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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ENVIRONMENTAL CHEMISTRY SECTION
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November 24, 1993

MEMORANDUM

SUBJECT: Baythroid® (Cyfluthrin) Method Evaluation - Report No. ECM003E1

FROM: Aubry E. Dupuy, Jr., Chief Aubry E. Dupuy Jr.
BEAD/ACB/Environmental Chemistry Section

TO: Henry M. Jacoby
EFED/Environmental Fate and Groundwater Branch (7507C)

THRU: Donald A. Marlow, Chief
BEAD/Analytical Chemistry Branch (7503W)

The EFED/Ecological Effects Branch has requested an Environmental Chemistry Method Validation on Cyfluthrin (Baythroid®) residues in water and sediment. The analytical methods are included in a report "Assessment of the Potential Ecological/Biological Effects of Baythroid® (Cyfluthrin) utilizing Artificial Pond Systems", submitted by the Agricultural Chemicals Division of Mobay Corporation. This report (ECM003E1) discusses the lab evaluation data we obtained for Baythroid® (Cyfluthrin) in sediment.

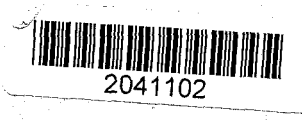
The report includes a summary, the analysis performance results in terms of precision, accuracy and experimental details including linearity curves, representative chromatograms and example calculations.

The fortification levels, which include the limit of quantitation (LOQ), were 5.0, 10.0 and 50.0 parts-per-billion (ppb). Triplicate analyses were performed on fortified samples and sample blanks.

If you have questions concerning the reports, please contact Henry Shoemaker at 601 688-1222 or Aubry Dupuy at 601-688-3212.

cc: Danny McDaniel, QA Officer
BEAD/ACB/ECS

Henry Shoemaker, Chemist
BEAD/ACB/ECS



Environmental Chemistry Method Validation Report Number ECM0003E1
Cyfluthrin (Baythroid™) in Sediment

Environmental Chemistry Section
Analytical Chemistry Branch
Biological and Economic Analysis Division

September 30, 1993

Prepared by: Henry Shoemaker 11/17/93
Henry Shoemaker, ECS Chemist

Reviewed by: Danny McDaniel 11/17/93
Danny McDaniel, QA Coordinator

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Part I
Summary and Conclusions

We have completed an Environmental Chemistry Method Validation on Cyfluthrin (Baythroid™) in sediment. This method submitted by the Agricultural Chemicals Division of Mobay Corporation appears to be suitable to gather residue data for Cyfluthrin from 10 parts per billion (ppb) to at least 50 (ppb) in sediment.

The analytical method involves extraction of the sediment matrix by stirring with acetone and transferring to acetonitrile and then hexane by roto-evaporation. The resultant extract is analyzed by Electron Capture Gas Chromatography. The fortification levels were at 5.0, 10.0, and 50.0 parts per billion (ppb) with triplicate analyses at each level.

The Method Limit of Detection (LOD) was 5.0 ppb and Limit of Quantitation (LOQ) was 10.0 ppb. Recoveries for Cyfluthrin in sediment at the (LOD) ranged from 70% to 118% with a mean of 91.3% and relative standard deviation (RSD) of 26.6%. Recoveries for Cyfluthrin at the (LOQ) and above ranged from 83% to 93% with a mean of 87.3% and relative standard deviation (RSD) of 4.7%.

Since there is no clean-up and the acetone would extract many other contaminants, the limit of detection of Cyfluthrin may be compromised in some samples. The (LOD) and (LOQ) may have to be adjusted for certain highly contaminated samples.

Part II
Analytical Results
EPA Recoveries of Cyfluthrin in Sediment

Sample	Added(ppb)	Found(ppb)	%Recovered	Mean	SD	RSD
Blank 1	0	0				
S-24	5.0	5.94	118			
S-25	5.0	3.52	70.4			
S-26	5.0	4.28	85.6			
				91.3%	24.3	26.6%
Blank 2	0	0				
S-27	10.0	9.00	90.0			
S-28	10.0	8.86	88.6			
S-29	10.0	8.34	83.4			
				87.3%	3.5	4.0%
Blank 3	0	0.3				
S-30	50.0	42.9	85.8			
S-31	50.0	46.7	93.4			
S-32	50.0	41.4	82.8			
				87.3%	5.5	6.3%

Part III
Experimental Details

Liquid-Solid Extraction

1. Before extraction, the sample is homogenized with a teflon or stainless steel spatula and a sample for dry weight analysis is removed from all samples if the final calculation is to be based on sediment dry weight.

2. 50 grams of sediment sample is weighed into a 225 ml amber glass jar. 50 ml of acetone is added to the sample in the jar and a stir bar is added. The sample is tightly capped and stirred at moderate speed for 15 minutes.

3. The extract is vacuum filtered into a 250 ml evaporating flask through a Buchner funnel lined with a disc of Whatman #41 filter paper and a 5-10 mm bed of Celite 545 which has been previously rinsed with acetone. The sample jar is rinsed with an additional 50ml of acetone and this fraction is filtered and combined with the first acetone extract. The acetone is allowed to evaporate in the roto-evaporator until water remains.

4. 125 ml of acetonitrile is added to the water fraction and the extracts are evaporated to dryness by gentle rotary evaporation. If the water was not totally evaporated, an additional 30 ml of acetonitrile is added to complete the evaporation of the water. 10 ml of hexane is added to dissolve the residues and the flask is sonicated for 2-3 minutes.

5. The hexane extract is carefully removed with a Pasteur pipet. Part of the sample is transferred directly to an amber autosampler vial for gas chromatographic analysis and the remainder is transferred to a labeled 8 ml amber storage vial and stored at -15 ± 10°C.

Analysis of Extracts

The extracts and standards are analyzed by high resolution gas chromatography using a 5 meter x 0.53 mm fused silica column. The non-polar methylsilicone stationary phase is 2.65 um thick. Samples are grouped by dose level along with appropriate standards. On-column injection is used with an injection volume

of two microliters. The injections are made using the auto injection system on the HP5890 gas chromatograph. In all cases, the injection volume of standards and samples must be identical. The oven is temperature programmed to allow the Cyfluthrin to migrate through the analytical column in a reasonable time. The chromatograms are stored on computer disk and printouts generated at the end of each analysis.

