Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Diazinon

MRID #: 414904-01

Matrix: Water

Analysis: GC/NPD

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Cover Sheet for

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DIAZINON
41-90 4-01

SPRINGBORN LABORATORIES, INC.
ENVIRONMENTAL SCIENCES DIVISION
CHEMISTRY DEPARTMENT

TITLE: A Gas-Liquid Chromatographic Method for the Measurement of Diazinon Residue in Pond Water

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ABSTRACT: A gas-liquid chromatographic (GC) method is described for the analysis of diazinon in pond water. The method employs a dichloromethane partition of the aqueous sample prior to analysis by GC utilizing nitrogen-specific detection. Recoveries of diazinon from pond water fortified in the range of 0.100 - 100 ppb resulted in a mean recovery of 105% with a recovery range of 82.3-140%. Control values were all < 0.0439 ppb.

DATE: July 18, 1989

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)

RESULTS AND DISCUSSION

Pond water samples were prepared which contained a variety of concentrations of diazinon. To each sample was added 10 mL of an aqueous saturated solution of NaCl. Each sample was then partitioned into dichloromethane, dried through sodium sulfate, rotary evaporated to approximately 0.5 mL, evaporated to dryness under nitrogen and dissolved in GC-grade hexane.

Recoveries from pond water fortified with diazinon at 100 ppb ranged from 92.7 to 98.7% with an average recovery of 95.6%; recoveries at 10.0 ppb ranged from 101 to 104% with an average recovery of 102%; recoveries at 1.00 ppb ranged from 82.3 to 103% with an average recovery of 92.8%; recoveries at 0.500 ppb ranged from 106 to 113% with an average recovery of 109%; recoveries at 0.100 ppb ranged from 117 to 140% with an average recovery of 126%. The minimum detectable level for diazinon was determined by linear regression analysis of the calculated value of one-half the mean of the peak areas of the lowest standard, resulting in an M.D.L. of less than 0.0439 ppb.

Linear regression analyses for the response of diazinon is shown in Figure 16A. Representative chromatograms of a diazinon standard, of an extracted diazinon pond water sample and a pond water control sample are shown in Figure 17A.

Table 19A. Analytical results for the recovery of diazinon from pond water.

Fortified Level (ppb)	Sample Volume (mL)	Level Found (ppb)	Percent Recovery (%)
100	250	92.7	92.7
100	250	95.4	95.4
100	250	98.7	98.7
10.0	250	10.1	101
10.0	250	10.1	101
10.0	250	10.4	104
1.00	250	0.823	82.3
1.00	250	0.929	92.9
1.00	250	1.03	103
0.500	250	0.563	113
0.500	250	0.537	107
0.500	250	0.530	106
0.100	250	0.117	117
0.100	250	0.120	120
0.100	250	0.140	140
Control	250	< 0.0439	NA
Control	250	< 0.0439	NA
Control	250	< 0.0439	NA

Average Recovery: 1..5% ± 13.7.

Theoretical minimum detectable concentration is < 0.0439 ppb for a 250-mL sample.

Figure 16A. **The linear regression analysis for diazinon standards used in the pond water recovery study.**

