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.

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