Calculations

Calculation of Cyfluthrin concentration in the sample is by direct comparison to the standards which were injected immediately before and after the sample. The analyte concentration in one milliliter of the sample extract may be calculated as follows:

$$\frac{\text{Conc. of Standard (ng/ml)}}{\text{Avg.Peak Area}} = \frac{\text{Conc. of Extract (ng/ml)}}{\text{Peak Area}}$$

The analyte concentration ng/g (ppb) in the original sample may be calculated as follows:

$$\text{Cyfluthrin Concentration in Sample (ng/g)} = \frac{\text{Extract Conc.(ng/ml)} \times \text{Extract Vol(ml)}}{\text{Original Sample Wt.(gram)}}$$

NOTE If concentration based on dry weight is needed, replace the original sample weight with its dry weight equivalent.

NOTE While this method of calculation is valid for samples of known fortification levels, it would not be suitable for samples of unknown quantities of Cyfluthrin. Calculations using a standard calibration curve would be more appropriate.

Source of Analytical Reference Standard

A standard of 1 gram of Cyfluthrin (Baythroid™) was received from The Agriculture Division of Miles, Inc., Kansas City, Missouri. In its neat state, Cyfluthrin is extremely difficult to routinely homogenize and manipulate because of its extremely thick syrupy nature. Therefore, the standard was supplied as a 50.2% Cyfluthrin solution in Cyclohexanone.

Source of Sample Matrix

Sediment was collected locally from the Pearl River near Stennis Space Center. Sediment was collected in wide mouth jars which had been previously rinsed with acetone and hexane then allowed to air dry. Sediment was refrigerated and brought to room temperature before use in the method trial.

Instrumentation for Quantitation

1. Gas Chromatograph - Hewlett-Packard Model 5890 with on-column capillary inlet, electron capture detector, and automatic injection system.

2. GC Column - 5 meter x 0.53 mm I.D. fused silica megabore capillary column with a 2.65 mm film of methylsilicone stationary phase (HP-1) and a 1 meter x .53 mm un-coated gap attached with a glass connector.

3. Carrier Gas - Hydrogen, make-up gas, methane/argon

4. GC Parameters

Oven Program
Starting Temp - 170°C for .5 minutes
Ramp - 15°C per minute
Final Temp - 240° C for 1 minute
Detector Temp - 325° C
Electrometer - Range 2, Attenuation 7
Inlet Head Pressure - 7 psi
Injection Volume - 2 microliters
Cyfluthrin Retention Time - (3.66± .02) minutes

Modification of Method

We made a slight change in the oven program. The registrant used a ramping rate of 40°C per minute to a final temperature of 290° C. A ramping rate of 15C per minute to a final temperature of 240° C gave us good results with a much more stable base line on our particular instrument.

Chromatograms and Linearity Check

Chromatogram #1 - Method Blank, Unfortified Sediment S-22

Chromatogram #2 - Method Blank, Unfortified Sediment S-23

Chromatogram #3 - Cyfluthrin Standard, 25 ng/ml

Chromatogram #4 - Sediment S-24, Fortified at 5 ppb.

Chromatogram #5 - Cyfluthrin Standard, 50 ng/ml.

Chromatogram #6 - Sediment S-27, Fortified at 10 ppb.

Chromatogram #7 - Cyfluthrin Standard, 250 ng/ml.
Injection Time: May 27, 12:12 p.m.

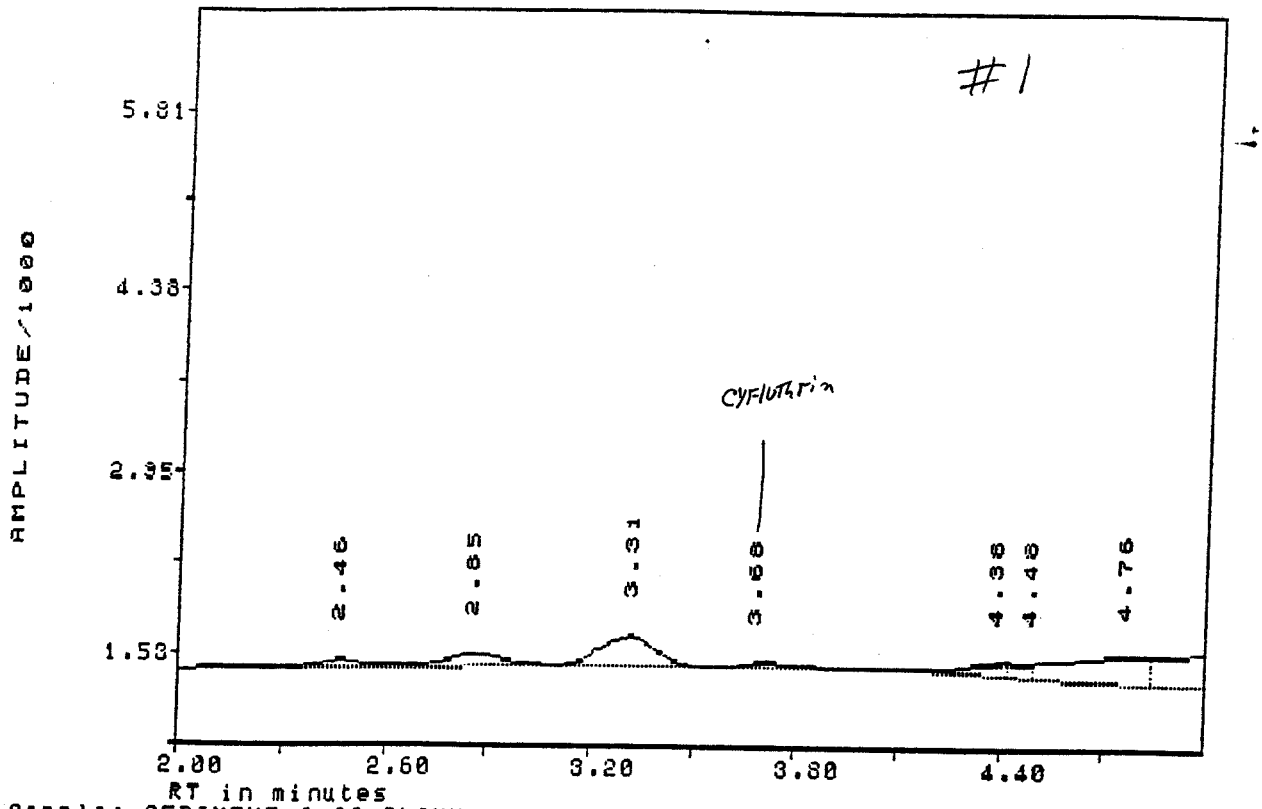
Chromatogram #8 - Sediment S-32, Fortified at 50 ppb.
Injection Time: May 27, 11:51 a.m.

