
	4	ND	121	116	126	119	120	**uwl:**	**129**
	5	ND	104	117	116	120	125	**lwl:**	**96.5**
								LCL:	**88.3**
Azinphos-methyl	1	ND	82.5	96.2	89.0	92.4	112	**Mean:**	**92.7**
	2	ND	89.5	79.6	82.4	118	126	**SD:**	**19.7**
	3	ND	73.0	112	84.2	70.2	99.0	**UCL:**	**152**
	4	ND	73.5	58.6	101	127	79.5	**uwl:**	**132**
	5	ND	63.5	87.8	89.7	100	131	**lwl:**	**53.3**
								LCL:	**33.6**
Azoxystrobin	1	ND	117	116	121	97.2	116	**Mean:**	**119**
	2	ND	122	126	113	90.8	102	**SD:**	**14.2**
	3	ND	119	127	128	103	123	**UCL:**	**162**
	4	ND	139	134	149	112	121	**uwl:**	**147**
	5	ND	120	139	139	103	109	**lwl:**	**90.6**
								LCL:	**76.4**
Bensulide	1	ND	87.0	98.4	112	99.6	118	**Mean:**	**108**
	2	ND	95.0	104	104	100	112	**SD:**	**10.4**
	3	ND	95.0	122	114	109	117	**UCL:**	**139**
	4	ND	116	119	128	112	123	**uwl:**	**129**
	5	ND	94.5	112	102	102	108	**lwl:**	**87.2**
								LCL:	**76.8**

Compound	Spike Level							Control Limits	
	MV Run	Blank	0.02 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb	%	
Bromacil	1	ND	94.5	108	110	95.2	109	**Mean:**	**106**
	2	ND	97.5	108	109	94.2	108	**SD:**	**7.76**
	3	ND	99.0	110	110	107	119	**UCL:**	**129**
	4	ND	97.0	99.0	109	113	117	**uwl:**	**122**
	5	ND	94.0	107	103	115	118	**lwl:**	**90.5**
								LCL:	**82.7**
Carbaryl	1	ND	101	104	107	94.8	111	**Mean:**	**109**
	2	ND	106	105	111	103	106	**SD:**	**5.74**
	3	ND	107	107	113	105	110	**UCL:**	**126**
	4	ND	119	110	118	109	108	**uwl:**	**120**
	5	ND	104	117	110	114	118	**lwl:**	**97.5**
								LCL:	**91.8**
Carbofuran	1	ND	100	107	115	99.2	114	**Mean:**	**109**
	2	ND	104	110	110	100	107	**SD:**	**6.00**
	3	ND	104	117	115	111	118	**UCL:**	**127**
	4	ND	103	102	107	106	114	**uwl:**	**121**
	5	ND	103	118	115	113	112	**lwl:**	**97.0**
								LCL:	**91.0**
Diazinon	1	ND	89.0	96.0	99.9	89.6	104	**Mean:**	**97.6**
	2	ND	72.0	80.2	89.5	91.2	93.0	**SD:**	**10.1**
	3	ND	87.0	106	99.4	93.6	102	**UCL:**	**128**
	4	ND	101	107	109	102	96.5	**uwl:**	**118**
	5	ND	92.0	113	106	108	114	**lwl:**	**77.4**
								LCL:	**67.3**
Dimethenamide	1	ND	91.5	99.4	101	88.6	107	**Mean:**	**99.1**
	2	ND	92.5	94.8	96.5	79.6	100	**SD:**	**8.84**
	3	ND	92.0	117	108	95.4	113	**UCL:**	**126**
	4	ND	102	97.6	107	96.2	109	**uwl:**	**117**
	5	ND	94.5	107	108	86.4	93.5	**lwl:**	**81.4**
								LCL:	**72.6**

