DPR 289

California Department of Food and Agriculture
Center for Analytical Chemistry
Environmental Monitoring Section
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Title: Determination of Organophosphate Pesticides in Surface water using Gas Chromatography

1. Scope:

   This section method (SM) documents the selected organophosphate pesticides analysis in surface water by all authorized section personnel.

2. Principle:

   The surface water sample is extracted with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated to almost dryness on a rotary evaporator and diluted to a final volume of 1.0 mL with acetone. The extract is then analyzed by a gas chromatograph equipped with flame photometric detector (FPD) and any positive result is confirmed by mass selective detector (MSD). The low level diazinon and chlorpyrifos (RL = 10 ppt) are analyzed only by mass selective detector using the same extract.

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

4. Interferences:

   There are matrix interferences that cause quantitative problems. Therefore the calibration standards will be made up in appropriate matrix.

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 Balance (Mettler PC 4400) or equivalent

5.5 Gas Chromatograph equipped with a flame photometric detector (FPD) in phosphorus mode
5.6 Gas Chromatograph equipped with mass selective detector (MSD)

6. Reagents and Supplies

6.1	Methylene Chloride, nanograde or equivalent pesticide grade	
6.2	Acetone, nanograde or equivalent pesticide grade	
6.3	Anhydrous Sodium Sulfate, granular	
6.4	Ethoprophos	CAS# 13194-48-4
6.5	Diazinon	CAS# 333-41-5
6.6	Disulfoton	CAS# 298-04-4
6.7	Chlorpyrifos	CAS# 2921-88-2
6.8	Malathion	CAS# 121-75-5
6.9	Methidation	CAS# 950-37-8
6.10	Fenamiphos	CAS# 22224-92-6
6.11	Azinphos Methyl	CAS# 86-50-0
6.12	Dichlorvos	CAS# 62-73-7
6.13	Phorate	CAS# 298-02-2
6.14	Fonofos	CAS# 66767-39-3
6.15	Dimethoate	CAS# 60-51-5
6.16	Parathion methyl	CAS# 298-00-0
6.17	Tribufos (DEF)	CAS# 13071-79-9
6.18	Profenofos	CAS# 41198-08-7

6.19 Conical tube with glass stopper, 15-mL graduated, 0.1 mL subdivision
6.20 Separatory funnel, 2 L
6.21 Boiling flask, 500 mL
6.22 Funnel, long stem, 10 mm diameter
6.23 Disposable Pasteur pipettes, and other laboratory ware as needed
6.24 Recommended analytical columns:

For FPD – Restek's Rtx® - OPPesticides (fused silica column), 30 m x 0.25 mm x 0.4 μm film thickness or 30 m x 0.32 mm x 0.5 μm film thickness, and Rtx® - OPPesticides2 (fused silica column), 30 m x 0.25 mm x 0.25 μm film thickness or 30 m x 0.32 mm x 0.32 μm film thickness.

For MSD - 5% phenyl Methylsilicone (HP-5ms or equivalent) fused silica column, 30 m x 0.25 mm x 0.25 μm film thickness.

7. Standards Preparation:

7.1 Dilute the 1 mg/mL Organophosphate standards obtained from the CDFA/CAC Standards Repository with acetone to make up a series of mixed working standards (see 10.2). These standards shall be prepared to cover the linear range from 0.025 ηg/μL to 1.0 ηg/μL for OP screen and 0.01 ηg/μL to 0.5 ηg/μL for low level diazinon and chlorpyrifos.

7.2 The calibration standards are added to matrix blank extracts (9.1.2.1) to correct for matrix background interference.

7.3 Keep all standards in designated refrigerator for storage.

7.4 The expiration date of each mixed working standard is six months from the preparation date.

8. Sample Preservation and Storage:

All water samples and sample extracts shall be stored in the refrigerator (3 ± 4 °C).

9. Test Sarnple Preparation:

9.1 Sample Preparation

9.1.1 Remove samples from refrigerator and allow samples to come to room temperature before extraction.

9.1.2 Preparation of matrix blank and matrix spike:

The Department of Pesticide Regulations (DPR) provides the background water for matrix blarık and spikes.

