## A Gas-Liquid Chromatographic Method for Measurement of Diazinon Residue in Pond Water

### INTRODUCTION

A method for determining diazinon [ O,O-Diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate ]in pond water is presented.

### PRINCIPLE AND APPLICATION

Diazinon is extracted from pond water (to which is added a saturated solution of sodium chloride) with dichloromethane which is subsequently dried through sodium sulfate, evaporated to dryness and dissolved in hexane. A gas-liquid chromatograph equipped with a thermionic detector operated in the nitrogen-specific mode measures the extracted residue and integrates the resulting peak. Linear regression analysis of diazinon peak areas for samples and reference standards permits calculation of each diazinon sample concentration.

### ANALYTICAL METHOD

#### Reagents

Dichloromethane, Fisher Optima, Reagent grade

Water, Burdick and Jackson, HPLC grade

Hexane, Burdick and Jackson, HPLC grade

Acetone, Burdick and Jackson, HPLC grade

Sodium chloride, Mallinckrodt, Reagent, A.C.S.

Sodium sulfate, Doe and Ingalls, Inc., Analytical Reagent

Diazinon, Lot No. S87-1185-1, 96.7% a.i., supplied by Ciba Geigy

#### Equipment

Balance, Ohaus Galaxy 160, four-place analytical balance

Flasks, volumetric, assorted sizes

Pipets, volumetric, assorted sizes

Separatory funnels, 500 mL

Glass funnels, assorted sizes

Glass wool, prewashed with dichloromethane

Roundbottom flasks, 500 mL

GC vials with crimp caps and Teflon-faced septa

Serum bottles, Wheaton, assorted sizes, with Teflon-lined lids and metal crimp caps

Syringes, Hamilton, assorted sizes

Rotary evaporator, Buchii Model R110, with vacuum pump, 40 °C water bath

**Detailed Procedure**

**I. Preparation of Stock Solution**

A. Diazinon (1 mg/mL)

1. Weigh 100 milligrams (a.i.) of diazinon on an analytical balance.
2. Transfer the diazinon to a 100-mL volumetric flask and dissolve to the mark with acetone.
3. Transfer the stock solution to a 100-mL amber serum vial and seal with a Teflon-lined crimp cap.
4. Store this stock solution in a refrigerator maintained at 4 °C.

**II. Control Sample Fortification**

A. Rinse all glassware with dichloromethane prior to fortification.

B. To each separatory funnel, add 250 mL of pond water.

C. Fortify each sample with diazinon by volumetric addition of dilutions of the primary stock solutions.

NOTE: The fortification levels produced in the control pond water samples for the method validation/recovery were 100, 10.0, 1.00, 0.500 and 0.100 ppb (three replicates at each level). An additional three pond water samples were left unfortified and utilized as control samples.

III. Extraction

A. Pond Water

1. Add 10 mL of an aqueous saturated sodium chloride solution to the sample.
2. Add 100 mL of dichloromethane to the 250 mL aqueous sample.
3. Shake the separatory funnel for 90 seconds and allow the phases to separate.
4. Drain the lower dichloromethane layer through approximately 30 grams of sodium sulfate (glass wool plug in glass funnel) into a 500-mL roundbottom flask.
5. Repeat steps 1-4, combining the dichloromethane extracts in the roundbottom flask.
6. Rinse the sodium sulfate with approximately 25 mL of dichloromethane and collect the rinse in the same flask.
7. Evaporate the sample to approximately 0.5 mL on a rotary evaporator.
8. Evaporate the remaining dichloromethane under a gentle stream of nitrogen.
9. Volumetrically pipet the requisite volume of reagent-grade hexane into the flask and swirl the flask in order to ensure complete dissolution of the diazinon residues.

NOTE: a) For the 0.100 ppb recovery samples a volume of 1 mL would yield a concentration of 25.0 µg/L.

b) The volume added for samples of unknown concentration would be such that the final concentration falls in the midrange of the standard curve.

10. Remove an aliquot of each solution and proceed to Section IV, Gas-Liquid Chromatography.

IV. Gas-Liquid Chromatography

A. Instrumental Conditions: Hewlett-Packard Model 5840 gas-liquid chromatograph equipped with Hewlett-Packard Model 7671A autosampler and thermionic detector.

| | |
|---|---|
| Column: | DB-17, 15 M x 0.53 mm ID with 1.0 µm film thickness (J & W Cat #125-1712) |
| Column Flowrate: | Helium @ 20 mL/minute |
| Detector: | Hydrogen @ 3.3-3.5 mL/minute |

| | |
|---|---|
| Air: | @ 80-90 mL/minute |
| Injector Temperature: | 250 °C |
| Column Temperature: | 170 °C (isothermal) |
| Detector Temperature: | N-P @ 275 °C |
| Chartspeed: | 0.3 cm/minute |
| Injection Volume: | 4 µL |
| Attenuation: | $2^5$ |
| Slope Sensitivity: | 0.20 |

C. Analysis

1. Prepare standard solutions containing diazinon. Standard solution concentrations used for the recovery study were 25.0, 50.0, 100, 300 and 500 µg/L.
2. Inject 4 µL of the 25.0 µg/L standard solution. Adjust the attenuation so that the peak signal results in at least a fifteen percent deflection from the baseline.
3. Inject 4 µL of each of the standards, document the peak areas, and determine the correlation coefficient of the line. Proceed to step 4 if the correlation coefficient is greater than or equal to 0.985.
4. Inject 4 µL of several samples.
5. After each set of samples, reinject 4 µL of each of the standards and document the peak areas.
6. Construct a standard curve for the analyte (using all standard results) by plotting peak area observed versus the concentration (µg/L) of the standard injected.
7. The standard linear regression analysis for diazinon is used to determine the concentration in each sample.
8. In order to determine the analytical result for each sample, the following equation is used:

Analytical Result (ppb) = A X D.F. / $d_s$

where:

Analytical Result = concentration of diazinon

| | |
|---|---|
| A = | concentration (µg/L) of sample from the regression analysis |
| D.F. = | dilution factor, ratio of the final volume (mL) of the sample to the initial volume (mL) of sample used |
| $d_s$ = | density of water (kg/L) |