Compound	Spike Level							Control Limits	
	MV Run	Blank	0.02 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb	%	
Dimethoate	1	ND	102	110	111	99.0	106	**Mean:**	**108**
	2	ND	104	113	109	102	110	**SD:**	**4.62**
	3	ND	103	112	110	102	110	**UCL:**	**122**
	4	ND	107	109	118	110	112	**uwl:**	**117**
	5	ND	102	114	109	112	109	**lwl:**	**98.8**
								LCL:	**94.1**
Diuron	1	ND	96.5	104	112	98.6	112	**Mean:**	**115**
	2	ND	104	107	110	102	113	**SD:**	**9.64**
	3	ND	108	119	117	112	121	**UCL:**	**144**
	4	ND	124	120	130	123	129	**uwl:**	**134**
	5	ND	109	121	118	129	126	**lwl:**	**95.7**
								LCL:	**86.1**
Ethofumesate NH4	1	ND	80.0	92.4	94.8	89.4	110	**Mean:**	**94.3**
	2	ND	79.0	84.0	84.1	72.2	95.5	**SD:**	**11.1**
	3	ND	88.0	105	99.8	88.0	118	**UCL:**	**128**
	4	ND	102	99.0	112	86.0	102	**uwl:**	**117**
	5	ND	89.5	102	100	86.0	99.5	**lwl:**	**72.1**
								LCL:	**61.0**
Fenamiphos	1	ND	78.0	86.2	96.2	90.0	109	**Mean:**	**96.4**
	2	ND	81.5	84.4	85.0	78.8	104	**SD:**	**11.3**
	3	ND	91.5	114	112	90.6	111	**UCL:**	**130**
	4	ND	98.5	98.8	103	90.6	96.5	**uwl:**	**119**
	5	ND	90.5	100	93.0	117	110	**lwl:**	**73.8**
								LCL:	**62.5**
Fludioxonil NH4	1	ND	90.5	92.8	85.7	84.4	102	**Mean:**	**93.6**
	2	ND	88.5	83.4	86.7	61.2	102	**SD:**	**12.7**
	3	ND	98.0	115	97.5	86.6	107	**UCL:**	**132**
	4	ND	106	101	110	86.0	114	**uwl:**	**119**
	5	ND	85.0	99.8	96.2	70.4	90.0	**lwl:**	**68.2**
								LCL:	**55.5**

Compound	Spike Level							Control Limits	
	MV Run	Blank	0.02 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb	%	
Imidacloprid	1	ND	106	110	117	99.8	114	**Mean:**	**112**
	2	ND	113	119	116	106	114	**SD:**	**5.66**
	3	ND	103	115	113	106	114	**UCL:**	**129**
	4	ND	110	111	120	114	119	**uwl:**	**123**
	5	ND	103	117	112	120	117	**lwl:**	**101**
								LCL:	**95.0**
Linuron	1	ND	95.0	107	112	104	114	**Mean:**	**111**
	2	ND	102	105	109	105	114	**SD:**	**6.83**
	3	ND	106	122	117	108	123	**UCL:**	**131**
	4	ND	114	110	117	113	121	**uwl:**	**125**
	5	ND	102	118	113	112	112	**lwl:**	**97.3**
								LCL:	**90.5**
Mefenoxam	1	ND	105	116	118	96.2	109	**Mean:**	**113**
	2	ND	109	115	113	98.2	109	**SD:**	**7.25**
	3	ND	106	116	114	114	123	**UCL:**	**135**
	4	ND	115	110	118	118	124	**uwl:**	**128**
	5	ND	102	114	114	121	122	**lwl:**	**98.5**
								LCL:	**91.3**
Methiocarb	1	ND	91.0	96.2	94.4	91.8	108	**Mean:**	**103**
	2	ND	94.0	93.6	96.5	82.2	104	**SD:**	**10.4**
	3	ND	94.0	109	98.9	102	116	**UCL:**	**134**
	4	ND	105	105	114	110	120	**uwl:**	**124**
	5	ND	90.0	107	109	114	124	**lwl:**	**82.2**
								LCL:	**71.8**
Metolachlor	1	ND	97.0	106	103	90.0	105	**Mean:**	**106**
	2	ND	96.0	106	99.8	89.4	102	**SD:**	**7.85**
	3	ND	102	113	108	107	120	**UCL:**	**130**
	4	ND	112	108	113	109	119	**uwl:**	**122**
	5	ND	111	116	108	109	112	**lwl:**	**90.3**
								LCL:	**82.5**