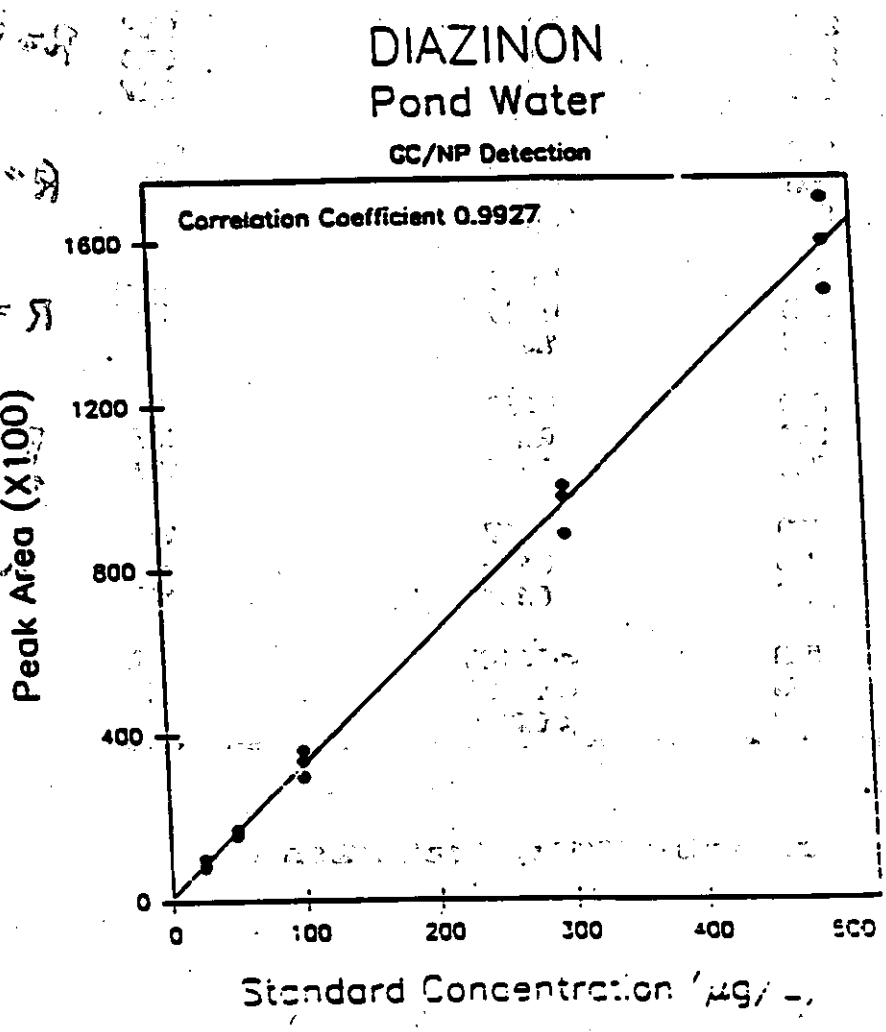


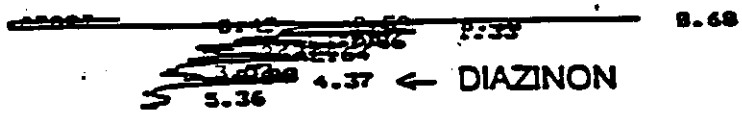
Figure 17A. Representative GC chromatograms of a diazinon standard (upper), of an extracted pond water sample (middle) and a control pond water sample (lower).

HP RUN # 19 JUN/22/89 TIME 18:26:44
BOTTLE 19
AREA %

Standard
500 ug/L

RT	AREA	AREA %
4.38	159388	100.000

DIL FACTOR: 1.0000 E+ 0

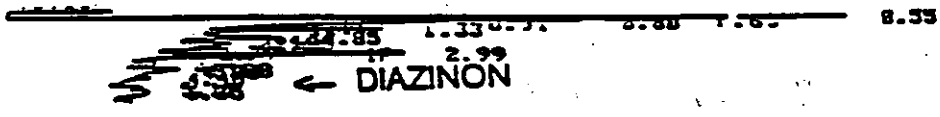


HP RUN # 23 JUN/22/89 TIME 18:58:43
BOTTLE 23
AREA %

Recovery
0.100 ug/L
A ug/mL

RT	AREA	AREA %
3.53	215	1.284
3.98	1727	10.314
4.04	1864	11.132
4.37	10296	61.451
5.36	2649	15.820

DIL FACTOR: 1.0000 E+ 0



HP RUN # 27 JUN/22/89 TIME 19:31:09
BOTTLE 27
AREA %

Recovery
Control
B

RT	AREA	AREA %
3.42	1456	18.383
3.98	2244	16.773
4.38	1489	18.531
4.48	2786	28.226
[illegible]	1636	12.228
[illegible]	3928	29.359

DIL FACTOR: 1.0000 E+ 0

6.0 APPENDIX III - METHOD VALIDATION: DIAZINON IN SEDIMENT