DETERMINATION OF RESIDUES OF TRANSFLUTHRIN AND PERMETHRIN IN AIR WHILE USING AN AEROSOL FORMULATION

BY

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OBJECTIVES

• To develop an analytical method to quantify the residues of Permethrin and Transfluthrin in air samples

• To establish an effective procedure to collect air samples following the use of Transfluthrin 0.6% w/w + Permethrin 0.8% w/w Aerosol in a closed chamber
AEROSOL DISPENSER SYSTEM

- Dispenser works on 15 minutes interval
- Declared volume in the can is 154 grams
- Life of the can is 28.9 ~ 30 days
- Spray Rate is 0.055 gram/spray
This residue study was conducted using an automatic aerosol dispenser.

The sprayer was switched on for 24 hours at a spray rate of 0.055g/spray once every 15 minutes.

The residues of permethrin and transfluthirun in air were estimated for a period of 24hrs in a pre-determined intervals (0, 2, 4, 6, 10 and 24 hours).

Air Samples were collected at 1.5 m height from the floor using cartridge.
500 mL of air sample was withdrawn from the chamber approx. 3-5 minutes after the spray.

The collected air sample was pre-concentrated and analyzed by a validated GC-ECD method.
1. Name of the compounds:
   i. Transfluthrin
   ii. Permethrin

2. Nature of the compound: Insecticide

3. Type of formulation: Aerosol

4. Percentage of active ingredient:
   i. Transfluthrin – 0.6%
   ii. Permethrin – 0.8%
• Shimadzu GC-17A GC-ECD, Auto injector AOC - 20i with GC-solution software. M/s Shimadzu Corop., Japan

• Mettler Toledo analytical balance AG-245, capable of weighing 0.01 mg supplied by M/s. Mettler Toledo, Switzerland.

• Buchi temperature controlled vacuum rotary evaporator supplied by M/s. Buchi Rotovapour, Switzerland.
Detector: $^{63}\text{Ni}$ Electron Capture Detector (ECD)

Column used: DB-210 Megabore (30m length x 0.53 mm I.D., 1.0 µm film thickness).

Temperature conditions:
- Oven: -150°C
- Injector: -240°C
- Detector: -260°C

Gas flow rate:
- Nitrogen: -10 mL/min
- Makeup: -30 mL/min

Retention time (approximate):
- Transfluthrin (Standard): -6.1 minutes
- Permethrin (Standard) Cis: -10.5 minutes
  Trans: -11.2 minutes

Column temperature program:

<table>
<thead>
<tr>
<th>Rate</th>
<th>Temperature °C</th>
<th>Hold time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>150</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>220</td>
<td>6.5</td>
</tr>
</tbody>
</table>
REPRESENTATIVE CHROMATOGRAM OF GC-ECD

- Transfluthrin
- Cis-permethrin
- Trans-permethrin
METHOD VALIDATION - LINEARITY

CALIBRATION CURVE - TRANSFLUTHRIN + PERMETHRIN

y = 1754879.2680x - 98.6728
R² = 0.9997

y = 727335.2533x - 138.7666
R² = 0.9992

Calibration range 0.001 – 2 mg/L
LOQ = 0.001 mg/L
METHOD VALIDATION - RECOVERY

Spikings: 1, 0.1 and 0.001 mg/L level on Carbon cartridge

Suction of 500mL of Clean air

Eluted with 10mL of Acetone

Analyzed 1µL by GC-ECD
<table>
<thead>
<tr>
<th>Fortified concentration (mg/L)</th>
<th>Transfluthrin Recovery (%)</th>
<th>Permethrin Recovery (%)</th>
<th>Transfluthrin mean Recovery (%) ±SD</th>
<th>Permethrin mean recovery (%) ±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>89.98</td>
<td>96.88</td>
<td>93.46±3.34</td>
<td>93.50±4.04</td>
</tr>
<tr>
<td>0.001</td>
<td>93.75</td>
<td>89.03</td>
<td>92.51±2.49</td>
<td>94.67±2.00</td>
</tr>
<tr>
<td>0.001</td>
<td>96.65</td>
<td>94.59</td>
<td>94.36±2.26</td>
<td>94.38±1.71</td>
</tr>
<tr>
<td>0.1</td>
<td>90.5</td>
<td>92.38</td>
<td>94.48</td>
<td>92.05</td>
</tr>
<tr>
<td>0.1</td>
<td>95.29</td>
<td>95.62</td>
<td>94.48</td>
<td>96.56</td>
</tr>
<tr>
<td>0.1</td>
<td>91.74</td>
<td>96.02</td>
<td>94.48</td>
<td>93.75</td>
</tr>
<tr>
<td>1</td>
<td>94.48</td>
<td>93.08</td>
<td>94.48</td>
<td>94.48</td>
</tr>
<tr>
<td>1</td>
<td>92.05</td>
<td>96.32</td>
<td>94.48</td>
<td>94.48</td>
</tr>
<tr>
<td>1</td>
<td>96.56</td>
<td>93.75</td>
<td>94.48</td>
<td>94.48</td>
</tr>
</tbody>
</table>