Chromatogram #9 - Cyfluthrin Standard, 250 ng/ml
Injection Time: May 27, 11:40 a.m.

#10 - Example Calculation for Sample S-32

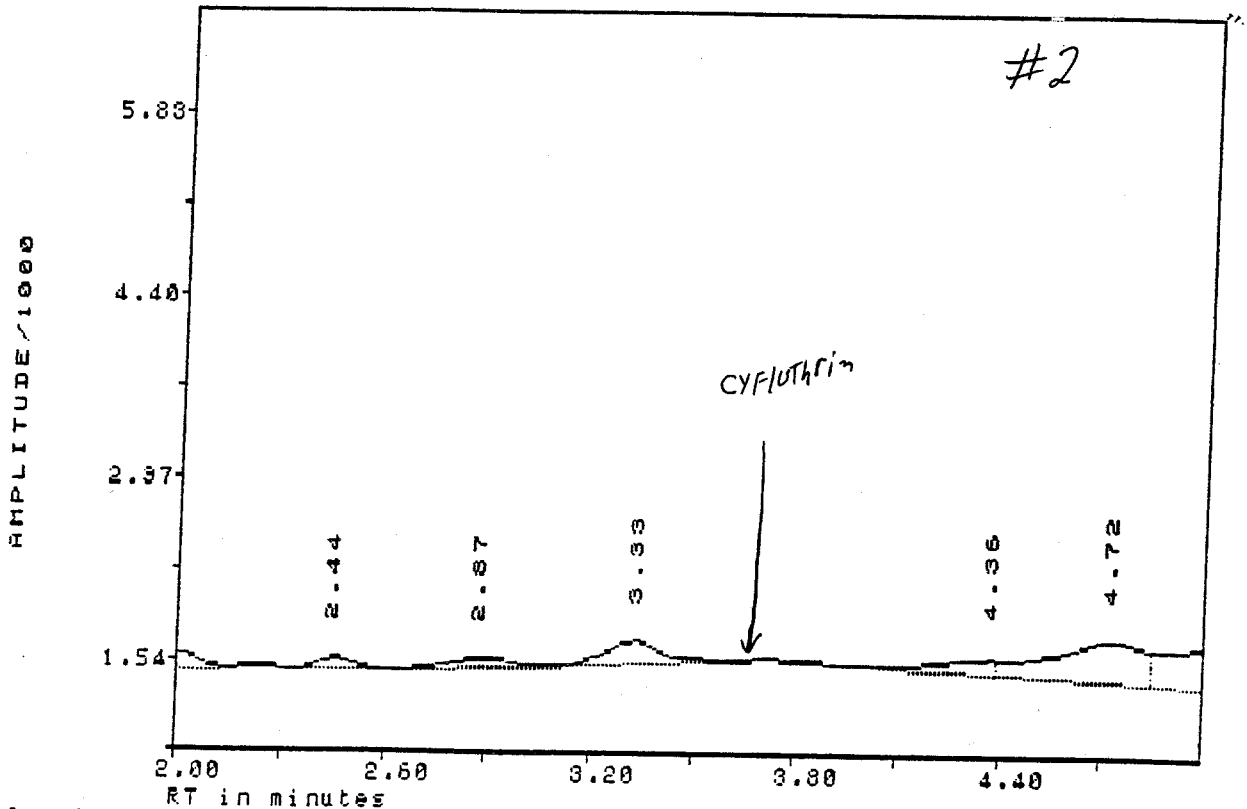
#11 - Linearity Check for Cyfluthrin (Baythroid™)