Compound	Spike Level							Control Limits	
	MV Run	Blank	0.02 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb	%	
Metribuzin	1	ND	73.0	84.0	88.4	80.2	90.0	**Mean:**	**85.1**
	2	ND	85.5	90.6	92.3	85.2	92.5	**SD:**	**11.8**
	3	ND	79.5	92.2	81.6	83.0	101	**UCL:**	**121**
	4	ND	55.5	61.4	71.0	97.4	97.0	**uwl:**	**109**
	5	ND	74.0	89.4	79.7	100	103	**lwl:**	**61.5**
								LCL:	**49.7**
Napropamide	1	ND	101	106	114	94.8	107	**Mean:**	**110**
	2	ND	99.5	104	107	93.0	105	**SD:**	**8.55**
	3	ND	103	118	116	112	125	**UCL:**	**136**
	4	ND	115	113	119	117	122	**uwl:**	**127**
	5	ND	105	110	109	121	120	**lwl:**	**92.9**
								LCL:	**84.4**
Norflurazon	1	ND	101	120	115	89.2	105	**Mean:**	**112**
	2	ND	101	106	101	100	109	**SD:**	**10.5**
	3	ND	118	128	114	104	111	**UCL:**	**144**
	4	ND	137	122	116	111	121	**uwl:**	**133**
	5	ND	117	126	107	111	110	**lwl:**	**91.0**
								LCL:	**80.5**
Oryzalin	1	ND	89.0	98.2	105	92.0	116	**Mean:**	**104**
	2	ND	91.0	95.4	101	97.6	109	**SD:**	**10.1**
	3	ND	94.0	116	111	97.0	109	**UCL:**	**134**
	4	ND	94.0	92.8	114	119	112	**uwl:**	**124**
	5	ND	107	123	116	96.4	110	**lwl:**	**83.8**
								LCL:	**73.7**
Prometon	1	ND	101	123	125	110	118	**Mean:**	**117**
	2	ND	120	117	114	108	112	**SD:**	**6.46**
	3	ND	109	121	119	110	120	**UCL:**	**136**
	4	ND	118	115	129	123	123	**uwl:**	**130**
	5	ND	109	119	117	121	122	**lwl:**	**104**
								LCL:	**97.6**

Compound	Spike Level							Control Limits	
	MV Run	Blank	0.02 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb	%	
Simazine	1	ND	97.5	107	114	104	118	**Mean:**	**113**
	2	ND	103	109	110	106	114	**SD:**	**6.67**
	3	ND	105	117	115	111	120	**UCL:**	**133**
	4	ND	113	110	120	120	120	**uwl:**	**126**
	5	ND	105	118	115	121	121	**lwl:**	**99.7**
								LCL:	**93.0**
Tebuthiuron	1	ND	105	116	118	96.8	110	**Mean:**	**111**
	2	ND	109	116	110	103	106	**SD:**	**5.97**
	3	ND	104	118	117	101	115	**UCL:**	**129**
	4	ND	110	109	120	110	116	**uwl:**	**123**
	5	ND	106	114	116	110	113	**lwl:**	**99.1**
								LCL:	**93.1**
Thiamethoxam	1	ND	88.5	100	97.6	82.2	95.5	**Mean:**	**99.4**
	2	ND	92.5	105	104	87.0	95.0	**SD:**	**7.05**
	3	ND	95.5	104	106	100	103	**UCL:**	**121**
	4	ND	97.5	103	113	105	107	**uwl:**	**114**
	5	ND	93.5	106	101	104	98.5	**lwl:**	**85.3**
								LCL:	**78.3**
Thiobencarb	1	ND	94.0	100	105	94.2	109	**Mean:**	**107**
	2	ND	97.5	99.8	103	95.8	106	**SD:**	**8.68**
	3	ND	96.0	111	112	107	116	**UCL:**	**133**
	4	ND	114	105	119	116	117	**uwl:**	**124**
	5	ND	99.0	113	115	115	124	**lwl:**	**89.6**
								LCL:	**81.0**
Uniconazole-p	1	ND	88.0	101	102	92.2	111	**Mean:**	**108**
	2	ND	97.0	99.8	101	89.6	107	**SD:**	**11.3**
	3	ND	111	124	119	97.0	111	**UCL:**	**142**
	4	ND	120	112	126	102	114	**uwl:**	**131**
	5	ND	117	130	113	100	106	**lwl:**	**85.4**
								LCL:	**74.1**

