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Studies on Deltamethrin Treated Mosquito Net

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Abstract: The focus of the present studies is to characterize mosquito net for its material of construction and qualitative as well as quantitative determination of the mosquito repellent chemical deltamethrin present in it. Further, the assessment of the mode of incorporation of the deltamethrin in the fabric of the mosquito net was done, *i.e.* whether the deltamethrin was present as a coating on the surface of the mosquito net or it was incorporated in the bulk of the material of construction of the mosquito net. The chromatographic technique has been used for quantitative estimation of deltamethrin extracted by two different solvents from the net. It has been found that the determination of deltamethrin in mosquito nets can vary with the method of extraction used. While extraction with acetone is good enough for estimating the chemical adsorbed on the surface, extraction with xylene provides complete information about the chemical present even in the bulk of the material.

Keywords: Mosquito net, Insecticide, Deltamethrin, HPLC, GC-MS.

Introduction

Mosquito nets or curtains have been in use for protection from mosquitoes and prevention of malaria since centuries. The nets made up of various materials like cotton, nylon, polyester *etc*. have been useful in preventing the mosquitoes to enter through. In order to ensure that mosquitoes do not stay even on the outer surface of the net, various chemicals have been tried to make the net repellent to mosquitoes. Products with deliberate treatment of net materials with mosquito repellents of various types including even DDT to provide additional protection against mosquitoes are already in the market[1]. In several endemic areas of the world, laboratory and field trials with untreated and treated mosquito nets have shown that treated mosquito nets show better protection as compared to untreated nets[1]. A study in Zaire has reported that the use of insecticide treated nets (ITNs) resulted in a reduction in the number of bites from malaria vector by 94%[2]. In Africa alone, over 1 mn children die from malaria every year. Hence, in 2006, Kenyan government initiated a program to provide 3.4 mn treated nets free to young children[3].

Some of the prominent mosquito repellents exploited commercially so far is from the group of pyrethroids, for example, deltamethrin and permethrin, lambdacyhalothrin *etc.,* all these repellents have been used to treat mosquito nets. Pyrethroid insecticides are currently the only chemicals recommended by WHO Pesticide Scheme (WHOPES) for net impregnation[3]. In 1990s, several small-scale trials in various countries demonstrated the effectiveness of nets treated with pyrethroids in reducing malaria and vector population[1]. Deltamethrin is one of the insecticides recommended by WHO for indoor spraying and for treatment of mosquito nets[4]. In China, trials of deltamethrin treated bednets for control of malaria transmitted by mosquito vectors have been done[5].

Since the nets are generally washable, the risk of loosing the mosquito repellent during washing has always been a cause of concern, especially for products where the repellent remains only as a coating on the surface of the net. Such nets have to be replaced or re-treated with insecticide after a few washes and therefore, do not serve as a long-term solution to the malaria problem. Hence, Long-lasting Insecticide treated Nets (LLINs) were developed. LLINs incorporate the insecticide into the net material and release the insecticide slowly over a period of time. However, the suppliers often avoid adding the mosquito repellents in the bulk of the material of the net to save the cost and this leaves the consumers at a disadvantage. Incidentally, there exists no standard method for checking whether the repellent exists only on the surface or it is incorporated in the bulk. Keeping this gap area in mind, this study was planned to assess the situation. We present herein a systematic approach for characterizing the deltamethrin treated mosquito net using sophisticated state-of-the-art instrumental techniques.

Experimental

Mosquito repellent nets were procured from the local market. Certified reference standard of deltamethrin from Reidel-de-Haen, acetone and xylene (HPLC grade) from s.d. fine chemicals and Helium gas of 99.9% purity were used. All chemicals were used as received. The equipment used in this study are: Fourier Transform Infra red spectroscope (Model: FTLA 2000, Make: ABB Bomem), differential scanning calorimeter (Model: Modulated DSC 2910, Make: TA Instruments), high performance liquid chromatograph (Model: SCL-10 AVP, Make: Shimadzu) equipped with UV-visible detector and autosampler for injection, Gas Chromatograph-Mass Spectrometer (Model: 6890 N with 5975 mass selective detector, Make: Agilent Technology) were used. The Gas Chromatograph was equipped with a 7683 series autosampler and split/splitless injector with electronic pressure controls.