SD - Standard deviation
An automatic insect control aerosol system was fixed on wall in one corner of the testing chamber.

Air samples were collected by placing the carbon cartridge at 5 centimeters distance from the sprayer nozzle.

500 ml of air samples were withdrawn from the chamber at 0-10, 10-20, 30-40 and 60-70 and 90-100 seconds after the spray at a rate of 3 L/min for 10 seconds using a cartridge connected to a vacuum pump equipped with flow regulator.

Trapped residues were eluted using 10 ml acetone twice.

Evaluated the residues of transfluthrin and permethrin using a validated GC-ECD method.
AIR CONCENTRATION CHAMBER - SETUP
STUDY DESIGN – AIR CONCENTRATION RECOVERY TRAP

Airflow 3L/min

Pump

Cartridge

Closed Chamber

1 m

5 cm

1 m
PRELIMINARY INVESTIGATIONS

- No residues were found when carbon trap was kept at 20, 30, 45 and 60 cm away from cartridge.

- Non-recovery of residues at longer distance can be attributed due to:
  - Low concentration of residues in air samples
  - Requirement of huge volume air sample to concentrate the residues on the cartridge in a shortest plausible time
  - 5 cm distance between tip of the nozzle and the carbon trap was found optimum.
PRE CONCENTRATION OF TRANSFLUTHRIN AND PERMETHRIN FOLLOWED BY 0.055 G/SPRAY USING CARBON CARTRIDGE KEPT AT VARIED DISTANCES

<table>
<thead>
<tr>
<th>Time gap between Spray and Sample Collection (sec)</th>
<th>Sample Collection Duration (sec)</th>
<th>Sample Collection flow rate (L/min)</th>
<th>Volume of air (mL)</th>
<th>Transfluthrin active content (mg/L)</th>
<th>Permethrin active content (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10</td>
<td>10</td>
<td>3</td>
<td>500</td>
<td>0.1559</td>
<td>0.1985</td>
</tr>
<tr>
<td>10-20</td>
<td>10</td>
<td>3</td>
<td>500</td>
<td>0.1228</td>
<td>0.1824</td>
</tr>
<tr>
<td>30-40</td>
<td>10</td>
<td>3</td>
<td>500</td>
<td>0.0864</td>
<td>0.1121</td>
</tr>
<tr>
<td>60-70</td>
<td>10</td>
<td>3</td>
<td>500</td>
<td>0.0254</td>
<td>0.0416</td>
</tr>
<tr>
<td>90-100</td>
<td>10</td>
<td>3</td>
<td>500</td>
<td>BLQ</td>
<td>BLQ</td>
</tr>
</tbody>
</table>

BLQ - Below Limit of Quantification
Air Concentrations of Actives in 1 m³ Chamber

- Transfluthrin
- Permethrin

Conc. mg/mL vs Time in sec
The residues of permethrin and transfluthrin were found to be below detectable level in all sampling occasions.

Non-recovery of residues can be attributed due to:
- Low concentration of the residues in air
- The actives may reduce quickly after the spray
- Huge volume of air sample may be required to pre-concentrate the residues on cartridge
- Sampling and extraction method need to be optimized

The present study is designed to minimize such influential parameters.
RESIDUE ACCUMULATION IN A ROOM DUE TO 8 HRS SPRAY
Aerosol sprayer was switched on for 8 hours in a dark 1m³ chamber by fixing the device on wall in one corner.