Compound	Spike Level							Control Limits	
	MV Run	Blank	0.02 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb	%	
Methoxyfenozide	1	ND	126	130	145	126	129	**Mean:**	**111**
	2	ND	117	124	117	104	150	**SD:**	**16.3**
	3	ND	92.0	101	100	94.0	107	**UCL:**	**160**
	4	ND	101	95.8	108	98.8	117	**uwl:**	**144**
	5	ND	97.0	102	97.0	91.2	111	**lwl:**	**78.4**
								LCL:	**62.1**
Methomyl	1	ND	92.0	102	102	90.4	102	**Mean:**	**102**
	2	ND	91.0	102	102	94.2	101	**SD:**	**6.76**
	3	ND	95.5	106	108	103	110	**UCL:**	**122**
	4	ND	100	104	115	109	112	**uwl:**	**116**
	5	ND	91.5	106	104	109	106	**lwl:**	**88.5**
								LCL:	**81.7**
Chlorantraniliprole	1	ND	90.5	99.8	104	94.4	110	**Mean:**	**105**
	2	ND	99.0	97.4	101	91.4	106	**SD:**	**8.68**
	3	ND	99.5	128	114	102	116	**UCL:**	**131**
	4	ND	107	105	115	108	117	**uwl:**	**122**
	5	ND	96.5	110	107	105	108	**lwl:**	**87.6**
								LCL:	**79.0**
Isoxaben	1	ND	74.5	82.8	89.3	72.4	101	**Mean:**	**88.2**
	2	ND	75.5	84.0	82.3	73.2	84.0	**SD:**	**9.60**
	3	ND	80.5	93.0	91.8	78.4	108	**UCL:**	**117**
	4	ND	91.0	87.2	98.0	91.4	104	**uwl:**	**107**
	5	ND	86.0	98.2	92.2	91.4	95.0	**lwl:**	**69.0**
								LCL:	**59.4**
Propiconazole	1	ND	93.5	103	105	94.4	106	**Mean:**	**105**
	2	ND	96.5	100	98.9	93.8	100	**SD:**	**7.28**
	3	ND	106	117	104	101	108	**UCL:**	**127**
	4	ND	108	108	113	114	120	**uwl:**	**120**
	5	ND	104	118	106	104	108	**lwl:**	**90.4**
								LCL:	**83.2**