9.1.2.1 Matrix blank: Weigh out 1000 g of background water and follow the test sample extraction procedure.

9.1.2.2 Matrix spike: Weigh out 1000 g of background water. Spike a client requested amount of organophosphate pesticides into the background water and let it stand for 1 minute. Follow the test sample extraction procedure.

9.2 Test Sample Extraction

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

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

9.2.3 After phases have separated, drain lower methylene chloride layer through 20 ± 4 g of anhydrous sodium sulfate and glasswool, into a 500 mL boiling flask.

9.2.4 Repeat steps 9.2.2 & 9.2.3 two more times using 80 ± 5 mL of methylene chloride each time. Combine the extracts in the same boiling flask.

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

9.2.6 Evaporate the sample extract to 2 - 4 mL on a rotary evaporator using a water bath at 35 ± 2 °C and 15 - 20 inch Hg vacuum. Add 2 - 4 mL of acetone and rotoevaporate to 1 - 2 mL. Transfer the extract to a calibrated 15 mL graduated test tube.

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

9.2.8 Evaporate the extract to a volume slightly less than 1 mL in a water bath at 38 ± 2 °C under a gentle stream of nitrogen. Then bring to a final volume of 1.0 mL with acetone, mix well and transfer into two autosampler vials.

9.2.9 Submit extract for GC analysis.

10. Instrument Calibration:

10.1 The calibration standards are added to a matrix blank extract to correct for matrix background interference.

10.2 A calibration standard curve consists of minimum of three levels. Standard concentrations of 0.01, 0.025, 0.05, 0.1, 0.25, 0.5 or 1.0 ηg/μL are recommended.

Calibration is obtained using a linear or quadratic regression with the correlation coefficient (r) equal to or greater than 0.995.

10.3 Suggested compositions of calibration mixed standards are as follow.

OP-1 Mixed Standard	**OP-2 Mixed Standard**
Ethoprophos	Dichlorvos
Diazinon	Phorate
Disulfoton	Fonofos
Chlorpyifos	Dimethoate
Malathion	Parthion-methyl
Methidathion	DEF
Fenamiphos	Profenofos
Azinphos-methyl	

Low level Mixed Standard
Diazinon
Chlorpyifos

11. Analysis:

11.1 Injection Scheme

Follow the sequence of Solvent, Calibration standards, Solvent, Matrix Bank, Matrix Spike, Test Samples (maximum of 10-12 samples) and Calibration standards. Inject an old sample or matrix blank before the sequence analysis to condition the instrument is recommended.

11.2 GC Instrumentation

11.2.1 Analyze OP pesticides by a gas chromatograph equipped with two flame photometric detectors and two different columns.

11.2.2 Recommended instrument (GC/FPD) parameters: Injector 250 °C; detector 250 °C; oven temperature 80 °C (hold 2 min.) to 180 °C @ 20 °C/min. to 280 °C @ 6 °C/min. (hold 6 min.); injection volume 3 µL.

11.2.3 Confirm OP pesticides by a gas chromatograph equipped with mass selective detector.

11.2.4 Recommended instrument (GC/MSD) parameters: Injector 250 °C; MSD transfer line heater 280 °C; initial oven temperature 80 °C, hold 2 min., ramp @ 20 °C/min. to 180 °C and then ramp @ 6 °C/min. to 250 °C, hold 4 min; injection volume 2 or 3 µL.

11.2.5 Analyze low level diazinon and chlorpyrifos by a gas chromatograph equipped with mass selective detector.

11.2.6 Recommended instrument (GC/MSD) parameters: Injector 250 °C; MSD transfer line heater 280 °C; oven temperature 80 °C, hold 2 min., ramp @ 20 °C/min. to 250 °C, hold 4 min.; injection volume 2 or 3 µL.

Ions Selected for SIM Acquisition:

Diazinon	137, 152, **179**, 304,	Retention time: 10.4 min.
Chlorpyrifos	**197**, 258, 286, 314,	Retention time: 11.6min.

(Quantitation ions are in bold)

12. Quality Control:

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

12.2 The matrix blank should be free of target compounds.

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

12.4 The retention time should be within ± 2 percent of that of the standard.

12.5 The sample must be diluted if results fall outside the linear range of the standard curve.

12.6 Bracketing standard curves should have a percent change less than 20 % for most of organophosphate compounds, and 20 – 35 % for late eluted OP compounds.

