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Allethrin in the Air During the Use of a Heated Mosquito Repellent Mat

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Allethrin containing formulations such as aerosol, smoke coils and electrical mats are most popular methods of personal protection against mosquitoes and several hundred tones per year of allethrin and related pyrethroids based formulations are used throughout the world (Ramesh and Vijaylakshmi 2002). Pyrethroids are generally considered to be safe insecticides due to their low toxicity to mammals. However it is not clearly established whether chronic inhalation of allethrin for 8-10 h every night would be judged safe and non-hazardous to human health, particularly children, pregnant women and people suffering from various diseases. Our survey revealed that 11.8% of the users of allethrin containing mosquito repellents across all age groups complained of a variety of acute toxicity effects within few hours of their use. Gas chromatographic methods are generally used for the determination of pyrethroids residues (Pang et al. 1994; Papadopoulou-Mourkidou 1983). Eitzer (1991) reported the cycling of indoor air concentration of allethrin following repeated pesticide applications. We have monitored the concentrations of allethrin in air at various time intervals during its use in mosquito mats and confirmed the presence of this residue in air sample using GCMS analysis.

MATERIALS AND METHODS

Allethrin was purchased from Chemicals Unlimited Mumbai, India, while HPLC grade methanol was obtained from Ranbaxy Fine chemicals, Delhi. Ultra pure nitrogen and helium were used as carrier gases for chromatographic analysis. Prallethrin was used as an internal standard. Mosquito repellent mat (Baygon) containing 4% allethrin marketed by Bayer India Ltd, Mumbai was used throughout the study.

A stock solution 10 $\mu g\ ml^{-1}$ of allethrin was prepared in methanol. The concentration range of 0.05-1.0 $\mu g\ ml^{-1}$ were used for the calibration curve of allethrin while the internal standard (0.01 $\mu g\ ml^{-1}$) was used throughout the study.

A Hewlett-Packard 5890 gas chromatograph fitted with Ni^{63} electron-capture detector and a Shimadzu CR8 integrator (Shimadzu Corporation, Japan) was used for the analysis. Nitrogen at the flow rate of 2.0 ml min^{-1} (split ratio 1:4)

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was used as carrier gas on fused silica capillary column TM^5 PTE (length 30 m, 0.25 mm id; Supelco Inc., USA) for the separation of allethrin and internal standard. The injector, oven and detector temperature were set at 210, 190 and 220 °C respectively.

A Varian CP 3800 gas chromatograph equipped with mass detector (Varian Satrun 2000 Corporation, USA) was used for GC-MS analysis. Chromatographic separation was carried out using a DB-5 capillary column supplied by Varian Pvt., Mumbai (30 m x 0.25 mm id with the film thickness of 0.25 μm). Ultra pure helium at a flow rate of 0.8 ml min^{-1} and in splitting ratio of 1:10 was used as carrier gas. The injector temperature was 200°C while the oven initial temperature was 15 °C increased to the final temperature of 200 °C at the rate of 2 °C min^{-1}. MS detector was operated at 70 ev in EI auto ionization mode. The trap temperature, manifold temperature and transfer line temperature were 170°C, 40°C and 270 °C respectively for MS detector.

Commercially available mosquito repellent mat (Casper, 4% allethrin) was allowed to heat by placing it on an electric element for 14 h in a room (3m x 3m x 2.5m fitted with an air cooler and a circulating fan). The temperature of the room varied from 30-32 °C with the relative humidity of 50%. Air samples were collected using an air sampler (Model APM-411, Envirotech Industries Ltd. Delhi) through a plunger fitted with 25 ml methanol. The air was pumped into the plunger at the rate of 500 ml min^{-1} and each sample was collected for 30 min of air flow, dried and kept at 4 °C until analysis.

To investigate the influence of environmental parameters, two different sets of air samples were collected from the room: i) window open and ii) window closed. The door of the room was closed in both cases. Samples were collected at 30 min and 3, 5, 8, 10 and 14 h after initiation of heating of the mosquito mat.

