May, 2002

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# Determination of Organophosphate Pesticides in Surface Water Using Gas Chromatography

## Scope:

This method is for the determination of organophosphate pesticides in surface water. The MDLs for the analytes were as follows by the HP-1 analysis method: 0.025 µg/L for Diazinon, 0.024 µg/L for DDVP, 0.022 µg/L for Ethoprophos, 0.020 µg/L for Dimethoate/Phorate, 0.020 µg/L for Fonofos, 0.020 µg/L for Methyl Parathion, 0.021 µg/L for Malathion, 0.019 µg/L for Chlorpyrifos, 0.019 µg/L for Methidathion, 0.016 µg/L for Phosmet and 0.016 µg/L for Azinfos methyl. The MDLs for the analytes were as follows by the HP-17 analysis method: 0.013 µg/L for Diazinon, 0.016 µg/L for DDVP, 0.015 µg/L for Ethoprophos, 0.017 µg/L for Dimethoate, 0.015 µg/L for Phorate, 0.018 µg/L for Fonofos, 0.019 µg/L for Methyl Parathion, 0.018 µg/L for Malathion, 0.019 µg/L for Chlorpyrifos, 0.016 µg/L for Methidathion, 0.017 µg/L for Phosmet and 0.017 µg/L for Azinfos methyl.

## Equipment and Reagents:

Equipment:

*Glassware and Miscellaneous Equipment*

Balance
Boiling flask, flat bottom 500 mL
Filter paper, Whatman #4, 15 cm
Nitrogen evaporator (Meyers Organomation Assoc.)
Separatory funnel, 2L
Syringes, microliter, various sizes
Test tube, 15 mL conical, graduated
Volumetric flask, various sizes
Volumetric pipette, various sizes
Vortex mixer

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Reagents and Standards:

*Solvents/Reagents*

All solvents were HPLC grade unless noted:

Acetone

Dichloromethane

Sodium Sulfate, anhydrous

*Standard Reference Substances*

The reference standards were supplied or purchase as shown below:

| Standard | Source | Lot Number | Expiration Date | Purity (%) |
|---|---|---|---|---|
| Azinphos-methyl/Guthion | Chem Service<br>Crescent Chemical Co. | 238-49B<br>90111 | 2/04<br>1/1/03 | 99<br>96.5 |
| Chlorpyriphos | Chem Service<br>Crescent Chemical Co. | 242-54B<br>80721 | ¾<br>8/1/02 | 99.5<br>99.0 |
| Diazinon | Chem Service<br>Crescent Chemical Co. | 252-102B<br>00406 | 11/03<br>5/1/03 | 99.4<br>94.0 |
| Dichlorvos/DDVP | Chem Service<br>Crescent Chemical Co. | 258-35B<br>00126 | 1/03<br>2/1/03 | 98.0<br>97.0 |
| Dimethoate | Chem Service | 244-90B | 4/03 | 98 |
| Ethoprophos | Chem Service<br>Crescent Chemical Co. | 249-114B<br>90212 | 9/03<br>3/1/02 | 98<br>92.0 |
| Fonophos | Chem Service<br>Crescent Chemical Co. | 256-32B<br>00103 | 7/02<br>1/1/04 | 99.0<br>97.0 |
| Malathion | Chem Service<br>Crescent Chemical Co. | 254-44C<br>70401 | 10/03<br>4/1/03 | 98<br>99.5 |
| Methidathion | Chem Service<br>Crescent Chemical Co. | 254-109B<br>81105 | 11/04<br>11/1/02 | 99<br>97.0 |
| Methyl parathion | Chem Service<br>Crescent Chemical Co. | 258-38A<br>90318 | 8/02<br>4/1/03 | 99.5<br>98.5 |
| Phorate | Chem Service<br>Crescent Chemical Co. | 252-110A<br>90413 | 11/03<br>4/1/03 | 98<br>94.5 |
| Phosmet/Imidan | Chem Service<br>Crescent Chemical Co. | 255-126A<br>90713 | 2/04<br>7/1/03 | 99<br>98.5 |

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The reference standards were concluded to be stable throughout the conduct of the study based on the comparison of chromatograms of the first and last analysis.

**Analytical Procedures**

Preparation of Sample:

All samples were received cool at PTRL West, Inc. and remained refrigerated until used for analysis.