12.7 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 water samples are spiked at 0.05 ppb for OP screen and 7 replicate water samples are spiked at 10

ppt for low level diazinon and chloripyrifos. 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.

12.8 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. Per client agreement, the RL is chosen in a range 1-5 times the MDL except in special cases. (See 15.5)

MDL data and the RL are tabulated in Appendix IA and IB.

12.9 Method Validation Recovery Data and Control Limits:

12.9.1 The method validation consisted of five sample sets. Each set included seven levels of fortification (0.05, 0.1, 0.25, 0.5, 1.0, 2.0, and 5.0 ppb) and a method blank. All spikes and method blank samples were processed through the entire analytical method.

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

12.9.3 The method validation for low level diazinon and chlorprifos consisted of five sample sets. Each set included three levels of fortification (12.5, 25 and 75 ppt) and a method blank. All spikes and method blank samples were processed through the entire analytical method.

Method validation results and control limits are tabulated in Appendix IIA and IIB.

12.10 Estimated Measurement Uncertainty:

Total uncertainty for this method is 11% at 95% confidence interval.

13. Calculations:

Quantitation is based on external standard (ESTD) calculation using either the peak area or height. The software uses a linear or quadratic curve fit, with all levels weighted equally. Alternatively, at chemist discretion, concentrations may be calculated using the response factor for the standard whose value is closest to the level in the sample.

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

14. Reporting Procedure:

14.1 Identification of Analyte

For responses within calibration range, compare the retention time of the peaks with the retention time of standards. For positive results retention times shall not vary from the standards more than 2 percent.

14.2 The Restek's Rtx® - OPPesticides column is used as the primary analytical column, the 2nd column, Rtx® - OPPesticides2 column and GC/MSD used as confirmation.
Sample results and the data reported in the Appendix IA and IIB were calculated from the Rtx® - OPPesticides column.

14.3 Sample results are reported out according to the client's analytical laboratory specifications.

15. Discussion and References:

15.1 Sample response and quantitation vary depending on matrix background in the samples. The calibration standards were added to a matrix blank extract to correct for matrix background interference.

15.2 Two different sizes of analytical column (ID of 0.25 and 0.32 mm) were used in this method. The column with larger ID (0.32 mm) seems to give more reproducible results, since 3 µL sample extract was injected.
The retention times for OP pesticides are tabulated in Appendix III.

These retention times were obtained when columns were newly installed. After columns had been trimmed, the retention times decreased.

15.3 Some of the late eluting compounds were observed to suffer gradual losses in sensitivity. We recommend changing the injector liner and trimming the column when this occurs.

15.4 The client requested a lower reporting limit for both diazinon and chlorpyrifos. We re-validated this method using GC/MSD as the analysis instrument to achieve the lower reporting limit for those two compounds.

15.5 The reporting limit for low level diazinon and chlorpyrifos is 9 - 10 times greater than its MDL. This is because the sample matrix can easily interfere with the ion spectrum at low levels compared to background water used for method validation. Therefore setting RL 9 - 10 times the MDL provides a confident limit for the chemist to report and has client approval.

16. References:

16.1 *EPA Method 507, Pesticides, Capillary Column*. EPA Test Method for Drinking Water and Raw Source Water, 1987.

16.2 Hsu, J. and Hernandez J. *Determination of Organophosphate Pesticides in Surface Water using Gas Chromatography*, 1997, Environmental Monitoring Method, Center for Analytical Chemistry, CDFA.

APPENDIX IA

The determination of Method Detection Limit (MDL) data and Reporting Limit (RL)

Spk \ Analyte	Ethoprophos	Diazinon	Disulfoton	Chlorpyrofos	Malathion
0.05 ppb spk1	0.0503	0.0580	0.0528	0.0573	0.0602
0.05 ppb spk2	0.0500	0.0561	0.0513	0.0552	0.0581
0.05 ppb spk3	0.0482	0.0524	0.0490	0.0534	0.0555
0.05 ppb spk4	0.0538	0.0582	0.0525	0.0616	0.0657
0.05 ppb spk5	0.0498	0.0548	0.0514	0.0574	0.0600
0.05 ppb spk6	0.0559	0.0593	0.0569	0.0617	0.0630
0.05 ppb spk7	0.0469	0.0496	0.0477	0.0534	0.0558
SD	0.00313	0.00349	0.00296	0.00348	0.00371
MDL	0.0098	0.0110	0.0093	0.0109	0.0117
RL	0.050	0.040	0.040	0.040	0.040