RESULTS AND DISCUSSION

The separation between allethrin and prallethrin (internal standard) was best achieved using nitrogen at the flow rate of 2 ml min^{-1} as carrier gas on fused silica capillary column TM^5 PTE (length 30m, 0.25 mm id) and Ni^{63} electron capture detector. The injector, oven and detector temperatures were fixed at 210, 190 and 220 °C respectively. Allethrin and prallethrin were resolved to base line with retention times of 9.0 and 9.8 min respectively. The limit of detection for allethrin was 2 ng ml^{-1} with a signal to noise ratio of 1:4. Figure 1 showed the chromatographic determination of allethrin in air sample taken at 3 hrs during heating of repellent mat Casper. The identity of allethrin in air sample was confirmed using a GC-MS method. The GC MS analysis of allethrin is given in Figure 1. The retention time for allethrin was 27.68 min (Figure 1b). The mass spectrum corresponding to allethrin peak is given in Figure 1(a). The base peak was obtained at 123 and the protonated molecular ion peak with low relative abundance was recorded at M/Z 303. The mass spectra of allethrin peak was confirmed by NIST and MS database search. Some peaks appeared in the

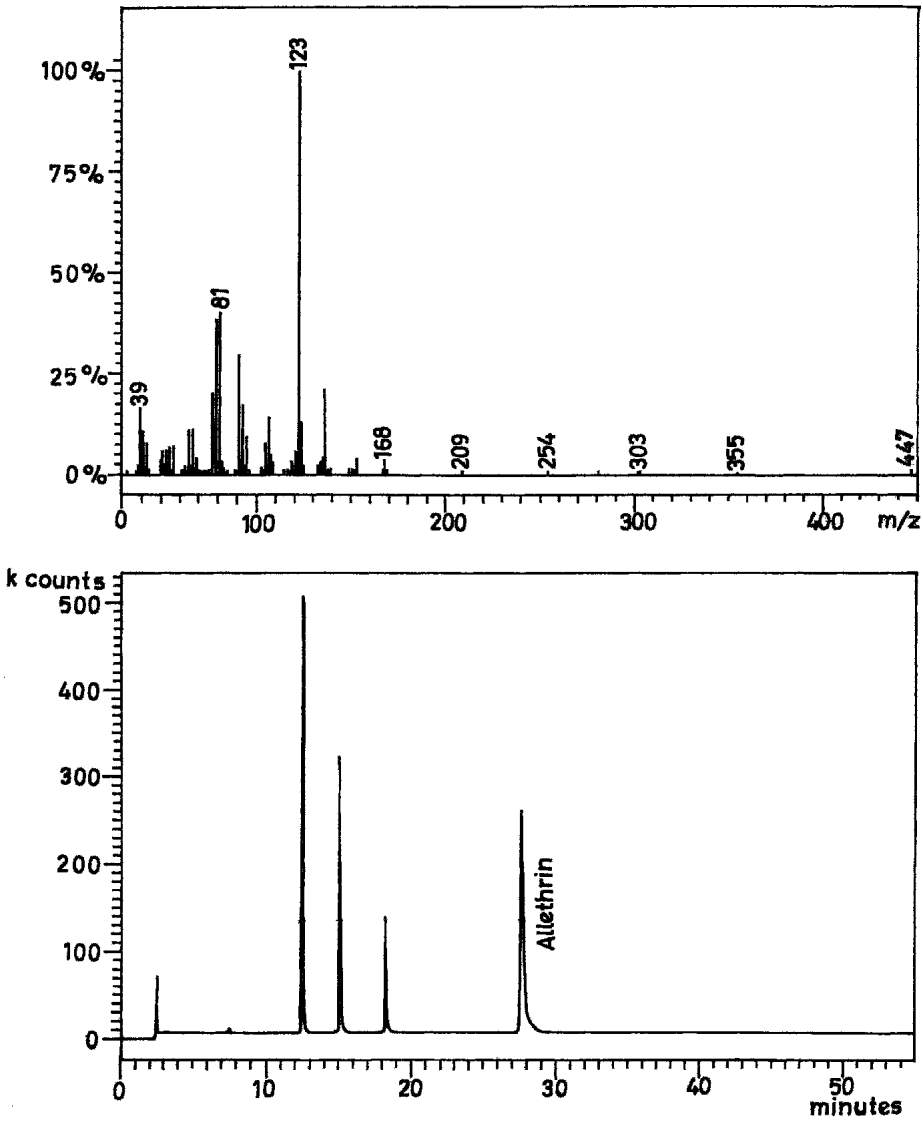

Figure 1. GC-MS analysis of allethrin in air using He at the flow of 0.8 ml min^{-1} as carrier gas on DB-5 capillary column (30 m x 0.25 id). Figure 2(a) mass spectra recorded due to the allethrin peak of GC analysis and 2(b) Gas chromatogram showing allethrin peak .