#1



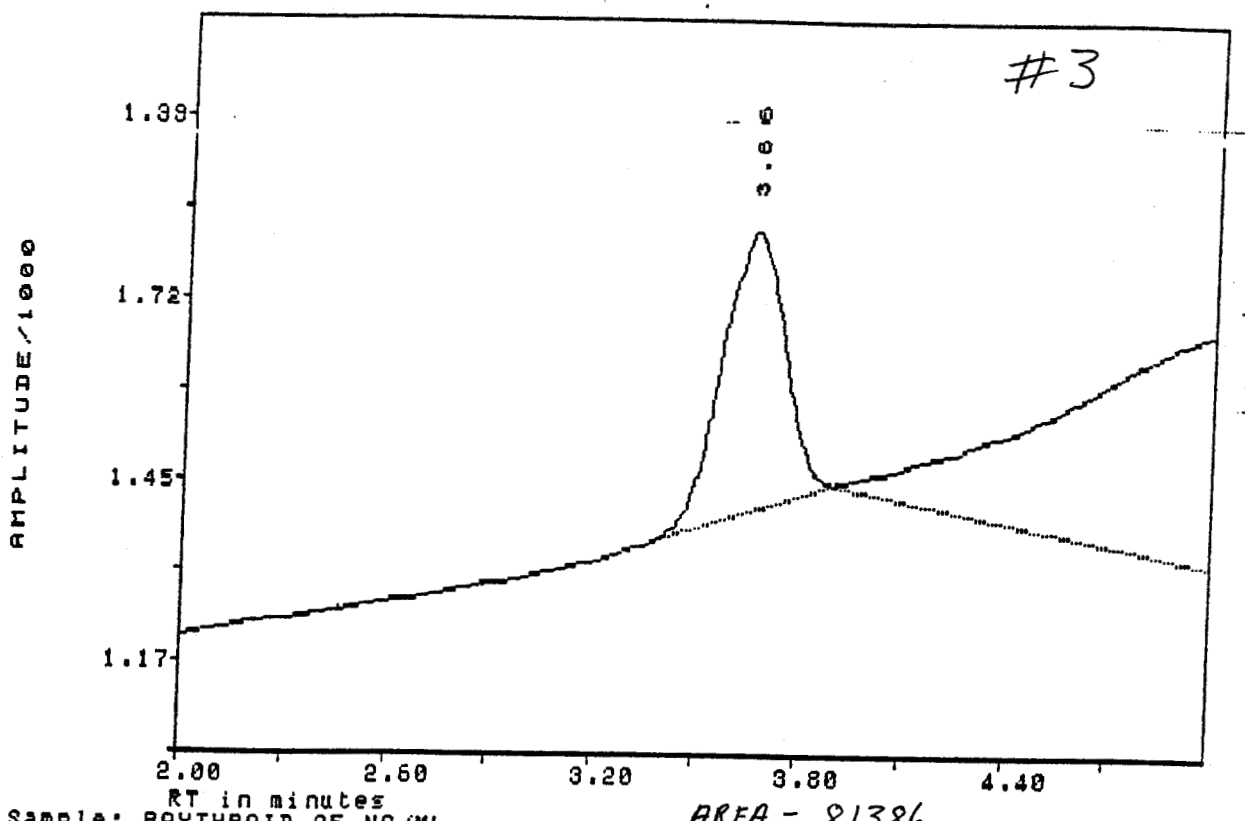
Sample: SEDIMENT S-22 BLANK
Method: /DATA/BAY.MTH
Result: BAY203
Injected on Thu May 27, 1993 8:05:15 am

#2



Sample: SEDIMENT S-23 BLANK
Method: /DATA/BAY.MTH
Result: BAY204
Injected on Thu May 27, 1993 8:16:00 am

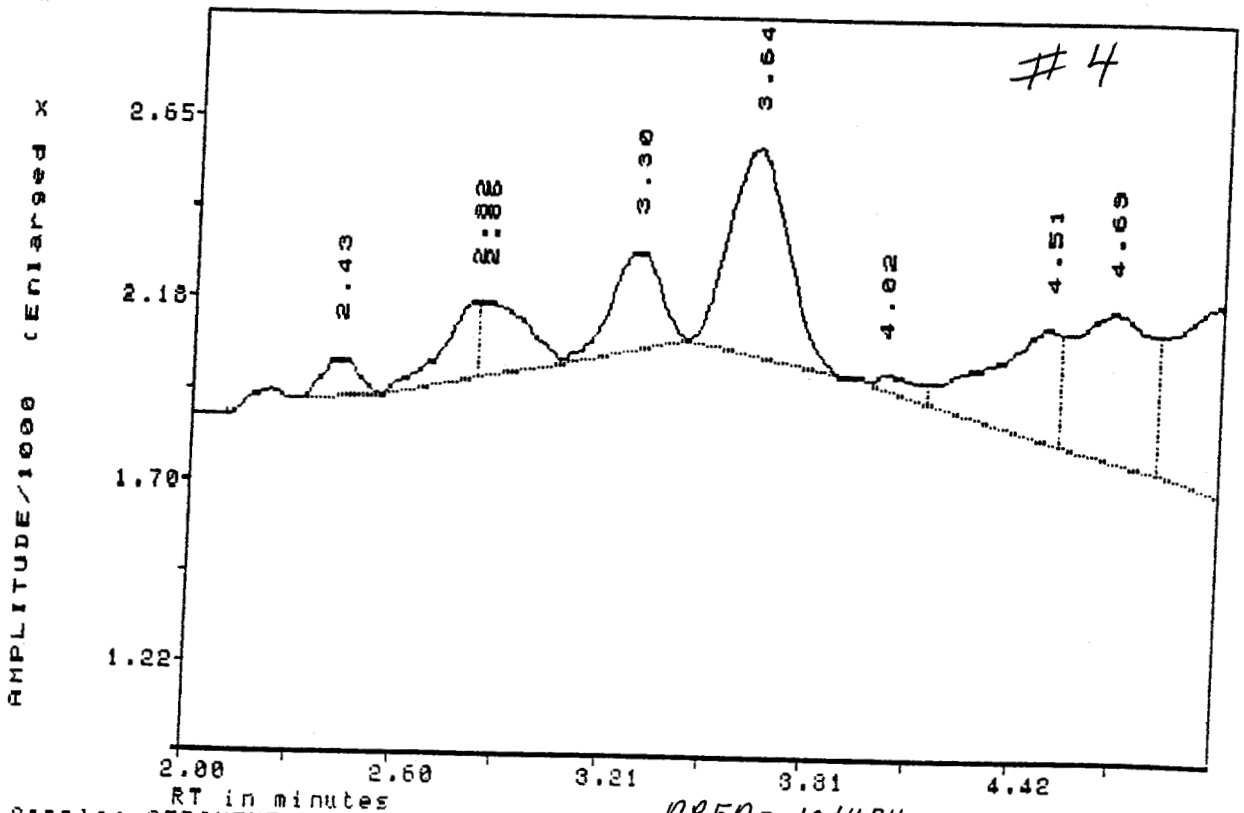
#3



Sample: BAYTHROID 25 NG/ML
Method: /DATA/BAY.MTH
Result: BAY207
Injected on Thu May 27, 1993 8:48:27 am