Spk \ Analyte	Methidathion	Fenamiphos	Dichlorvos	Phorate	Fonofos
0.05 ppb spk1	0.0576	0.0610	0.0417	0.0458	0.0476
0.05 ppb spk2	0.0574	0.0585	0.0476	0.0468	0.0486
0.05 ppb spk3	0.0540	0.0587	0.0461	0.0474	0.0493
0.05 ppb spk4	0.0643	0.0683	0.0393	0.0404	0.0430
0.05 ppb spk5	0.0613	0.0638	0.0398	0.0459	0.0485
0.05 ppb spk6	0.0628	0.0674	0.0422	0.0429	0.0451
0.05 ppb spk7	0.0599	0.0608	0.0416	0.0476	0.0503
SD	0.00355	0.00397	0.00311	0.00266	0.00256
MDL	0.0111	0.0125	0.0098	0.0083	0.0080
RL	0.050	0.050	0.050	0.050	0.040

Spk \ Analyte	Dimethoate	Propenofos	DEF	Parathion Methyl	Azinophos Methyl
0.05 ppb spk1	0.0502	0.0538	0.0558	0.0495	0.0612
0.05 ppb spk2	0.0502	0.0541	0.0555	0.0503	0.0606
0.05 ppb spk3	0.0495	0.0526	0.0544	0.0501	0.0621
0.05 ppb spk4	0.0468	0.0519	0.0520	0.0464	0.0678
0.05 ppb spk5	0.0472	0.0535	0.0576	0.0499	0.0631
0.05 ppb spk6	0.0431	0.0440	0.0448	0.0440	0.0671
0.05 ppb spk7	0.0486	0.0545	0.0579	0.0509	0.0598
SD	0.00253	0.00371	0.00452	0.00254	0.00316
MDL	0.0079	0.0114	0.0142	0.0080	0.0099
RL	0.040	0.050	0.050	0.030	0.050

All concentrations are expressed in ppb.

APPENDIX IB

The determination of Method Detection Limit (MDL) data and Reporting Limit (RL) for low level Diazinon and Chlorpyrifos

Spk \ Analyte	**Diazinon**	**Chlorpyrifos**
10 ppt spk1	10.06	10.12
10 ppt spk2	9.55	9.38
10 ppt spk3	9.80	9.92
10 ppt spk4	9.38	9.69
10 ppt spk5	9.43	9.46
10 ppt spk6	8.92	9.78
10 ppt spk7	9.87	9.74
SD	0.3789	0.2542
MDL	1.191	0.799
RL	10.0	10.0

All concentrations are expressed in ppt.

APPENDIX IIA

Method Validation Data and Control Limit for low level diazinon and chlorpyrifos

Analyte	Spike ppt	Recovery (%) Set 1	Set 2	Set 3	Set 4	Set 5	%
Diazinon	12.5	87.2	96.8	100.8	88.8	88.0	Mean: 93.0
	25.0	88.8	100.8	107.6	79.6	85.2	SD: 7.90
	75.0	87.9	102.5	98.3	86.7	95.6	UCL: 116.7
							UWL: 108.8
							LWL: 77.2
							LCL: 69.3
Chlorpyrifos	12.5	91.2	100.8	100	88.8	97.6	Mean: 94.1
	25.0	85.2	98.8	109.2	79.2	84.4	SD: 8.45
	75.0	87.9	103.9	99.6	87.3	97.9	UCL: 119.45
							UWL: 111
							LWL: 77.2
							LCL: 68.75

