Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Esfenvalerate (Asana)

MRID #: 417880-01

Matrix: Water

Analysis: GC/ECD

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ABSTRACT

Twenty-four samples of spray tank mixtures from six application times of the cypermethrin mesocosm were analyzed for cypermethrin for independent laboratory confirmation of spray application mixtures. Water samples were prepared and analyzed as described by FMC method number RAN-0226 with the exception that a 0.53 mm id fused silica column was used in place of the packed column system described in the method for GC analysis. Simultaneously with sample analysis, two laboratory fortifications and a laboratory control were prepared and analyzed to ensure analytical accuracy. Sample fortifications did not vary more than ±20% from their nominal values while laboratory controls did not exhibit any interferences with the analyte. Field control samples from each application time did not exhibit any interferences with the analyte. Concentrations of cypermethrin ranged from a maximum of 26.55 ppm to a minimum of 18.37 ppm in spray tank samples.

INTRODUCTION

Twenty-four samples of spray tank mixtures from six application times were analyzed for cypermethrin for independent laboratory confirmation of spray application mixtures from the cypermethrin mesocosm study. Water samples were prepared and analyzed as described by FMC method reported in RAN-0226 with the exception that a 0.53 mm i.d. fused silica column was used in place of the packed column system described in the method for GC analysis.

MATERIALS AND METHODS

MATRICES:

Twenty-four spray tank mixture samples from FMC Mesocosm study A89-2847 were received at PTRL-West on December 10, 1990. Samples consisted of six sets of four samples, with each set composed of a field control, recovery spike, initial tank and tank end aliquots. All samples were received frozen and remained frozen until analysis.

REAGENTS:

Ethyl acetate, Fisher Scientific, Optima Grade
Ethanol, Gold Shield Chemical, 200 proof
Inert ingredients mixture of Ammo 2.5 EC Insecticide, FMC Corporation

STANDARDS:

Standards of cis- and trans-cypermethrin were received at PTRL-West on December 10, 1990 and January 29, 1991. Stock solutions of 1 mg/ml and 10 mg/ml total cypermethrin were prepared in ethanol to be used for dilute standard preparation and sample fortifications. Analytical reference standards were returned to sponsor after preparation of stock solutions. Stock solutions were stored at <0°C until used for sample or standard preparation. Diluted standard solutions of 0.025, 0.05, 0.1, 0.2 and 0.4 ng/µl were prepared in ethyl acetate for calibration and linearity standards. These were stored at <0°C until used for analysis.

ANALYTICAL METHOD:

Frozen aqueous samples were thawed by standing at room temperature overnight. Once thawed, the samples were vigorously shaken for approximately 15 seconds to thoroughly mix the sample.

The laboratory control was prepared by the adding 58 µl of the Ammo 2.5 EC Inert Ingredients to 1 liter of tap water in a stoppered graduated cylinder and shaking for 15 seconds to produce a homogeneous solution. Laboratory control (1 liter tap water with 58µl inerts) was prepared on the following dates: January 29 (set #1), February 7 (sets #2 and 3), February 8 (sets #4 and 5), and February 13 (set #6). Two 200-ml aliquots were removed to 250-ml stopped graduated cylinders and a third aliquot removed for the laboratory control sample. One 200-ml aliquot was fortified with 200 µl of 10 mg/ml cypermethrin stock solution and the second with 600 µl to produce solutions of 10 and 30 ppm cypermethrin respectively.

One-milliliter aliquots were removed from the samples, laboratory control and laboratory prepared fortifications and added to 190 ml of ethyl acetate in stoppered 250-ml graduated cylinders. The volume was adjusted to 200 ml with ethyl acetate and mixed thoroughly by shaking 15 seconds. Aliquots of the diluted samples and laboratory prepared samples were placed into GC auto-sampler vials for analysis.

GC ANALYSIS:

Samples were analyzed by the instrumentation outlined below. Using these parameters, a retention time of approximately 3.4 minutes was obtained for the analyte.

The standard eluted as a single broad peak even though composed of more than a single isomer. Standard and sample injection volumes were held constant. Samples were injected in the following order: 2 ethyl acetate blanks, linearity standards, 0.1 ng/µl calibration standard, sample, sample, 0.1 ng/µl calibration standard, sample, sample etc. Samples were bracketed by calibration standards at both the beginning and end of the run. If the variability of the calibration standard between runs was greater than ±20%, the sample set was reanalyzed. In addition, if the linear regression of the standards yielded an r^2 of <0.95, the sample set was reinjected or reanalyzed.