Preparation of Standards:

Stock solutions of each reference standard were prepared in acetone, as described under the "Method of Calculations" section. A 1 mg/mL stock solution was prepared in acetotone for the following analytes: Azinphos methyl, Chlorpyrifos, Diazinon, DDVP, Dimethoate, Ethoprophos, Fonofos, Malathion, Methidathion, Methyl Parathion, Phorate, and Phosmet. Working solutions were made by diluting the stock standards to prepare fortification standards and calibration standard solutions, as described below. Microliter syringes, volumetric pipettes and volumetric flasks were used throughout.

Fortification Procedure:

Fortification of untreated surface water was conducted to determine the percent recovery within each sample set for Azinphos methyl, Chlorpyrifos, Diazinon, DDVP, Dimethoate, Ethoprophos, Fonofos, Malathion, Methidathion, Methyl Parathion, Phorate, and Phosmet. Fortification of control water was conducted in duplicate within sample sets. A mixed 50 µg/mL fortification stock was prepared by aliquoting 5 mL for each 1 mg/mL stock into a 100 mL volumetric flask and diluting to the mark with acetone. A mixed 5.0 µg/mL fortification stock was prepared by aliquoting 10 mL of the 50 µg/mL fortification stock and diluting to 100 mL with acetone. A mixed 0.5 µg/mL fortification stock was prepared by aliquoting 10 mL of the 5.0 µg/mL fortification stock and diluting to 100 mL with acetone.

The following fortifications were conducted:

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*Method Validation:*

| Fortification Level (µg/L) | OPs |
|---|---|
| 10.0 | 2 mL of 5.0 µg/mL Mixed Fort Stock |
| 5.0 | 1 mL of 5.0 µg/mL Mixed Fort Stock |
| 1.0 | 0.2 mL of 5.0 µg/mL Mixed Fort Stock |
| 0.5 | 1 mL of 0.5 µg/mL Mixed Fort Stock |
| 0.1 | 0.2 mL of 0.5 µg/mL Mixed Fort Stock |

*Sample Set Analysis:*

| Fortification Level (µg/L) | OPs |
|---|---|
| 0.2 | 400 µL of 0.5 ug/mL |

Preparation of Mixed Linearity Standards:

All mixed OPs dilutions made with acetone.

| Concentration (ng/mL) | Preparation: |
|---|---|
| 300 | 6 mL of 5.0 µg/mL mixed OP stock diluted to 100 mL |
| 100 | 20 mL of 0.5 µg/mL mixed OP stock diluted to 100 mL |
| 50 | 10 mL of 0.5 µg/mL mixed OP stock diluted to 100 mL |
| 40 | 8 mL of 0.5 µg/mL mixed OP stock diluted to 100 mL |
| 20 | 4 mL of 0.5 µg/mL mixed OP stock diluted to 100 mL |
| 10 | 2 mL of 0.5 µg/mL mixed OP stock diluted to 100 mL |
| 5 | 1 mL of 0.5 µg/mL mixed OP stock diluted to 100 mL |

All dilutions were prepared in volumetric flasks using Hamilton syringes and volumetric pipettes.

A set of calibration curves were generated with each sample set to determine linearity and to quantitate each triazine, see "Methods of Calculation" for example.

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Extraction Method for OPs in Water:

1. Remove water samples from refrigerator and allow them to come to room temperature.
2. Record weight of water by weighing sample bottle before and after water has been transferred into a separatory funnel.
3. Extract sample by shaking with 100 mL of methylene chloride for 2 minutes. Vent frequently to relieve pressure.
4. After the phases have separated, drain the lower methylene chloride layer through 20 g of anhydrous sodium sulfate, into a boiling flask.
5. Repeat steps 3 & 4 two more times, using 80 mL of methylene chloride each time.
6. After draining the final extraction, rinse the sodium sulfate with 25 mL of methylene chloride.
7. Evaporate the sample extract to just dryness on a rotary evaporator under vacuum, using a 35 °C water bath.
8. Add 5 mL of acetone and swirl to dissolve the residue in the flask. Transfer the extract to a calibrated 15-mL graduated conical test tube.
9. Rinse flask 2 more times, each time with 2 mL of acetone and transfer each rinse to the same test tube.
10. Under a gentle stream of nitrogen with no heat applied, evaporate the extract to a volume slightly less than 2 mL. Then, bring to a final volume of 2 mL with acetone.
11. Submit extract to GC analysis.