Spray Rate is 0.55g/spray once in 15 minutes time intervals.

Air sampling was done from different locations of the chamber - Top, Middle & Bottom.

<table>
<thead>
<tr>
<th>Insecticide formulation</th>
<th>Time of collection (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permethrin 0.8% w/w + Transfluthrin 0.6% w/w</td>
<td>0.5, 1, 2, 4, 6 and 8</td>
</tr>
</tbody>
</table>
EXPERIMENTAL DETAILS

✓ 500 CC Volume of air samples were collected using cartridge in each location from the room.
✓ Collected samples were dissolved in 10mL of acetone and quantified by GC-ECD.
✓ Once again all the samples were pooled and reduced the volume to 1mL and analyzed by GC-ECD to determine the total residue concentration.
✓ Surface concentration was measured after completion of 8 hours.
✓ Floor of the chamber was covered with poly propylene sheet.
✓ Poly propylene sheet was cut into pieces and extracted with 250 mL of acetone using end-over-end mechanical shaker.
✓ Volume of acetone was reduced to 1 mL using rotary evaporator and analyzed by GC-ECD.
**CONCENTRATION OF TRANSFLUTHRIN AND PERMETHRIN IN AIR AT DIFFERENT LOCATIONS IN THE ROOM**

<table>
<thead>
<tr>
<th>Sampling Occasion (hours)</th>
<th>Locations</th>
<th>Transfluthrin (mg/L)</th>
<th>Permethrin (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Top</td>
<td>Middle</td>
<td>Bottom</td>
</tr>
<tr>
<td>0.5*</td>
<td>BLQ</td>
<td>BLQ</td>
<td>BLQ</td>
</tr>
<tr>
<td>1*</td>
<td>BLQ</td>
<td>BLQ</td>
<td>BLQ</td>
</tr>
<tr>
<td>2</td>
<td>BLQ</td>
<td>BLQ</td>
<td>0.0013</td>
</tr>
<tr>
<td>4</td>
<td>0.0011</td>
<td>0.0017</td>
<td>0.0019</td>
</tr>
<tr>
<td>6</td>
<td>0.0015</td>
<td>0.0024</td>
<td>0.0036</td>
</tr>
<tr>
<td>8</td>
<td>0.0028</td>
<td>0.0062</td>
<td>0.0081</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Top</td>
<td>Middle</td>
<td>Bottom</td>
</tr>
<tr>
<td></td>
<td>BLQ</td>
<td>BLQ</td>
<td>BLQ</td>
</tr>
<tr>
<td></td>
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<td>BLQ</td>
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<tr>
<td></td>
<td>BLQ</td>
<td>BLQ</td>
<td>0.0016</td>
</tr>
<tr>
<td></td>
<td>0.0013</td>
<td>0.0015</td>
<td>0.0021</td>
</tr>
<tr>
<td></td>
<td>0.0019</td>
<td>0.0028</td>
<td>0.0047</td>
</tr>
<tr>
<td></td>
<td>0.0033</td>
<td>0.0071</td>
<td>0.0093</td>
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BLQ - Below Limit of Quantification

* - Pooled samples were analysed
DEPOSITIONS OF TRANSFLUTHRIN AND PERMETHRIN ON FLOOR IN THE CHAMBER

<table>
<thead>
<tr>
<th>Sampling Occasion (hours)</th>
<th>Residue (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Transfluthrin</td>
</tr>
<tr>
<td>8</td>
<td>0.282</td>
</tr>
</tbody>
</table>
CONFIRMATION OF RESIDUES BY GC – MS

Instrument - Shimadzu GCMS QP5050A
Column - DB-5 (30 m x 0.25 mm I.D x1.0 µm)

Temperature conditions
Oven -150°C
Injector -240°C
Detector -260°C

Gas flow rate
Helium -1.0
Spit ratio - 1:20

Ion Monitered
Transfluthrin - 127,163 m/z
Permethrin - 163,183 m/z

Retention time (approximate)
Transfluthrin (Standard) -6.1 minutes
Permethrin (Standard) Cis -14.5 minutes
Trans -15.2 minutes

Column temperature program

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<tr>
<td>20</td>
<td>220</td>
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MS SPECTRA - TRANSFLUTHRIN

![MS Spectrogram of Transfluthrin](image)