INSTRUMENTATION: Hewlett Packard 5980A Gas chromatograph equipped with electron capture detector, 3396A integrator, 7376A Autosampler or equivalent

COLUMN: DB-17 fused silica column, 15 m x 0.53 mm id, 1.0 µm film thickness, (J&W Scientific)

TEMPERATURES:

Injector A: 250°C
Detector B (ECD): 300°C
Oven Temperature: 240 °C (isothermal)

GASES:

Carrier Gas =N2 @ 50 ml/min
Makeup Gas =Methane (5%) in Ar @ 50 ml/min

INJECTION VOLUME = 2 µl

Example chromatograms as shown in Appendix B.

QUANTITATION:

The calculations were performed by the computer program Microsoft Excel™, on a Macintosh SE computer. The gas chromatographic peak height and external calibration standards were used to calculate the amount of cypermethrin in a sample. For all analyses, the calibration factor (CF) or [(response/ng compound injected)$^{-1}$] was calculated by

CF = ng injected standard/standard peak height

This response factor was updated after the injection of each calibration standard by averaging with the previous response factors. The updated calibration factor was used to calculate the residues in the samples using the formula:

$$ppm\ (ng/mg) = CF \times [sample\ peak\ height] \times DF$$

where DF is the dilution factor representing l/mg of sample injected. A sample calculation is shown below from Set #3.

Run #1702 was the 10 ppm fortified sample with a peak height of 786

CF average = 1.334×10^4

DF= 1/0.01 mg= 100/mg

ppm = 1.334×10^4 ng/peak height x 786 peak height x 100/mg = 10.48 ppm

These results are shown in Table II and Appendix C.

RESULTS AND DISCUSSION

RESIDUES:

Of the six field control samples, none were found to have any residues of cypermethrin. Field recovery spikes ranged in concentration from 21.34 to 29.01 ppm. Initial tank aliquots ranged in concentration from 18.68 to 26.55 ppm and in general were slightly greater than the tank end concentrations ranging from 17.60 ppm to 22.73 ppm.

RECOVERIES:

Recoveries for laboratory prepared fortifications ranged from a minimum of 84% for set #2, 10 ppm fortification to a maximum of 120% for set #6, 10 ppm fortification. Recoveries were within the protocol limits of 80 and 120%. Lab control samples were not found to have any interferences with the analyte of interest.

CONCLUSIONS

Samples of tank spray mix prepared for pond application in FMC's cypermethrin mesocosm study were analyzed by PTRL-West for independent laboratory concentration confirmation. Recoveries for laboratory prepared samples were within accepted limits and control samples, both field and laboratory were not found to have any interferences with

the analyte when analyzed by gas chromatography. The method was modified in that a DB-17, 0.53 mm fused silica column was used for GC analysis in place of the recommended packed OV-17 column with no significant difference in retention time or sensitivity.

Table I: Calculated Concentrations of Cypermethrin in Spray Tank Mixtures

Study Day	Sample Number	Date of Analysis	Sample Type	Amount Cypermethrin Found (ppm)
Day 35	318B	February 13, 1991	Control	0.00
	310A		Recovery Spike	25.84
	320B		Tank Inital	26.55
	321B		Tank End	21.33
Day 42	1068B	February 8, 1991	Control	0.00
	1054B		Recovery Spike	21.34
	1064B		Tank Inital	18.68
	1066B		Tank End	17.60
Day 49	2142B	February 12, 1991	Control	0.00
	2132B		Recovery Spike	29.01
	2144B		Tank Inital	19.62
	2146B		Tank End	18.37
Day 56	2718B	February 11, 1991	Control	0.00
	2710B		Recovery Spike	24.64
	2720B		Tank Inital	23.30
	2722B		Tank End	22.73
Day 63	3309B	February 11, 1991	Control	0.00
	3306B		Recovery Spike	22.80
	3271B		Tank Inital	19.21
	3272B		Tank End	22.13
Day 70	3862B	February 14, 1991	Control	0.00
	3856B		Recovery Spike	23.81
	3863B		Tank Inital	23.28
	3864B		Tank End	20.06

Table II: Recoveries of Cypermethrin from Laboratory Prepared Fortifications

Set Number	Fortification Level (ppm)	Calculated Concentration (ppm)	% Recovery
Set 1	Lab Control	0.00	NA*
	10	10.31	103
	30	31.85	106
Set 2	Lab Control	0.00	NA
	10	8.37	84
	30	27.25	91
Set 3	Lab Control	0.00	NA
	10	10.48	105
	30	31.16	104
Set 4	Lab Control	0.00	NA
	10	10.73	107
	30	31.16	102
Set 5	Lab Control	0.00	NA
	10	10.07	101
	30	27.16	91
Set 6	Lab Control	0.00	NA
	10	12.00	120
	30	33.11	110

*: NA = Not Applicable

Average % Recovery 102

Standard Deviation ±9.6

APPENDIX A: Protocol and Protocol Deviations for PTRL-Project #275W