**Analysis Method**

Gas Chromatograph:

*Primary Analysis:*

Instrument: Hewlett Packard 5890 GC with FPD
Column: HP-1 (10 m x 0.53 mm x 2.65 µm (film)
Carrier Gas: Helium (20 mL/min)
Injector Temperature: 220 °C
Detector Temperature: 250 °C
Injection Volume: 1 or 2 µL
Oven Temperature:
Initial temperature: 150 °C, Hold for 1 minute
Ramp 1: 10 °C/min

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Final Temperature: 200 °C, hold for 2 minutes
Ramp 2: 20 °C/min
Final Temperature: 250 °C, hold for 5 minutes

*Confirmatory Analysis:*

Instrument: Hewlett Packard 5890 GC with FPD
Column: HP-17 (10 m x 0.53 mm x 2.0 µm (film)
Carrier Gas: Helium (20 mL/min)
Injector Temperature: 220 °C
Detector Temperature: 250 °C
Injection Volume: 1 or 2 µL
Oven Temperature:
Same as primary analysis conditions

| | Retention Times (minutes) | |
|---|---|---|
| Chemicals: | HP-1 | HP-17 |
| DDVP | 0.45 | 0.65 |
| Ethoprop | 2.03 | 2.94 |
| Phorate | 2.47 | 3.42 |
| Dimethoate | 2.48 | 4.82 |
| Fonophos | 3.07 | 4.30 |
| Diazinon | 3.30 | 4.18 |
| Methyl Parathion | 3.82 | 5.74 |
| Malathion | 4.53 | 6.22 |
| Chlorpyrifos | 4.72 | 6.04 |
| Methidathion | 5.48 | 8.71 |
| Phosmet | 8.78 | 11.63 |
| Azinphos methyl | 9.48 | 12.55 |

Separation of the analyte was achieved by gas chromatography. The analytes were identified by the coincidence of their retention times with the reference standards, and quantitated by integration of the peak area for the relevant ion(s). Phorate and dimethoate could not be separated on the HP-1 chromatographic column. Since these two analytes

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separated on the HP-17 column, both methods were used for analysis where phorate and/or dimethoate were present.

A typical injection sequence for triazine water samples as analyzed by GC was: solvent blank, solvent blank, 10 ng/mL mixed standard, 10 ng/mL mixed standard, control sample, control sample, fortified #1 sample, fortified #1 sample, fortified #2 sample, fortified #2 sample, 20 ng/mL mixed standard, 20 ng/mL mixed standard, treated #1 sample, treated #1 sample, treated #2 sample, treated #2 sample, treated #3 sample, treated #3 sample, 40 ng/mL mixed standard, 40 ng/mL mixed standard, etc.

**Statistical Methods**

The residue data included the following statistical calculations: means, averages, standard deviations, relative standard deviations and linear regression analysis.

**Method Detection Limit**

The limit of quantitation was determined according to SOP Number QAQC001.00, wherein the 0.05 µg/mL mixed standard was injected seven times. The MDLs for the analytes were as follows by the HP-1 analysis method: 0.025 µg/L for Diazinon, 0.024 µg/L for DDVP, 0.022 µg/L for Ethoprophos, 0.020 µg/L for Dimethoate/Phorate, 0.020 µg/L for Fonofos, 0.020 µg/L for Methyl Parathion, 0.021 µg/L for Malathion, 0.019 µg/L for Chlorpyrifos, 0.019 µg/L for Methidathion, 0.016 µg/L for Phosmet and 0.016 µg/L for Azinfos methyl. The MDLs for the analytes were as follows by the HP-17 analysis method: 0.013 µg/L for Diazinon, 0.016 µg/L for DDVP, 0.015 µg/L for Ethoprophos, 0.017 µg/L for Dimethoate, 0.015 µg/L for Phorate, 0.018 µg/L for Fonofos, 0.019 µg/L for Methyl Parathion, 0.018 µg/L for Malathion, 0.019 µg/L for Chlorpyrifos, 0.016 µg/L for Methidathion, 0.017 µg/L for Phosmet and 0.017 µg/L for Azinfos methyl.