Compound	Spike Level							Control Limits	
	MV Run	Blank	0.02 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb	%	
Pyraclostrobin	1	ND	99.5	107	112	96.6	109	**Mean:**	**111**
	2	ND	105	109	107	94.4	104	**SD:**	**7.68**
	3	ND	108	126	121	109	120	**UCL:**	**134**
	4	ND	119	114	118	112	115	**uwl:**	**126**
	5	ND	107	120	115	109	111	**lwl:**	**95.6**
								LCL:	**88.0**
Cyprodinil	1	ND	91.0	101	111	102	113	**Mean:**	**114**
	2	ND	107	103	109	105	112	**SD:**	**9.24**
	3	ND	111	120	115	115	126	**UCL:**	**142**
	4	ND	121	119	126	121	124	**uwl:**	**132**
	5	ND	111	119	120	127	125	**lwl:**	**95.5**
								LCL:	**86.3**
Flutriafol	1	ND	94.5	104	105	113	122	**Mean:**	**111**
	2	ND	102	103	104	103	115	**SD:**	**8.58**
	3	ND	103	112	113	120	133	**UCL:**	**137**
	4	ND	108	110	115	122	118	**uwl:**	**128**
	5	ND	100	111	108	117	115	**lwl:**	**93.8**
								LCL:	**85.3**
Alachlor	1	ND	93.5	103	109	90.8	107	**Mean:**	**106**
	2	ND	95.5	104	102	86.0	102	**SD:**	**8.69**
	3	ND	99.0	112	109	108	119	**UCL:**	**132**
	4	ND	111	105	112	115	118	**uwl:**	**123**
	5	ND	104	113	109	115	119	**lwl:**	**88.6**
								LCL:	**79.9**
Bentazon	1	ND	92.5	107	109	97.0	112	**Mean:**	**105**
	2	ND	101	95.6	105	103	113	**SD:**	**6.02**
	3	ND	115	103	108	105	113	**UCL:**	**123**
	4	ND	100	104	102	105	112	**uwl:**	**117**
	5	ND	97.5	108	107	106	114	**lwl:**	**93.0**
								LCL:	**86.9**

Appendix III

MDL Determination (Fortified at 0.02 µg/L) by GC/MS/MS

Compound Name	Blank	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7	SD	MDL	RL
Clomazone	ND	0.0268	0.0238	0.0228	0.0201	0.0204	0.0260	0.0236	0.00254	0.00799	0.050
Dichlobenil	ND	0.0256	0.0235	0.0225	0.0198	0.0201	0.0208	0.0203	0.00216	0.00678	0.030
Dichloran	ND	0.0252	0.0227	0.0222	0.0192	0.0201	0.0173	0.0148	0.00351	0.01103	0.050
Disulfoton	ND	0.0121	0.0119	0.0209	0.0166	0.0167	0.0190	0.0164	0.00331	0.01040	0.050
Ethoprophos	ND	0.0228	0.0216	0.0220	0.0201	0.0201	0.0204	0.0179	0.00161	0.00506	0.030
Fonofos	ND	0.0253	0.0229	0.0254	0.0214	0.0206	0.0247	0.0220	0.00196	0.00616	0.030
Malathion	ND	0.0247	0.0214	0.0223	0.0192	0.0189	0.0238	0.0206	0.00220	0.00691	0.030
Parathion Ethyl	ND	0.0233	0.0207	0.0224	0.0189	0.0182	0.0227	0.0192	0.00206	0.00646	0.030
Parathion Methyl	ND	0.0246	0.0209	0.0223	0.0192	0.0189	0.0217	0.0192	0.00208	0.00655	0.030
Phorate	ND	0.0232	0.0211	0.0222	0.0193	0.0192	0.0207	0.0188	0.00166	0.00521	0.030
Piperonyl Butoxide	ND	0.0220	0.0187	0.0220	0.0181	0.0168	0.0202	0.0155	0.00250	0.00785	0.030
Prometryn	ND	0.0255	0.0228	0.0233	0.0198	0.0195	0.0250	0.0216	0.00235	0.00738	0.030
Propanil	ND	0.0287	0.0250	0.0249	0.0217	0.0211	0.0265	0.0235	0.00266	0.00836	0.050
Triallate	ND	0.0248	0.0229	0.0225	0.0195	0.0194	0.0233	0.0209	0.00203	0.00638	0.030