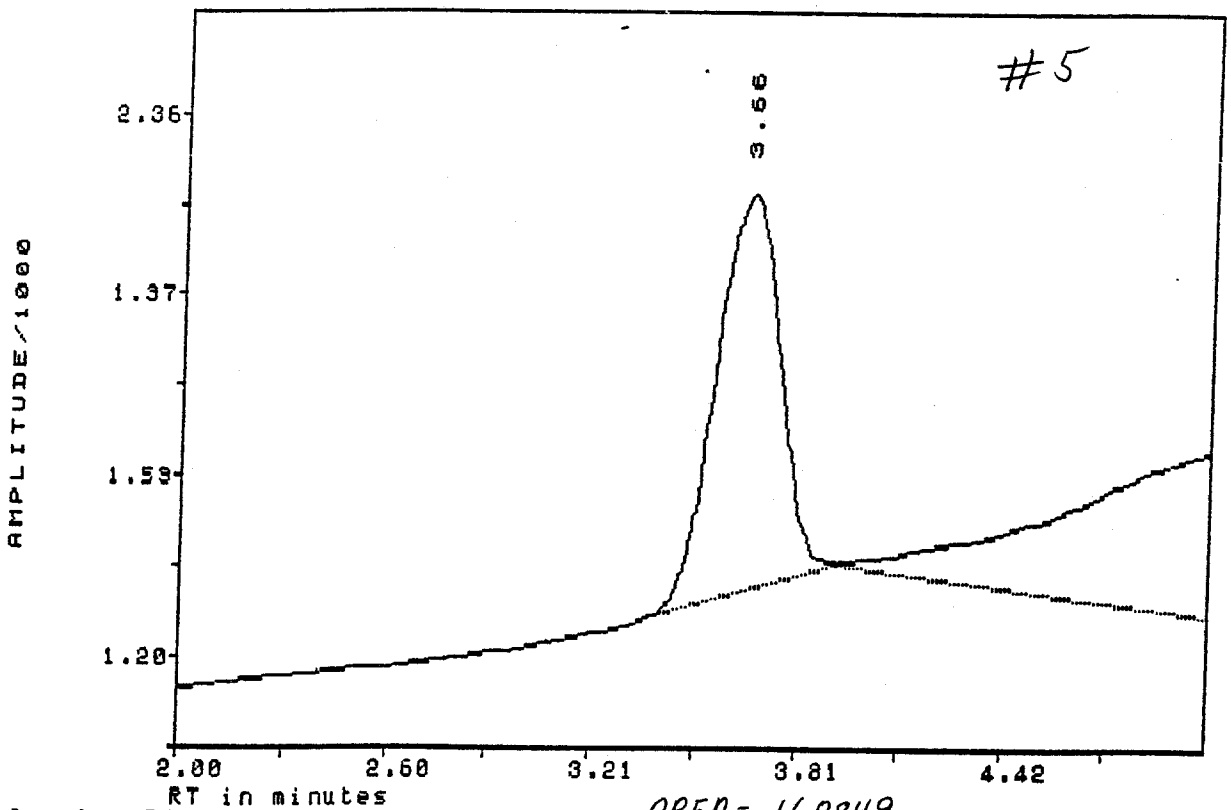
AREA = 81386

#4



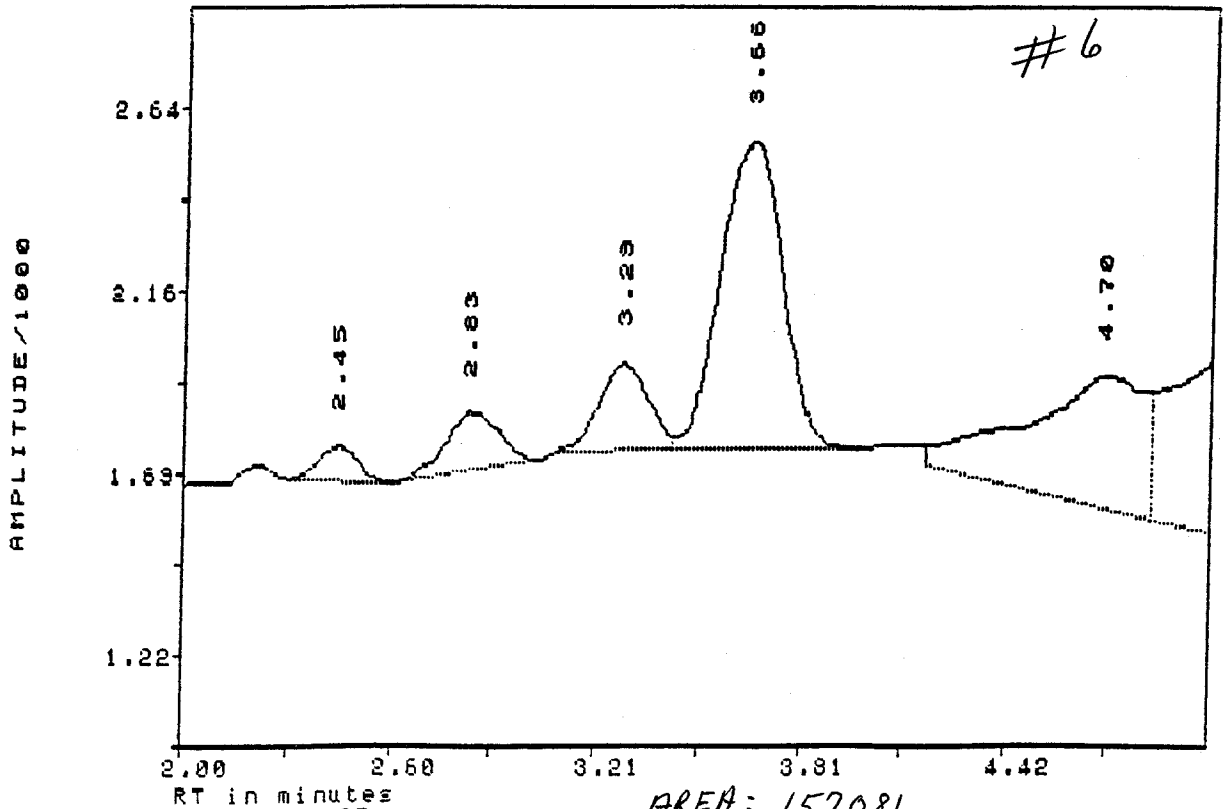
Sample: SEDIMENT S-24
Method: /DATA/BAY.MTH
Result: BAY206
Injected on Thu May 27, 1993 8:37:37 am