**Methods of Calculation**

Preparation of Stock Standards:

$$\text{Volume of solvent (mL)} = \frac{(W) \times (P)}{(FC)}$$

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where W = Milligrams of neat standard
P = Chemical purity of neat standard
FC = Final Concentration (mg/mL)

Residue in Water:

Linear regression formula for each analyte,

calibration curve $y = mx + b$

where y = peak area
x = ng/mL analyte injected
m = Slope
b = Calibration intercept

The residue in water was calculated as follows:

$$\text{Analyte } (\mu g/L) = \frac{\mu g/mL \text{ (from standard curve) x final volume (mL)}}{\text{Sample weight (g)}} \times \frac{1000\,g}{L} \times \text{Dilution Factor}$$

Or

$$\text{Analyte } (\mu g/L) = \frac{\mu g/mL \text{ (from standard curve) x final volume (mL)}}{\text{Sample volume (L)}} \times \text{Dilution Factor}$$

Residues in fortified water were corrected for background by subtracting residue in control water.

**Method Performance:**

Quality Control:

1. Sample Storage: All field samples were refrigerated at 4 °C until extracted.
2. Sample extraction: All extracts were kept refrigerated at 4 °C until analyzed.
3. For each set of samples, at least one matrix blank and two matrix spikes were included.

Recovery data:

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The analytical method was validated by conducting 5 sets of samples using the provided background river water. Each set contained 5 different levels of spike and a matrix blank. Each set was processed through the entire analytical method on a different day. Each sample was injected twice on a HP-1 and HP-17 column. The results are presented in Appendix A.

Method Detection Limit (MDL):

Method Detection Limit (MDL) refers to the lowest concentration of analytes that a method can detect reliably. To determine the MDL, 7 replicate background samples were spiked at 0.05 µg/mL. The standard deviation from the spiked samples was used to calculate the MDL using the following equation:

$MDL = tS$

Where t is the Student t 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. See Appendix B for the recovery data from the determination of the Method Detection Limits.

The Reporting Limit (RL) refers to the level at which quantitative results may be obtained. By convention, the RL is chosen in a range 1-5 times the MDL. The Reporting Limit for this method was 0.05 µg/L for all analytes.

Discussion:

The method provided to PTRL West was slightly modified by increasing the final sample volume to 2 mL, which was dealt with as a dilution factor.

Reference

"Determination of Organophosphate Pesticides in Surface Water using Gas Chromatography," Method #EM 46.0, Jean Hsu, Jorge L. Hernandez, and Catherine Cooper, California Department of Food and Agriculture, May 1, 1997

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# Appendix A

## Method Validation Results

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Analytical Data for P999W

**RECOVERY of ORGANOPHOSPHATE PESTICIDES in SURFACE WATER**

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HP1 Analysis Method

| Organophosphate Pesticide | Spiked Level (µg/L) | # Spiked (n) | Mean Recovery (%) | Standard Deviation (Based on % Recovery) |
|---|---|---|---|---|
| DDVP | 0.1 | 5 | **69.2%** | 9.47% |
| | 0.5 | 5 | 104% | **20.3%** |
| | 1.0 | 5 | 96.0% | 10.6% |
| | 5.0 | 5 | 96.6% | **26.2%** |
| | 10.0 | 5 | 92.0% | 12.6% |
| Ethoprophos | 0.1 | 5 | 93.6% | 15.2% |
| | 0.5 | 5 | 112% | 14.4% |
| | 1.0 | 5 | 106% | 9.83% |
| | 5.0 | 5 | 109% | **22.6%** |
| | 10.0 | 5 | 103% | 10.8% |
| Phorate/Dimethoate | 0.1 | 5 | 97.4% | 14.8% |
| | 0.5 | 5 | 115% | 14.4% |
| | 1.0 | 5 | 111% | 13.4% |
| | 5.0 | 5 | 111% | **24.4%** |
| | 10.0 | 5 | 104% | 9.40% |
| Fonofos | 0.1 | 5 | 94.6% | 13.2% |
| | 0.5 | 5 | 111% | 14.4% |
| | 1.0 | 5 | 108% | 11.7% |
| | 5.0 | 5 | 109% | **23.7%** |
| | 10.0 | 5 | 103% | 10.6% |
| Diazinon | 0.1 | 5 | 93.0% | 14.7% |
| | 0.5 | 5 | 111% | 14.0% |
| | 1.0 | 5 | 109% | 12.7% |
| | 5.0 | 5 | 110% | **22.1%** |
| | 10.0 | 5 | 105% | 10.4% |
| Methyl Parathion | 0.1 | 5 | 101% | 14.0% |
| | 0.5 | 5 | 118% | 16.8% |
| | 1.0 | 5 | 114% | 14.7% |
| | 5.0 | 5 | 111% | **23.3%** |
| | 10.0 | 5 | 105% | 11.5% |
| Malathion | 0.1 | 5 | 98.8% | 14.0% |
| | 0.5 | 5 | 117% | 15.5% |
| | 1.0 | 5 | 114% | 15.4% |
| | 5.0 | 5 | 112% | **21.2%** |
| | 10.0 | 5 | 106% | 10.2% |