Identification and confirmation of material of construction of mosquito net

The material of construction of the mosquito net was identified by differential scanning calorimetry (DSC). For this, one mosquito net sample was taken as such and another was washed with detergent to remove impurities present on its surface. The DSC was carried out at a heating rate of 10 °C / minute from room temperature to 400 °C under nitrogen atmosphere.

Identification of insecticide present in the mosquito net

A known weight of the net sample was extracted in 50 to 60 mL of acetone. It was filtered and then evaporated to dryness in a Rota evaporator. This was then made up to 10 mL in mobile phase, *i.e.* a mixture of acetonitrile and water in the ratio of 85: 15 v/v. 20 µL of this solution was injected into HPLC. Another sample of certified reference standard of deltamethrin was injected for the second run.

HPLC analysis was carried out under the following conditions: λ-$_{max}$: 245 nm, Detector: UV Column: Perfectsil 100 ODS-3 5 µm (250 x 4.6 mm) Flow rate: 1.2 mL/min.

For gas chromatography-mass spectrometric analysis; a known weight of the net sample was cut into small pieces, immersed in acetone and shaken for one hour. The sample was filtered and the solution was concentrated to 2 mL. This concentrated solution was used to conduct GC-MS analysis under the following conditions:

GC-conditions

Injector temperature: 280 ºC, Split 10:1 Column: HP-17 MS (30 m x 0.25 mm x 0.25 µm) Capillary column Oven temperature: 200 ºC-300 ºC @ 2 ºC/min. (30 min-hold) Carrier Gas: Helium (1 mL/min) Transfer line temperature: 300 ^{o}C, MS conditions: MS Source: 230 ^{o}C, MS Quadrupole: 150 ^{o}C, Scan Range: 40-550 AMU.

Assessment of the mode of incorporation of deltamethrin

A common solvent for material of construction of the mosquito net and deltamethrin was taken, which in this case, is xylene. A known weight of the acetone extracted net sample was dissolved in boiling xylene and then allowed to cool. The polymer was observed to settle down on cooling. The solution was filtered through syringe filter. The filtrate was concentrated and then used for GC-MS analysis under the same conditions of GC-MS as mentioned earlier.

Results and Discussion

Identification and confirmation of material of construction of mosquito net

The thermal analysis of the net sample was done by using differential scanning calorimetry. The results of DSC for the mosquito net before and after washing with detergent solution are presented in Figures 1 & 2 respectively. The thermogram obtained for the net sample without washing shows a peak at 136.82 ºC (Figure.1), which indicates the melting point of the material of construction of the net sample. Although the peak is within the range of 130 ºC to 138 ºC, which is an acceptable melting point of polyethylene, the peak is not very sharp and shows the presence of some noise, which could be due to the impurities.

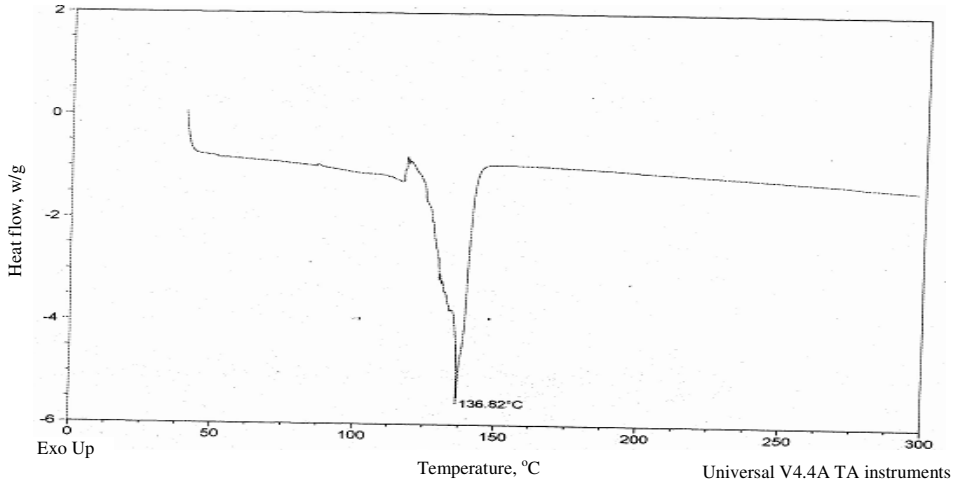


Figure 1. DSC thermogram of the unwashed mosquito net.