APPENDIX IIB

Method Validation Data and Control Limit

Analyte	Spike ppb	Recovery (%) Set 1	Set 2	Set 3	Set 4	Set 5	%
Ethoprophos	0.05	95.6	64.2	100.0	79.0	91.8	Mean: 91.6
	0.10	88.0	76.1	100.5	94.6	88.4	SD: 10.48
	0.25	84.8	90.8	86.0	90.0	82.0	
	0.50	91.2	88.0	100.6	84.0	84.8	UCL: 123.0
	1.0	83.7	82.6	87.9	76.2	96.7	UWL: 112.6
	2.0	107.2	103.9	95.6	91.6	90.8	LWL: 70.7
	5.0	113.1	108.9	97.2	107.6	103.2	LCL: 60.2
Diazinon	0.05	100.8	69.2	104.0	85.2	96.2	Mean: 96.6
	0.10	173.0	80.0	102.3	95.3	90.7	SD: 16.83
	0.25	90.0	94.0	88.0	91.2	84.0	
	0.50	93.4	89.8	100.8	88.6	87.2	UCL: 147.0
	1.0	85.4	87.2	88.1	79.9	97.9	UWL: 130.2
	2.0	106.5	104.4	96.7	92.1	92.6	LWL: 62.9
	5.0	109.4	123.5	98.3	113.6	100.1	LCL: 46.1
Disulfoton	0.05	95.2	58.8	92.4	80.2	83.0	Mean: 88.3
	0.10	88.0	70.5	96.7	92.3	82.2	SD: 10.09
	0.25	87.2	87.2	84.0	76.4	84.7	
	0.50	91.6	82.6	98.0	78.8	80.0	UCL: 118.6
	1.0	83.9	82.5	83.6	75.3	92.0	UWL: 108.5
	2.0	100.1	100.7	94.3	87.6	90.0	LWL: 68.1
	5.0	103.8	103.7	96.2	106.8	96.4	LCL: 58.0
Chlorpyrifos	0.05	95.6	69.0	102.0	90.2	94.2	Mean: 94.5
	0.10	92.5	83.1	101.5	97.1	91.1	SD: 8.84
	0.25	92.4	95.2	88.4	90.0	116.4	
	0.50	95.0	89.4	99.6	91.6	86.4	UCL: 121.1
	1.0	86.0	91.9	87.6	81.7	97.7	UWL: 112.2
	2.0	102.8	101.2	96.3	90.1	91.2	LWL: 76.9
	5.0	105.8	107.5	98.1	111.4	98.7	LCL: 68.0

APPENDIX IIB (Continued)

Method Validation Data and Control Limit

Analyte	Spike ppb	Recovery (%) Set 1	Set 2	Set 3	Set 4	Set 5	%
Malathion	0.05	97.4	66.4	102.2	88.2	95.2	Mean: 95.7
	0.10	91.1	86.4	100.6	94.4	91.8	SD: 10.01
	0.25	92.8	97.6	90.0	86.8	84.0	
	0.50	95.4	91.0	100.2	95.4	88.6	UCL: 125.7
	1.0	85.8	91.5	86.8	87.7	96.3	UWL: 115.7
	2.0	109.4	110.5	101.0	96.1	96.3	LWL: 75.7
	5.0	114.	112.6	102.5	117.8	105.0	LCL: 65.7
Methidathion	0.05	101.0	66.2	103.6	89.0	93.4	Mean: 95.9
	0.10	91.8	84.3	101.3	94.4	93.0	SD: 10.65
	0.25	92.0	89.6	88.8	84.0	84.8	
	0.50	93.0	89.4	99.6	95.0	89.8	UCL: 127.8
	1.0	84.9	93.0	86.0	93.3	96.7	UWL: 117.2
	2.0	111.1	111.3	102.0	97.3	96.8	LWL: 74.6
	5.0	116.4	113.7	106.0	118.6	104.4	LCL: 63.9
Fenamiphos	0.05	99.4	67.8	104.0	93.6	90.4	Mean: 96.2
	0.10	90.8	90.3	104.2	98.2	94.4	SD: 9.43
	0.25	92.8	97.2	90.0	90.0	84.4	
	0.50	95.4	90.4	100.0	95.6	88.4	UCL: 124.5
	1.0	85.8	94.6	88.2	86.3	97.5	UWL: 115.1
	2.0	108.9	106.3	101.7	94.6	97.2	LWL: 77.3
	5.0	110.3	113.0	103.4	117.8	104.0	LCL: 67.9
Azinphos Methyl	0.05	85.4	59.0	98.6	71.2	92.8	Mean: 93.2
	0.10	79.6	74.2	96.0	107.4	95.2	SD: 14.58
	0.25	83.2	86.8	84.0	84.8	89.6	
	0.50	82.6	80.0	99.4	83.4	91.6	UCL: 136.9
	1.0	77.1	90.2	83.7	113.1	90.0	UWL: 122.3
	2.0	108.3	113.5	101.1	96.6	92.2	LWL: 64.0
	5.0	124.9	113.6	112.5	118.8	101.2	LCL: 49.4