AREA = 101474



AREA = 168849

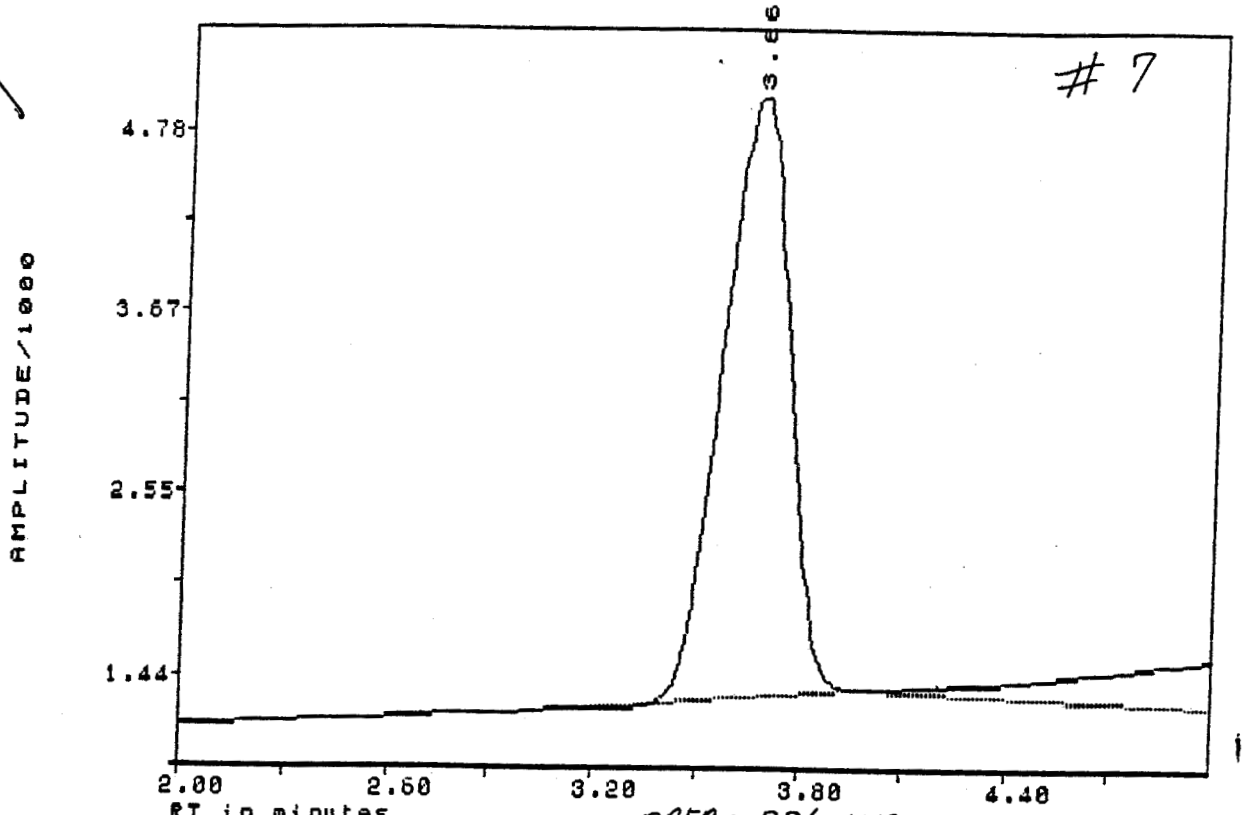
Sample: BAYTHROID 50 NG/ML
Method: /DATA/BAY.MTH
Result: BAY214
Injected on Thu May 27, 1993 10:03:51 am



AREA: 157081

Sample: SEDIMENT S-27
Method: /DATA/BAY.MTH
Result: BAY213
Injected on Thu May 27, 1993 9:58:07 am