When the net sample was washed with detergent solution in water and studied using DSC, the thermogram obtained showed a sharp peak at 133.6 ºC (Figure 2). The fact that the washed sample showed a sharp peak indicates the presence of certain impurities or a coating on the material surface, which gets washed off during washing. The presence of these impurities is responsible for the shift in the melting point of the material, which is being indicated at 136.82 ºC. The melting point of the washed net sample matches with that of the standard polyethylene sample showing peak at 133.08 ºC (Figure 3). Thus, the material of construction of net is polyethylene.

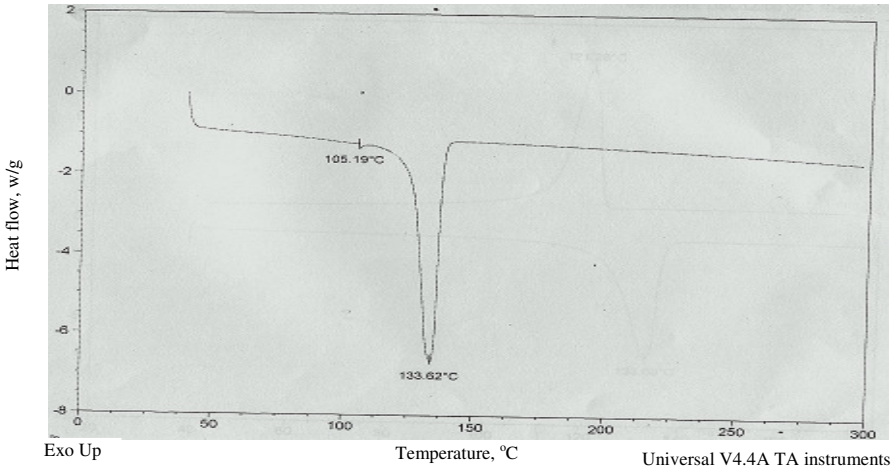


Figure 2. DSC thermogram of washed net sample

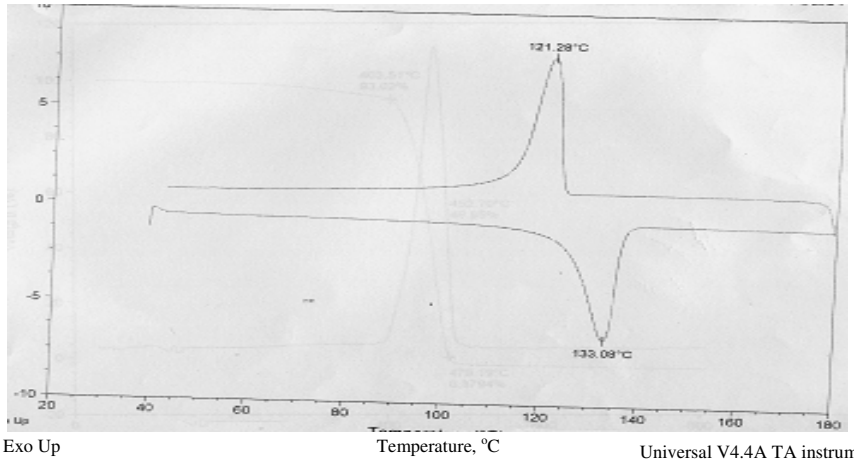
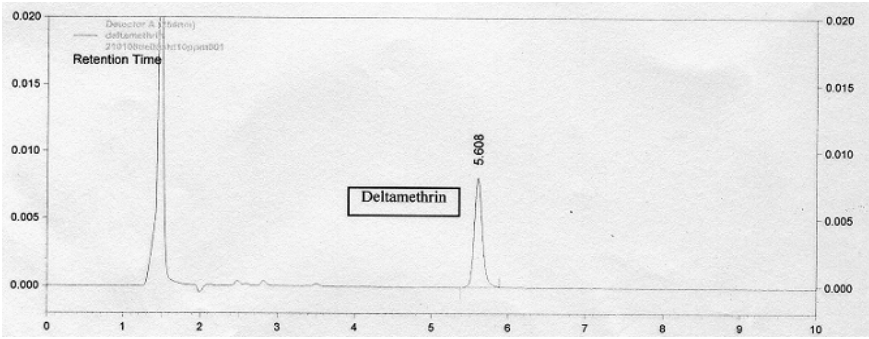