APPENDIX IIB (Continued)

Method Validation Data and Control Limit

Analyte	Spike ppb	Recovery (%) Set 1	Set 2	Set 3	Set 4	Set 5	%
Dichlorvos	0.05	72.6	95.6	95.2	72.6	82.6	Mean: 82.6
	0.10	92.3	91.5	91.1	82.3	81.1	SD: 7.80
	0.25	87.2	78.0	77.6	87.2	77.2	
	0.50	83.0	79.0	85.0	83.0	55.6	UCL: 106.0
	1.0	82.9	82.3	79.1	82.9	77.2	UWL: 98.2
	2.0	82.1	82.5	92.2	80.7	78.7	LWL: 67.0
	5.0	83.5	99.0	81.6	90.0	76.2	LCL: 59.2
Phorate	0.05	83.4	89.0	95.6	83.4	86.8	Mean: 87.9
	0.10	82.8	90.5	97.6	82.8	85.3	SD: 7.21
	0.25	90.4	86.0	83.2	90.4	80.8	
	0.50	85.2	83.4	94.2	852	75.6	UCL: 109.5
	1.0	80.7	79.5	87.5	80.7	78.7	UWL: 102.3
	2.0	92.1	86.1	100.3	91.3	84.1	LWL: 73.5
	5.0	100.6	106.2	90.9	102.5	84.0	LCL: 66.3
Fonofos	0.05	88.2	92.0	101.4	88.2	89.4	Mean: 90.3
	0.10	85.9	92.2	100.4	85.9	87.3	SD: 7.40
	0.25	91.6	86.8	86.0	91.6	82.8	
	0.50	86.0	83.4	97.2	86.0	79.2	UCL: 112.5
	1.0	81.6	78.2	91.1	81.6	81.6	UWL: 105.1
	2.0	94.7	88.9	105.1	95.1	88.1	LWL: 75.5
	5.0	97.9	107.3	95.4	104.7	88.1	LCL: 68.1
Dimethoate	0.05	96.2	96.6	88.4	96.2	84.6	Mean: 90.5
	0.10	82.7	95.4	95.8	82.7	86.5	SD: 8.67
	0.25	93.2	82.4	82.8	93.2	78.8	
	0.50	91.8	76.0	97.8	91.8	79.2	UCL: 116.6
	1.0	104.2	68.2	97.7	104.2	83.2	UWL: 107.9
	2.0	88.5	89.7	103.6	93.6	90.8	LWL: 73.2
	5.0	92.6	101.0	86.4	106.2	87.0	LCL: 64.5

APPENDIX IIB (Continued)

Method Validation Data and Control Limit

Analyte	Spike ppb	Recovery (%) Set 1	Set 2	Set 3	Set 4	Set 5	%
Parathion Methyl	0.05	93.2	99.0	97.2	93.2	91.4	Mean: 93.7
	0.10	86.1	98.6	101.4	86.1	88.1	SD: 8.55
	0.25	97.2	87.2	92.8	97.2	82.4	
	0.50	91.4	81.2	105.2	91.4	79.8	UCL: 119.3
	1.0	98.9	73.4	110.8	98.9	84.2	UWL: 110.8
	2.0	91.9	90.3	105.9	98.6	91.6	LWL: 76.6
	5.0	97.2	105.1	90.2	111.5	90.5	LCL: 68.0
DEF	0.05	96.6	97.2	102.4	96.6	92.6	Mean: 95.3
	0.10	91.6	98.3	106.7	91.6	90.3	SD: 10.2
	0.25	94.0	88.0	96.0	94.0	84.8	
	0.50	92.2	77.6	112.0	92.2	83.4	UCL: 126.0
	1.0	84.3	69.4	108.7	84.3	84.9	UWL: 115.8
	2.0	99.7	94.4	115.1	103.2	93.8	LWL: 74.9
	5.0	103.5	99.7	104.2	118.1	95.9	LCL: 64.7
Profenofos	0.05	96.8	105.2	104.0	97.8	85.4	Mean: 94.3
	0.10	88.0	100.4	104.3	88.0	87.0	SD: 10.06
	0.25	102.0	84.0	94.8	102.0	83.2	
	0.50	95.6	73.0	107.0	95.6	79.8	UCL: 124.5
	1.0	98.5	63.5	105.8	98.5	87.9	UWL: 114.5
	2.0	93.6	91.5	106.5	99.	91.6	LWL: 74.2
	5.0	96.8	96.4	93.5	112.3	92.1	LCL: 64.1