chromatogram before allethrin peak which could be due to the presence of other components present in the mosquito repellent mat. Chang and Lin (1998) have found aliphatic aldehydes and allethrin in mosquito coil smoke. Figure 2 showed the concentration profile of allethrin in air samples taken at various time intervals during the heating of mosquito repellent mat in a room fitted with an air cooler and a circulating fan.

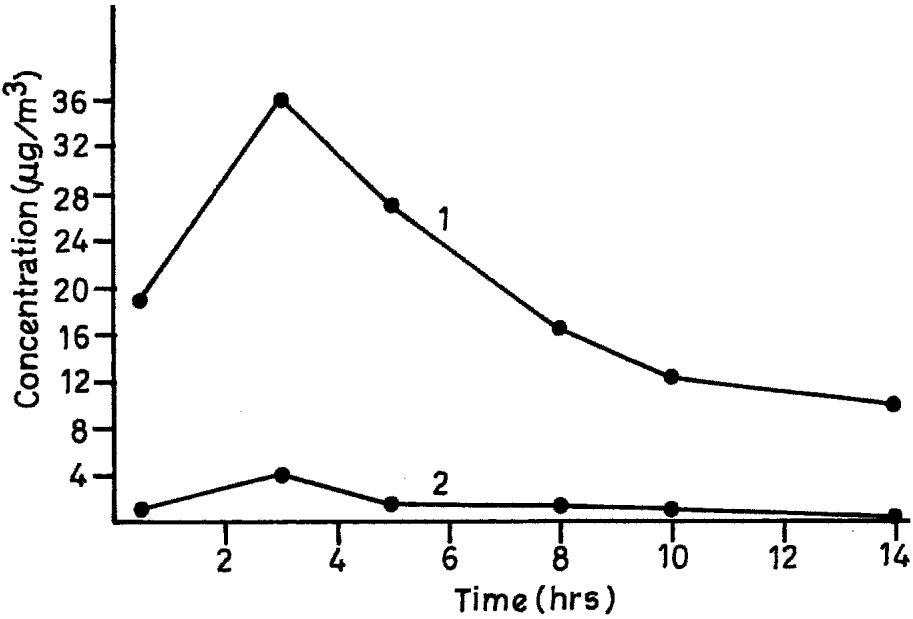

Figure 2. Allethrin concentration profile in air samples taken at various time intervals during heating of mosquito repellent mat casper (4% allethrin) in a room (3 x 3 x 2.5 m). Line 1. window closed; Line 2. window open.

The allethrin concentration in air at 30 min, 3, 5, 8, 10 and 14 h were 19, 36, 27, 16.5, 12.3 and 10.2 µ gm^{-3} respectively in the room with closed window while they were 1. 4. 1.7.1.3.1 and 0.3 µg m^{-3} respectively in the room with window open. Maximum concentration of allethrin was recorded at 3 h after initiation of heating of the mat irrespective of either the window closed or opened. The results revealed that there is a drastic reduction in the concentration of allethrin residue in air in the room when the window was open.

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REFERENCES

Chang JY, Lin JM (1998) Aliphatic aldehydes and allethrin in mosquito-coil smoke. Chemosphere 36: 617-624

Eitzer BD (1991) Cycling of indoor air concentrations of d-*trans* allethrin following repeated pesticide application. Bull Environ Contam Toxicol 47 : 406-412.

Pang GF, Fan CL, Chao YZ, Zhao TS (1994) Rapid method for the determination of multiple pyrethroid residues in fruits and vegetables by capillary column gas chromatography. J Chromatogr 667: 348-53

Papadopoulou-Mourkidou E (1983) Analysis of established pyrethroid insecticides. Residue Rev 89: 179-208

Ramesh A, Vijaylakshmi A (2002) Impact of long-term exposure to mosquito coils : residual deposition and dissipation of d-*trans*-allethrin in a room. J Environ Monit 4: 202-204