Appendix IV

Method Validation Data for GC/MS/MS Compounds

Compound	Spike Level							Control Limits	
	MV Run	Blank	0.025 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb	%	
Clomazone	1	ND	75.8	85.1	90.6	89.5	91.8	**Mean:**	**98.8**
	2	ND	111	124	124	121	102	**SD:**	**12.69**
	3	ND	90.6	96.8	94.3	91.8	107	**UCL:**	**137**
	4	ND	96.4	88.2	94.3	83.5	94.3	**uwl:**	**124**
	5	ND	112	109	108	96.6	91.5	**lwl:**	**73.4**
								LCL:	**60.7**
Dichlobenil	1	ND	72.0	75.5	83.2	85.8	85.8	**Mean:**	**92.7**
	2	ND	102	119	113	111	96.0	**SD:**	**12.26**
	3	ND	85.4	94.7	92.8	111	111	**UCL:**	**129**
	4	ND	84.2	80.6	89.1	88.8	88.8	**uwl:**	**117**
	5	ND	93.6	92.4	88.5	80.4	93.0	**lwl:**	**68.2**
								LCL:	**55.9**
Dichloran	1	ND	76.2	82.8	91.5	90.1	92.8	**Mean:**	**95.1**
	2	ND	112	122	127	134	106	**SD:**	**17.36**
	3	ND	88.2	96.0	90.6	96.9	113	**UCL:**	**147**
	4	ND	61.8	77.1	86.5	91.1	79.0	**uwl:**	**130**
	5	ND	67.2	97.2	102	97.8	98.0	**lwl:**	**60.4**
								LCL:	**43.0**
Disulfoton	1	ND	72.8	75.4	77.2	85.8	76.5	**Mean:**	**79.0**
	2	ND	52.4	54.7	58.6	89.7	95.5	**SD:**	**11.57**
	3	ND	68.4	70.6	82.7	81.9	101	**UCL:**	**114**
	4	ND	83.6	79.8	84.9	78.3	90.5	**uwl:**	**102**
	5	ND	85.2	84.4	80.6	78.4	86.5	**lwl:**	**55.9**
								LCL:	**44.3**

Compound	Spike Level							Control Limits	
	MV Run	Blank	0.025 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb	%	
Ethoprophos	1	ND	79.8	79.8	82.8	81.6	83.5	**Mean:**	**92.1**
	2	ND	99.0	118	117	120	103	**SD:**	**12.04**
	3	ND	87.0	91.2	88.9	87.8	103	**UCL:**	**128**
	4	ND	80.6	82.4	91.0	80.8	92.3	**uwl:**	**116**
	5	ND	94.4	96.8	88.5	82.4	90.0	**lwl:**	**68.0**
Fonofos	1	ND	82.8	88.0	92.3	90.5	93.3	**Mean:**	**98.0**
	2	ND	108	119	120	120	102	**SD:**	**10.75**
	3	ND	90.2	100	100	96.6	107	**UCL:**	**130**
	4	ND	91.8	86.7	91.7	82.5	94.0	**uwl:**	**119**
	5	ND	105	105	100	91.6	91.0	**lwl:**	**76.5**
								LCL:	**65.7**
Malathion	1	ND	73.6	81.9	86.9	87.2	88.3	**Mean:**	**94.3**
	2	ND	110	118	116	115	96.3	**SD:**	**11.91**
	3	ND	87.2	87.9	86.6	84.1	103	**UCL:**	**130**
	4	ND	92.2	91.2	93.8	80.7	95.8	**uwl:**	**118**
	5	ND	110	103	93.4	84.6	90.0	**lwl:**	**70.5**
								LCL:	**58.5**
Parathion Ethyl	1	ND	68.8	78.3	84.0	84.3	84.5	**Mean:**	**91.9**
	2	ND	112	116	115	117	96.0	**SD:**	**12.91**
	3	ND	84.2	84.1	83.0	82.9	102.0	**UCL:**	**131**
	4	ND	90.0	87.4	91.2	79.6	93.0	**uwl:**	**118**
	5	ND	106.0	99.4	89.1	82.0	87.0	**lwl:**	**66.0**
								LCL:	**53.1**
Parathion Methyl	1	ND	74.8	80.8	86.7	84.5	87.8	**Mean:**	**94.1**
	2	ND	108	119	120	122	101	**SD:**	**12.42**
	3	ND	87.2	89.6	87.6	87.2	103	**UCL:**	**131**
	4	ND	89.0	89.4	91.3	82.0	94.0	**uwl:**	**119**
	5	ND	103	99.0	93.3	85.4	88.0	**lwl:**	**69.3**
								LCL:	**56.9**