APPENDIX III

Retention Time for OP Pesticides:

RT(min.) / Op Pesticides	Rtx® -OPPesticides column		Rtx® -OPPesticides2 column	
	30m x 0.25mm x 0.4µm	30m x 0.32mm x 0.5µm	30m x 0.25mm x 0.25µm	30m x 0.25mm x 0.32µm
Ethoprophos	11.7	9.7	11.7	9.6
Diazinon	12.5	10.4	13.6	11.2
Disulfoton	13.1	10.9	13.9	11.5
Chlorpyrifos	15.2	12.8	16.5	13.8
Malathion	16.3	13.8	16.2	13.5
Methidation	18.2	15.5	18.7	15.8
Fenamiphos	18.9	16.3	18.9	16.1
Azinphos methyl	23.9	21.0	25.1	21.8
Dichlorvos	8.4	7.0	7.8	6.3
Phorate	11.8	9.8	12.5	10.2
Fonofos	13.0	10.8	13.8	11.3
Dimethoate	14.4	12.0	13.6	11.1
Parathion methyl	16.4	13.8	15.5	12.8
Tribufos (DEF)	17.5	15.0	19.1	16.1
Profenofos	18.3	15.7	19.3	16.3

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Revision Log:

Date	What was Revised? Why?
01/22/04	Section 6.22 deleted, as whatman filter paper is not used in the method.
	Section 9.2.3, "and glass wool" incorporated.
04/12/04	Appendix I, RL for Malathion and Dimethoate , changed from 0.05 to 0.04. (Typing error) Appendix II, Malathion , Set 3, changed from 1002 to 100.2 (Typing error). Appendix II, Azinphos Methyl, Set 2, changed from 4.2 to 74.2 (Typing error). Section 12.10, Measurement uncertainty estimation included.
04/20/04	Section 11.2.2, injection volume, Change from 4 µL to 3 µL.
	Section 11.2.4, injection volume, Change from 4 µL to 2 or 3 µL.
	Section 15.2, injection volume, Change from 4 µL to 3 µL
07/14/04	Section 8, the refrigerator temperature, changed from (32 - 40 °F) to (3 ± 4 °C).
	Section 9.2.1, Record the weight of water sample to 0.1g, (add 0.1 g)
	Section 9.2.6, water bath temperature, Change from ~ 35 ° C to 35 ± 2 ° C.
	Section 9.2.8, water bath temperature, Change from 25 to 35 ° C to 38 ± 2 ° C.
	Section 15.2, "These retention times were obtained when columns were newly installed. After columns had been trimmed the retention times decreased." Added.
09/02/04	The following items were added to this method due to the client's request for analysis of low level diazinon and chlorpyrifos sharing the same sample extract for OP screening.
	Section 2, Principle: "The low level diazinon and chlorpyrifos are only analyzed by mass selective using the same extract." included
	Section 7.1, "and 0.01 ηg/µL to 0.5 ηg/µL for low level diazinon and chlorpyrifos." included
	Section 10.2, Standard concentrations "0.01" ηg/µL added.
	Section 10.3, Low level mixed standards added.
	Section 11.2.5, 11.2.6 and 12.9.3 added.
	Section 12.7, "and 7 replicate water samples are spiked at 10 ppt for low level Diazinon and chloripyrifos." included.
	Section 15.4 and 15.5 included.
	Appendix IB and IIA added, Appendix I and II change to IA and IIB.