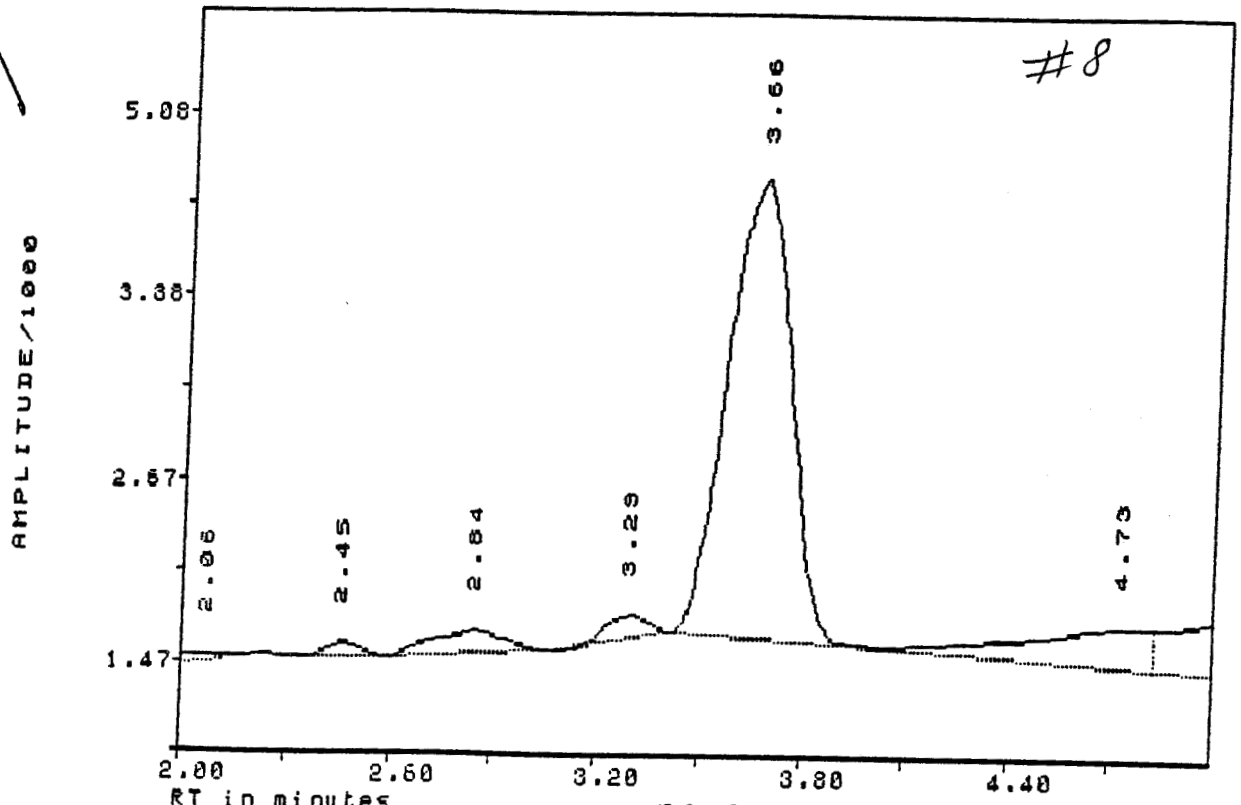
#7



Sample: BAYTHROID 250NG/ML
Method: /DATA/BAY.MTH

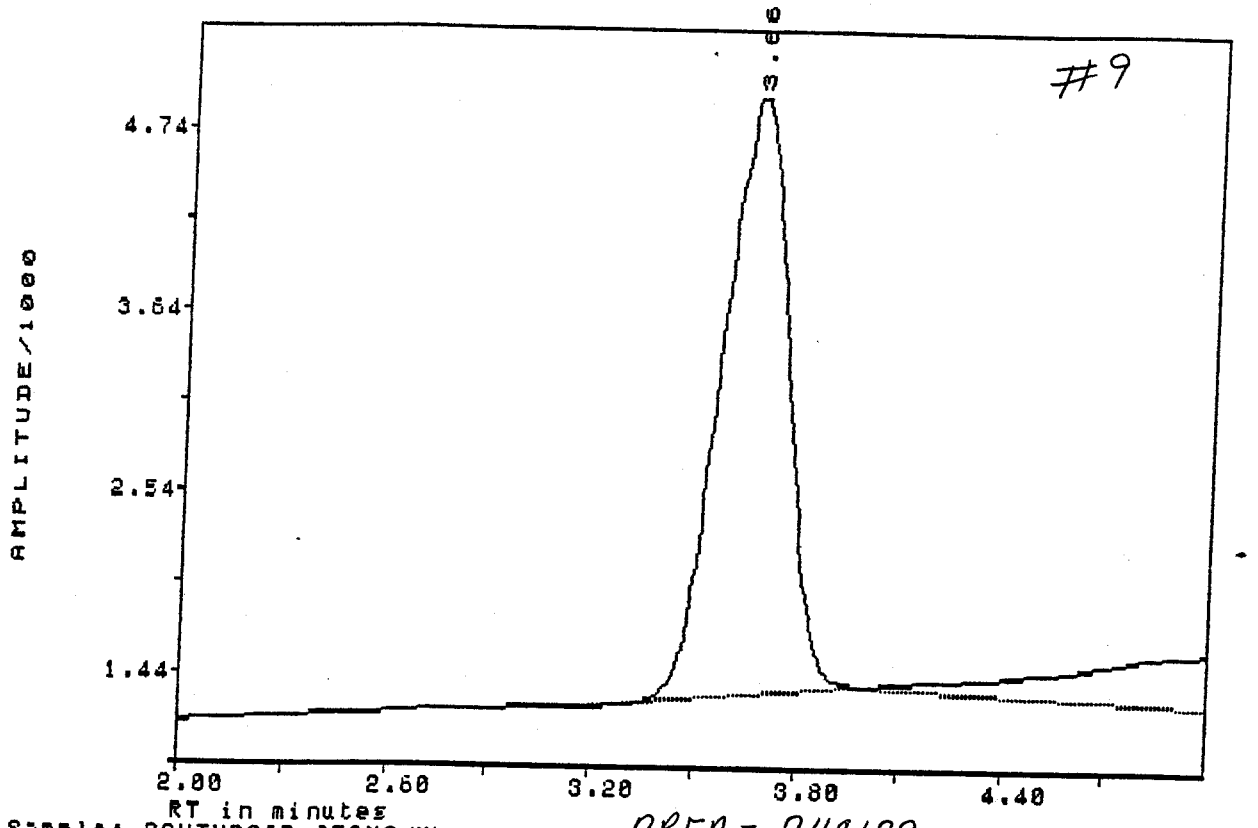
AREA = 776415

#8



Sample: SEDIMENT S-32
Method: /DATA/BAY.MTH
Result: BAY324
Injected on Thu May 27, 1988 11:51:31 am

AREA = 631333



AREA = 748179

#10 EXAMPLE CALCULATION for sample S-32

(1) AVERAGE AREA Response of standards injected before and after the sample.

$[776415 + 748179] \div 2 = 762297$

(2) $\frac{\text{conc. of extract (ng/ml)}}{631333} = \frac{250 \text{ ng/ml}}{762297}$