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Analytical Data for P999W

**RECOVERY of ORGANOPHOSPHATE PESTICIDES in SURFACE WATER**

California Department of Pesticide Regulation Study

HP1 Analysis Method

| Organophosphate Pesticide | Spiked Level (µg/L) | # Spiked (n) | Mean Recovery (%) | Standard Deviation (Based on % Recovery) |
|---|---|---|---|---|
| Chlorpyrifos | 0.1 | 5 | 94.6% | 13.5% |
| | 0.5 | 5 | 112% | 18.7% |
| | 1.0 | 5 | 111% | 14.5% |
| | 5.0 | 5 | 110% | **21.5%** |
| | 10.0 | 5 | 105% | 11.7% |
| Methidathion | 0.1 | 5 | 105% | 12.0% |
| | 0.5 | 5 | **122%** | 16.0% |
| | 1.0 | 5 | 115% | 14.8% |
| | 5.0 | 5 | 113% | **22.7%** |
| | 10.0 | 5 | 107% | 11.0% |
| Phosmet | 0.1 | 5 | 102% | **21.4%** |
| | 0.5 | 5 | **124%** | **25.1%** |
| | 1.0 | 5 | 108% | 7.63% |
| | 5.0 | 5 | 107% | 17.6% |
| | 10.0 | 5 | 94.4% | 10.6% |
| Azinphos Methyl | 0.1 | 5 | 115% | 13.2% |
| | 0.5 | 5 | **135%** | **26.5%** |
| | 1.0 | 5 | 116% | 4.72% |
| | 5.0 | 5 | 109% | **23.0%** |
| | 10.0 | 5 | 98.2% | 9.26% |

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Analytical Data for P999W

**RECOVERY of ORGANOPHOSPHATE PESTICIDES in SURFACE WATER**

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HP17 Analysis Method

| Organophosphate Pesticide | Spiked Level (µg/L) | # Spiked (n) | Mean Recovery (%) | Standard Deviation (Based on % Recovery) |
|---|---|---|---|---|
| DDVP | 0.1 | 5 | 79.6% | 9.18% |
| | 0.5 | 5 | 101% | 20.3% |
| | 1.0 | 5 | 96.6% | 15.5% |
| | 5.0 | 5 | 91.0% | 15.8% |
| | 10.0 | 5 | 96.0% | 19.8% |
| Ethoprophos | 0.1 | 5 | 96.0% | 8.97% |
| | 0.5 | 5 | 103% | 16.0% |
| | 1.0 | 5 | 100% | 6.20% |
| | 5.0 | 5 | 101% | 11.2% |
| | 10.0 | 5 | 101% | 10.5% |
| Phorate | 0.1 | 5 | 93.0% | 8.77% |
| | 0.5 | 5 | 98.2% | 13.4% |
| | 1.0 | 5 | 97.4% | 7.83% |
| | 5.0 | 5 | 97.8% | 8.11% |
| | 10.0 | 5 | 99.4% | 9.13% |
| Diazinon | 0.1 | 5 | 95.8% | 11.3% |
| | 0.5 | 5 | 107% | 16.8% |
| | 1.0 | 5 | 102% | 6.31% |
| | 5.0 | 5 | 97.8% | 6.10% |
| | 10.0 | 5 | 106% | 11.1% |
| Fonofos | 0.1 | 5 | 97.4% | 9.13% |
| | 0.5 | 5 | 99.0% | 16.2% |
| | 1.0 | 5 | 98.4% | 8.02% |
| | 5.0 | 5 | 101% | 12.0% |
| | 10.0 | 5 | 103% | 12.1% |
| Dimethoate | 0.1 | 5 | 98.8% | 10.2% |
| | 0.5 | 5 | 105% | 15.3% |
| | 1.0 | 5 | 104% | 9.78% |
| | 5.0 | 5 | 102% | 6.89% |
| | 10.0 | 5 | 103% | 11.7% |
| Methyl Parathion | 0.1 | 5 | 99.8% | 9.55% |
| | 0.5 | 5 | 106% | 15.4% |
| | 1.0 | 5 | 105% | 9.28% |
| | 5.0 | 5 | 100% | 5.98% |
| | 10.0 | 5 | 104% | 10.3% |

