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Method #: 7.0
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Determination of Bifenthrin in Water by GC/ECD

Scope: This method is for the determination of bifenthrin in water. The reporting limit of this method is 0.05 ppb.

Principle: The water is extracted with ethyl acetate. The extract is then dried with sodium sulfate. The dried extract is concentrated and analyzed by gas chromatography with an electron capture detector (ECD).

Reagents, Equipment and Instrument:

Reagents:

1. Bifenthrin, CAS# 82657-04-3, 1.0 mg/mL in acetone, obtained from CDFA Standard Repository (Center for Analytical Chemistry, California Department of Food and Agriculture)
2. Ethyl acetate, pesticide residue grade
3. Sodium sulfate, anhydrous, granular, ACS 10-60 mesh

Equipment:

1. Separatory funnels, 1000 mL
2. Beakers, 600 mL
3. Boiling flasks, flat-bottomed, 24/40 joints, 500 mL
4. Rotary evaporator, Büchi-Brinkmann, Model RE 111
5. Graduated conical test tubes, 15 mL
6. Nitrogen evaporator, Organomation, Model 112
7. Vortex mixer, Fisher Scientific, Model Vortex-Genie 2

Instrument:

1. GC: Hewlett Packard 5890 Series II gas chromatograph with ECD
2. Column: HP-1, 30 m x 0.53 mm x 2.65um

Analysis:

Sample Extraction:

1. Remove samples from refrigerated storage and allow them to come to room temperature (± 5 °C).
2. Shake each sample, weigh out 500 ± 1 grams or record sample weight. Place this aliquot into a 1-liter separatory funnel.
3. Extract samples by adding 120 mL of ethyl acetate and shaking vigorously for two minutes. **Vent frequently to relieve pressure.**
4. After the layers have separated, drain the aqueous layer into a 600-mL beaker.
5. Pour the organic layer from the top of the separatory funnel into a 500-mL boiling flask through a funnel filled with 20 g of anhydrous sodium sulfate.
6. Transfer the aqueous layer back to the separatory funnel.
7. Repeat steps 3 through 6 two more times with 100 mL of ethyl acetate. Combine the ethyl acetate extract.
8. Rinse the sodium sulfate twice with 20 mL of ethyl acetate and combine in the flask.
9. Concentrate the extract to ~ 2 mL on a rotary evaporator using 50 °C water bath and a vacuum of 23 inches Hg.
10. Transfer the concentrated extract into a calibrated conical test tube.
11. Rinse the flask twice with 2 mL of ethyl acetate each and combine the extract.
12. Place extract on a nitrogen evaporator with a 45 °C water bath and evaporate to 1.0 mL under a gentle stream of nitrogen.
13. Vortex for about 15 seconds and transfer the contents into an autosampler vial for analysis.

Instrument Conditions:

Primary analysis:

Instrument: Hewlett Packard 5890 Series II gas chromatograph with ECD, a 7673 autosampler and HP 3365 Series II ChemStation (Version A.03.21)
Column: HP-1, 30 m x 0.53 mm x 2.65 µm
Injector: 220 °C
Detector: 320 °C
Oven temperature program: Initial 120 °C, held 1 minute
Rate 20 °C/minute
Final 280 °C, held 15 minutes
Volume injected: 2 µL
Retention Time: approximately 15.7 ± 0.1 minutes

Confirmation analysis:

Instrument: Hewlett Packard 6890 Series gas chromatograph with mass selective detector (MSD) and HP ChemStation (Version B.02.06)
Column: HP-5MS, 30 m x 0.25 mm x 0.25 µm
Injector: 250 °C
Detector: 280 °C

Confirmation analysis: continued

Oven temperature program: Initial 70 °C, held 1 minute
Rate 20 °C/minute
Final 260 °C, held 10 minutes

SIM parameters: 165, 166, 181

Volume injected: 1 μL

Retention Time: approximately 13.9 ± 0.1 minutes

Calculations:

$$ppb = \frac{(\text{sample peak ht.})(\text{response factor, } \eta g)(\text{sample final vol., mL})(1000\mu L/mL)}{(\text{sample vol. injected, } \mu L)(\text{sample wt., g})}$$

$$\text{where: response factor } (\eta g) = \frac{\Sigma[(\text{std. conc.}_n, \eta g/\mu L)\ (\text{std. vol. injected, } \mu L)/\ (\text{std. peak ht.}_n)]}{n}$$

n = number of standards

Method Performance:

Quality Control:

1. A 4-point calibration curve of 0.02, 0.05, 0.1, and 0.2ηg/μL bifenthrin was obtained at the beginning and the end of each set of samples for calculating the response factor.
2. Each sample shall be injected two times to insure reliability of the analysis. If the signal of a sample is greater than that of the highest standard in the calibration curve, dilute the sample. Re-inject the diluted sample together with standards twice more. A sample set is usually comprised of 12 ~ 14 samples, a blank and a spike.