Compound	Spike Level							Control Limits	
	MV Run	Blank	0.025 ppb	0.05 ppb	0.1 ppb	0.5 ppb	2.0 ppb	%	
Phorate	1	ND	71.0	76.7	82.3	84.8	85.0	**Mean:**	**93.7**
	2	ND	98.6	108	110	112	95.8	**SD:**	**12.03**
	3	ND	85.6	89.2	90.1	112	103	**UCL:**	**130**
	4	ND	85.0	81.7	86.1	112	90.0	**uwl:**	**118**
	5	ND	96.8	97.2	88.6	112	89.0	**lwl:**	**69.6**
								LCL:	**57.6**
Piperonyl Butoxide	1	ND	57.8	67.1	73.8	73.4	81.3	**Mean:**	**84**
	2	ND	99.2	102	108	110	82.8	**SD:**	**12.4**
	3	ND	78.6	79.9	82.6	81.0	102	**UCL:**	**121**
	4	ND	78.0	75.9	81.5	74.6	87.5	**uwl:**	**109**
	5	ND	90.4	87.8	82.4	77.0	85.5	**lwl:**	**59.2**
								LCL:	**46.7**
Prometryn	1	ND	79.6	81.0	86.7	89.2	90.5	**Mean:**	**91.0**
	2	ND	112	115	116	117	94.3	**SD:**	**11.07**
	3	ND	89.8	89.3	87.2	87.2	105	**UCL:**	**124**
	4	ND	95.6	94.4	93.8	82.9	96.5	**uwl:**	**113**
	5	ND	108	107	97.2	90.0	91.0	**lwl:**	**68.9**
								LCL:	**57.8**
Propanil	1	ND	84.4	87.1	91.3	89.7	96.0	**Mean:**	**98.4**
	2	ND	125	132	125	125	97.5	**SD:**	**13.73**
	3	ND	101	94.0	90.9	87.8	107	**UCL:**	**140**
	4	ND	97.2	93.6	93.1	84.7	96.8	**uwl:**	**126**
	5	ND	88.0	93.4	101	89.8	89.0	**lwl:**	**71.0**
								LCL:	**57.2**
Triallate	1	ND	78.4	82.8	89.6	90.4	93.3	**Mean:**	**94.7**
	2	ND	105	118	117	115	98.5	**SD:**	**10.56**
	3	ND	86.0	92.8	91.0	89.1	105	**UCL:**	**126**
	4	ND	90.2	85.6	92.2	82.2	92.8	**uwl:**	**116**
	5	ND	101	100	95.0	86.8	90.5	**lwl:**	**73.6**
								LCL:	**63.1**

Appendix V

Storage Stability Study

A storage stability study was done for all compounds at an earlier date. The results show that all compounds are stable up to 28 days. The storage study was extracted using the wrong extraction method for days 0, 2, 4 and 7. Days 21 and 28 were extracted correctly and show that the stability is good to day 28. The storage study will be redone and added to this SOP at a later date.

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Date	What was revised? Why?
2/22/22	Reformatted the entire document in accordance with web accessibility requirements
	Revised the title of method for consistency with the method outline
	Made multiple editorial revisions throughout the document for improved readability
	Updated procedures for standards preparation to reflect current practices
	Added a title to the table of LC/MS/MS Instrument Conditions
	Added a title to the table of GC/MS/MS Instrument Conditions
	Revised Table 3 to include malathion, parathion ethyl, piperonyl butoxide, and prometryn.
	Reorganized the tables in Appendix I-IV to match the order of the compounds listed in Section 6.