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Analytical Data for P999W

**RECOVERY of ORGANOPHOSPHATE PESTICIDES in SURFACE WATER**

California Department of Pesticide Regulation Study

HP17 Analysis Method

| Organophosphate Pesticide | Spiked Level (µg/L) | # Spiked (n) | Mean Recovery (%) | Standard Deviation (Based on % Recovery) |
|---|---|---|---|---|
| Chlorpyrifos | 0.1 | 5 | 101% | 9.34% |
| | 0.5 | 5 | 106% | 15.0% |
| | 1.0 | 5 | 104% | 8.11% |
| | 5.0 | 5 | 96.6% | 12.5% |
| | 10.0 | 5 | 105% | 9.70% |
| Malathion | 0.1 | 5 | 98.2% | 11.9% |
| | 0.5 | 5 | 104% | 15.1% |
| | 1.0 | 5 | 105% | 11.9% |
| | 5.0 | 5 | 105% | 9.25% |
| | 10.0 | 5 | 106% | 10.1% |
| Methidathion | 0.1 | 5 | 101% | 10.7% |
| | 0.5 | 5 | 108% | 12.7% |
| | 1.0 | 5 | 106% | 9.89% |
| | 5.0 | 5 | 103% | 10.9% |
| | 10.0 | 5 | 105% | 10.2% |
| Phosmet | 0.1 | 5 | 101% | 5.03% |
| | 0.5 | 5 | 105% | 18.1% |
| | 1.0 | 5 | 102% | 6.12% |
| | 5.0 | 5 | 92.4% | 6.19% |
| | 10.0 | 5 | 96.4% | 15.8% |
| Azinphos Methyl | 0.1 | 5 | 113% | 6.02% |
| | 0.5 | 5 | 116% | 16.4% |
| | 1.0 | 5 | 110% | 8.84% |
| | 5.0 | 5 | 93.4% | 11.8% |
| | 10.0 | 5 | 101% | 10.4% |

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# Appendix B

## Method Detection Limit Results

Analytical Data Set for P999W

## METHOD DETECTION LIMITS

California Department of Pesticide Regulation Study

Description: Method Detection Limits
Analysis Location: PTRL WEST, INC.
Analysis Method: GC/FPD HP1 Column
Analysis Date: 3/13/01
Date of Extraction: 3/13/01

3.14.01

| | | Peak Area | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Name | Sample Volume (L) | Diazinon | DDVP | Ethoprophos | Phorate/Dimethoate | Fonofos | Methyl Parathion | Malathion | Chlorpyrifos | Methidathion | Phosmet | Azinphos Methyl |
| Control MDL | 1.00 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.05µg/mL MDL | 1.00 | 40,642,652 | 49,418,537 | 50,505,582 | 104,336,768 | 57,052,203 | 50,504,232 | 40,318,689 | 38,967,552 | 39,722,693 | 36,258,974 | 38,133,560 |
| 0.05µg/mL MDL | 1.00 | 58,546,780 | 37,210,540 | 63,290,763 | 128,480,955 | 75,181,915 | 66,486,201 | 47,696,615 | 49,386,965 | 50,077,483 | 34,261,267 | 41,029,351 |
| 0.05µg/mL MDL | 1.00 | 64,272,690 | 42,802,477 | 71,723,524 | 143,288,323 | 78,621,604 | 64,581,297 | 55,855,903 | 55,731,917 | 54,092,766 | 41,777,483 | 46,037,019 |
| 0.05µg/mL MDL | 1.00 | 67,409,479 | 64,590,937 | 78,858,688 | 156,156,277 | 82,578,903 | 73,820,044 | 60,002,401 | 58,327,570 | 58,749,790 | 46,814,117 | 48,063,223 |
| 0.05µg/mL MDL | 1.00 | 54,406,910 | 52,815,647 | 66,047,692 | 127,350,150 | 66,734,795 | 61,606,442 | 49,866,997 | 49,258,800 | 50,735,463 | 42,353,579 | 38,553,591 |
| 0.05µg/mL MDL | 1.00 | 60,158,070 | 59,813,134 | 68,069,285 | 135,039,804 | 74,639,774 | 60,605,441 | 49,952,224 | 46,673,809 | 51,173,067 | 38,430,662 | 40,613,129 |
| 0.05µg/mL MDL | 1.00 | 61,625,627 | 57,898,141 | 71,435,356 | 137,173,293 | 73,078,477 | 62,992,089 | 52,995,353 | 51,025,832 | 52,546,742 | 41,427,283 | 46,005,808 |