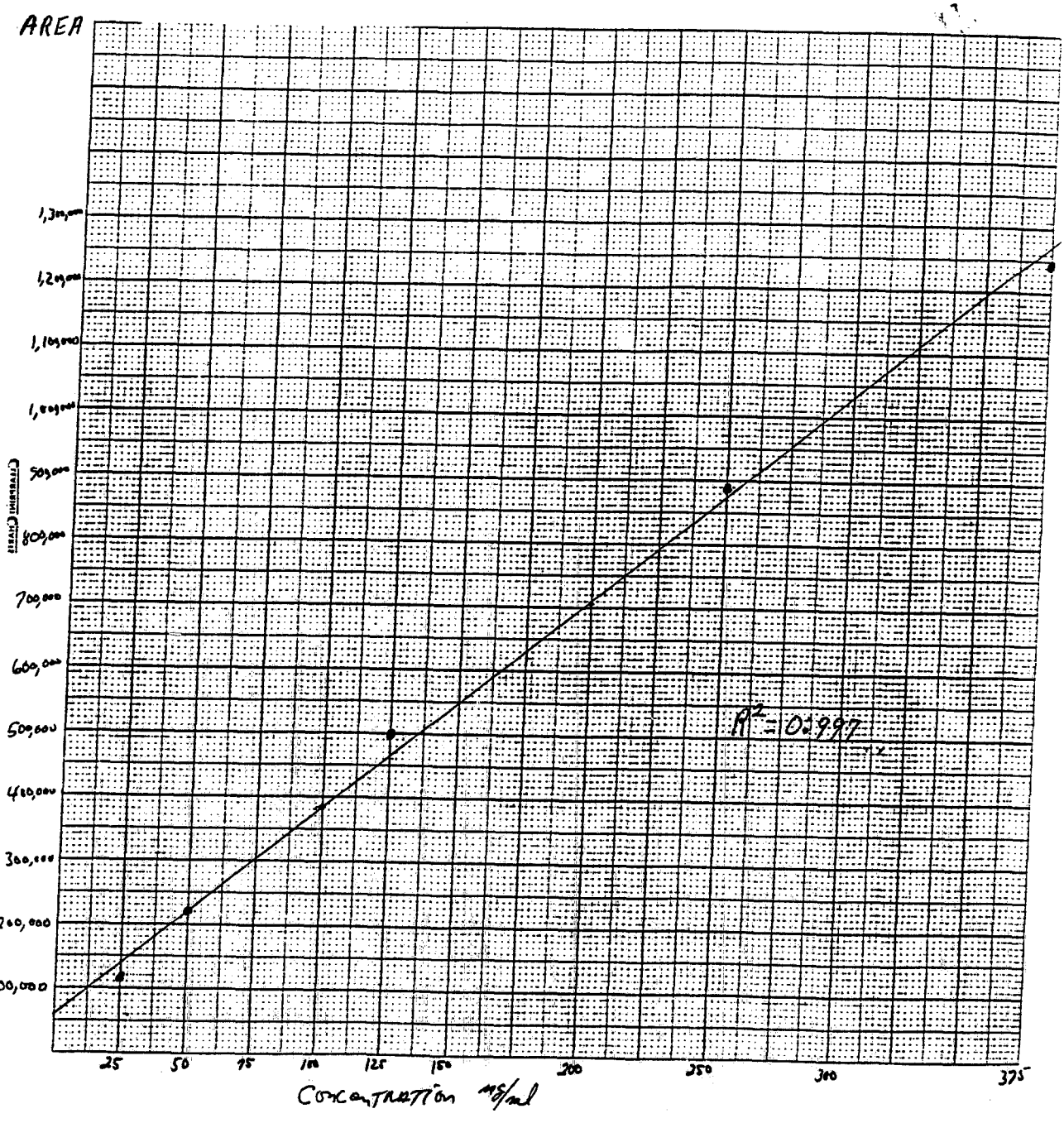
Conc. of EXTRACT = 207.05 ng/ml

(3) Conc. of CYFLUTHRIN in 50 gram sample is:

$207.05 \text{ ng/ml} \times \frac{10 \text{ ml}}{50 \text{ g}} = 41.4 \text{ ng/g}$ or 41.4 ppb

DATA Points

Std.	Response
25 ng/ml	116,574
50 ng/ml	220,149
125 ng/ml	494,466
250 ng/ml	888,376
375 ng/ml	1,240,050



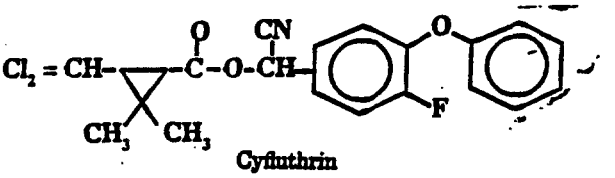
Baythroid*

Identification

COMMON NAME: Cyfluthrin.
OTHER NAMES: BAY FCR 1272, Baythroid* H, Solfac*.
CODE NUMBERS: CAS 14816-18-3; SHA 598800.

Chemistry

COMPOSITION: Cyano(4-fluoro-3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate.
FAMILY: Synthetic pyrethroid.
PROPERTIES: Colorless crystals. Tech grade product is mixture of 4 diastero-isomeric enantiomer pairs (I-IV).



Cyfluthrin

Action/Use

ACTION: Nonsystemic synthetic pyrethroid.
USE: Foliar insecticide controls chewing insects on a variety of crops such as corn, cotton, deciduous fruit, peanuts, potatoes, vegetables, and others. Baythroid* Tempo H*, Solfac* for numerous species of household, industrial, stored product, turf and ornamental, and hygienic pests.
FORMULATIONS: Aerosol, emulsifiable concentrate, granular, oil in water emulsion, ULV, wettable powder.

Registration Notes

Registered on cotton in U.S.

Environmental Guidelines

SOLUBILITY: Practically insoluble in water. Hardly soluble in n-hexane, 2-propanol. Readily in dichloromethane, toluene, 2-propanol.

Emergency Guidelines

SIGNAL WORD: DANGER. Eye irritation.
TOXICITY CLASS: II.
TOXICITY: Tech (Rat): Oral LD_{50} approx. 900 mg/kg. Dermal LD_{50} > 5000 mg/kg.
PROTECTIVE CLOTHING: Wear protective clothing, rubber gloves, goggles, face shield or safety glasses.
HANDLING AND STORAGE CAUTIONS: See label. Store in original container, preferably in a locked area, away from children, food, feed.

Emergency Guidelines

FLASHPOINT: 105°F (set-a-flash).
FIRE EXTINGUISHING MEDIA: DCP, water spray, foam, CO_2.
ANTIDOTE: None.
FIRST AID: Treat symptomatically. Get medical aid as necessary. Eyes, hold lids open and flush with a steady, gentle stream of water for 15 minutes. Skin, wash immediately with soap and water. Inhalation, remove to fresh air. If not breathing, give artificial respiration, preferably mouth-to-mouth. Ingestion, drink promptly a large quantity of milk, egg white, gelatin solution, or if these are not available, large quantities of water. Avoid alcohol.
EMERGENCY TELEPHONE: 816-242-2582 (Mobay).
BP: Bayer AG
Mobay Corp.