Method Detection Limit (MDL):

Method Detection Limit (MDL) refers to the lowest concentration of analyte that a method can detect reliably in either a sample or a blank. To determine the MDL, spike 7 samples, 500 ± 1 g of background water each, with 0.1 ppb of bifenthrin for the surface water and 0.2ppb of bifenthrin for the well water and process each through the entire method along with a blank. The standard deviation was computed from the 7 results (ppb). The MDL was computed as follows:

$$MDL = t_{(n-1,\ 1-\alpha\ =\ 0.99)}S$$

Where: $t_{(n-1,\ 1-\alpha\ =\ 0.99)}$ = the student "t" value for the 99% confidence level with n-1 degrees of freedom (for seven replicates, t = 3.143 with 6 degrees of freedom)

n = the number of replicates

S = the standard deviation obtained from replicate analysis

The results for the standard deviations and MDL are in Appendix, Table 1and 2.

Reporting Limit (RL):

Reporting Limit (RL) refers to level above which quantitative results may be obtained. In this method the RL is set at 0.05 ppb for bifenthrin.

Recovery Data:

In surface water, preparing five sets of method validation samples. Each set contained a blank and four levels of spikes. In well water, preparing three sets of method validation samples. Each set contained a blank and three levels of spikes. The background water (American River water or well water) was obtained from Department of Pesticide Regulation. Each set was extracted by a different person or on separate days. Recovery of bifenthrin is shown in Appendix, Table 3 and 4.

Discussion:

Starting from the beginning, both methylene chloride and ethyl acetate were successfully developed for extraction. Due to environmental concern, we decided to extract residue using ethyl acetate. When we analyzed the samples, a column of HP-5, 30 m x 0.53 mm x 2.65 um was used for analysis because the HP-1 column was not available. Bifenthrin was detected at 9.2 ± 0.1 minutes with an isotherm 280 °C temperature. The recovery of the spiking was 84.4% and the positive result was confirmed with MSD. Therefore, the HP-5 column could also be used in this method.

References:

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Appendix: Table 1. Bifenthrin Spike Results (ppb) for MDL Determination in surface water

0.1ppb Spike #	**Bifenthrin** (ppb)
1	0.0986
2	0.0929
3	0.0855
4	0.0895
5	0.0811
6	0.103
7	0.119
S =	0.0127 ppb
MDL = 3.143 x S =	0.0399 ppb

Table 2. Bifenthrin Spike Results (ppb) for MDL Determination in well water

0.1ppb Spike #	**Bifenthrin** (ppb)
1	0.206
2	0.201
3	0.209
4	0.194
5	0.192
6	0.190
7	0.215
S =	0.00945 ppb
MDL = 3.143 x S =	0.0297 ppb

Table 3. Bifenthrin Method Validation Results and Recovery in surface water

	Bifenthrin	
Spike Level (ppb)	Result (ppb)	Recovery (%)
0.1	0.0965	96.5
	0.104	104
	0.0876	87.6
	0.125	125
	0.0940	94.0
5.0	4.83	96.6
	5.30	106
	4.54	90.8
	5.15	103
	5.11	102
20	18.0	90.0
	19.4	97.0
	15.8	79.0
	14.8	74.0
	18.4	92.0
50	45.4	90.8
	50.3	101
	47.1	94.2
	47.1	94.2
	49.0	98.0

Table 4. Bifenthrin Method Validation Results and Recovery in well water

	Bifenthrin	
Spike Level (ppb)	Result (ppb)	Recovery (%)
0.1	0.0857	85.7
	0.0932	93.2
	0.0797	79.7
1.0	0.792	79.2
	0.821	82.1
	0.758	75.8
10	8.79	87.9
	8.61	86.1
	8.15	81.5