| | | Calculated Conc. (µg/L) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Name | Sample Volume (L) | Diazinon | DDVP | Ethoprophos | Phorate/Dimethoate | Fonofos | Methyl Parathion | Malathion | Chlorpyrifos | Methidathion | Phosmet | Azinphos Methyl |
| 0.05µg/mL MDL | 1.00 | 0.036 | 0.038 | 0.040 | 0.041 | 0.042 | 0.045 | 0.041 | 0.039 | 0.040 | 0.048 | 0.052 |
| 0.05µg/mL MDL | 1.00 | 0.053 | 0.028 | 0.050 | 0.050 | 0.055 | 0.059 | 0.049 | 0.049 | 0.051 | 0.046 | 0.056 |
| 0.05µg/mL MDL | 1.00 | 0.058 | 0.033 | 0.057 | 0.056 | 0.058 | 0.057 | 0.057 | 0.055 | 0.055 | 0.055 | 0.062 |
| 0.05µg/mL MDL | 1.00 | 0.061 | 0.050 | 0.062 | 0.061 | 0.061 | 0.065 | 0.062 | 0.058 | 0.060 | 0.061 | 0.065 |
| 0.05µg/mL MDL | 1.00 | 0.049 | 0.041 | 0.052 | 0.050 | 0.049 | 0.055 | 0.051 | 0.049 | 0.052 | 0.055 | 0.053 |
| 0.05µg/mL MDL | 1.00 | 0.054 | 0.046 | 0.054 | 0.053 | 0.055 | 0.054 | 0.051 | 0.046 | 0.052 | 0.051 | 0.055 |
| 0.05µg/mL MDL | 1.00 | 0.056 | 0.045 | 0.057 | 0.054 | 0.053 | 0.056 | 0.054 | 0.051 | 0.054 | 0.054 | 0.062 |
| | Average = | 0.052 | 0.040 | 0.053 | 0.052 | 0.053 | 0.056 | 0.052 | 0.050 | 0.052 | 0.053 | 0.058 |
| | Std Dev = | 0.008 | 0.008 | 0.007 | 0.006 | 0.006 | 0.006 | 0.007 | 0.006 | 0.006 | 0.005 | 0.005 |
| | t Value = | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 |
| | MDL = | 0.025 | 0.024 | 0.022 | 0.020 | 0.020 | 0.020 | 0.021 | 0.019 | 0.019 | 0.016 | 0.016 |

3.14.01



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Analytical Data Set for P999W

## METHOD DETECTION LIMITS

California Department of Pesticide Regulation Study

Description: Method Detection Limits
Analysis Location: PTRL WEST, INC.
Analysis Method: GC/FPD using HP-17 GC Column
Analysis Date: 3/15/01
Date of Extraction: 3/13/01

| | | Peak Area | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Name | Sample Volume (L) | DDVP | Ethoprophos | Phorate | Diazinon | Fonofos | Dimethoate | Methyl Parathion | Chlorpyrifos | Malathion | Methidathion | Phosmet | Azinphos Methyl |
| Control MDL | 1.00 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.05µg/mL MDL | 1.00 | 52,799,878 | 68,486,920 | 63,368,212 | 58,750,909 | 72,430,396 | 74,667,421 | 59,041,658 | 43,794,209 | 46,404,950 | 52,635,286 | 45,033,631 | 41,847,448 |
| 0.05µg/mL MDL | 1.00 | 72,782,514 | 86,054,590 | 82,251,514 | 67,063,116 | 96,704,743 | 94,364,297 | 79,530,072 | 59,502,329 | 62,276,756 | 68,233,133 | 57,302,331 | 51,806,658 |
| 0.05µg/mL MDL | 1.00 | 63,976,930 | 86,186,240 | 81,246,986 | 69,019,011 | 95,801,665 | 95,418,222 | 80,787,081 | 59,716,515 | 60,394,130 | 68,511,212 | 60,782,611 | 50,542,227 |
| 0.05µg/mL MDL | 1.00 | 76,697,207 | 91,273,434 | 85,161,338 | 74,795,704 | 99,833,748 | 101,495,645 | 85,205,164 | 64,627,262 | 68,956,561 | 71,502,087 | 63,369,889 | 52,858,423 |
| 0.05µg/mL MDL | 1.00 | 65,773,394 | 78,382,479 | 74,388,291 | 61,099,410 | 81,535,391 | 83,926,994 | 73,746,672 | 55,736,284 | 56,874,382 | 63,505,665 | 57,239,340 | 45,135,280 |
| 0.05µg/mL MDL | 1.00 | 71,492,600 | 78,451,944 | 80,693,155 | 66,346,691 | 84,515,651 | 88,107,367 | 73,471,867 | 57,796,847 | 59,399,000 | 60,720,630 | 57,049,760 | 49,080,373 |
| 0.05µg/mL MDL | 1.00 | 74,608,604 | 77,328,708 | 77,667,727 | 65,044,439 | 83,214,306 | 83,630,838 | 72,273,723 | 56,573,244 | 58,525,718 | 64,332,888 | 51,822,323 | 51,892,038 |

| | | Peak Area | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Name | Sample Volume (L) | DDVP | Ethoprophos | Phorate | Diazinon | Fonofos | Dimethoate | Methyl Parathion | Chlorpyrifos | Malathion | Methidathion | Phosmet | Azinphos Methyl |
| 0.05µg/mL MDL | 1.00 | 0.033 | 0.044 | 0.043 | 0.047 | 0.044 | 0.046 | 0.043 | 0.040 | 0.041 | 0.046 | 0.045 | 0.049 |
| 0.05µg/mL MDL | 1.00 | 0.045 | 0.055 | 0.055 | 0.054 | 0.058 | 0.057 | 0.057 | 0.055 | 0.054 | 0.058 | 0.057 | 0.060 |
| 0.05µg/mL MDL | 1.00 | 0.040 | 0.055 | 0.054 | 0.055 | 0.058 | 0.058 | 0.058 | 0.055 | 0.052 | 0.058 | 0.060 | 0.058 |
| 0.05µg/mL MDL | 1.00 | 0.048 | 0.058 | 0.057 | 0.060 | 0.060 | 0.061 | 0.061 | 0.059 | 0.060 | 0.061 | 0.062 | 0.061 |
| 0.05µg/mL MDL | 1.00 | 0.041 | 0.050 | 0.050 | 0.049 | 0.050 | 0.051 | 0.053 | 0.051 | 0.049 | 0.054 | 0.057 | 0.053 |
| 0.05µg/mL MDL | 1.00 | 0.045 | 0.051 | 0.054 | 0.053 | 0.051 | 0.054 | 0.053 | 0.053 | 0.052 | 0.052 | 0.056 | 0.057 |
| 0.05µg/mL MDL | 1.00 | 0.046 | 0.050 | 0.052 | 0.052 | 0.050 | 0.051 | 0.052 | 0.052 | 0.051 | 0.055 | 0.052 | 0.060 |
| | Average = | 0.043 | 0.052 | 0.052 | 0.053 | 0.053 | 0.054 | 0.054 | 0.052 | 0.051 | 0.055 | 0.056 | 0.057 |
| | Std Dev = | 0.005 | 0.005 | 0.005 | 0.004 | 0.006 | 0.005 | 0.006 | 0.006 | 0.006 | 0.005 | 0.006 | 0.004 |
| | t Value = | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 | 3.143 | 4.143 |
| | MDL = | 0.016 | 0.015 | 0.015 | 0.013 | 0.018 | 0.017 | 0.019 | 0.019 | 0.018 | 0.016 | 0.017 | 0.017 |

3.16.01



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