Figure 3. DSC thermogram for standard polyethylene

Identification of insecticide present in the mosquito net

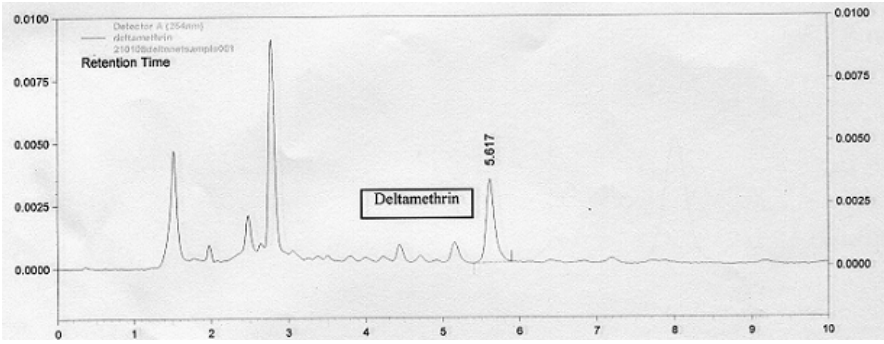
It is known that deltamethrin has high solubility in acetone and hence, the acetone extract could be used in HPLC and GC-MS analysis. As determined by HPLC using acetonitrile/ water as the mobile phase, it is clear that the extract obtained from the net sample contained deltamethrin. The chromatogram obtained from HPLC analysis of standard deltamethrin is shown in Figure 4.



Minutes

Figure 4. HPLC chromatogram of standard deltamethrin

The peak identified as that of deltamethrin in the sample (Figure 5) eluted exactly at the same retention time as that of the standard, confirming the presence of deltamethrin in the sample.



Minutes

Figure 5. HPLC chromatogram of acetone extract of deltamethrin from mosquito net

Since deltamethrin was identified in the mosquito net sample, its confirmation was conducted using gas chromatography-mass spectrometry. The mass spectra of the peak for deltamethrin was compared to that in the NIST library and identified as that of deltamethrin. The GC-MS chromatograms of reference standard of deltamethrin (100 ppm concentration) and of acetone extract of net sample are given in Figures 6 and 7 respectively.

The area under the peak of deltamethrin obtained by injecting the extracts of the net sample using GC-MS and HPLC was compared with that of the area under the peak obtained by injecting standard deltamethrin of known purity and calculated using the following formula:
Deltamethrin content = $(A_1/A_2) \times (C_{std} / C_{spl}) \times$ Percent purity of reference standard of Deltamethrin.

Where, A_1 is the area counts for the deltamethrin peak in the sample solution. A_2 is the area counts for the deltamethrin peak in the solution of the reference standard of deltamethrin. C_{std} is the concentration of the standard solution of deltamethrin. C_{spl} is the concentration of the sample solution. Deltamethrin content in the outer coating of the net sample as determined by GC-MS technique was found to be 103 mg/ kg.

Assessment of the mode of incorporation of deltamethrin

Although the coated deltamethrin was extracted in acetone, yet the possibility of its being incorporated in the material of construction of net and getting leached out from the core during extraction cannot be ruled out.

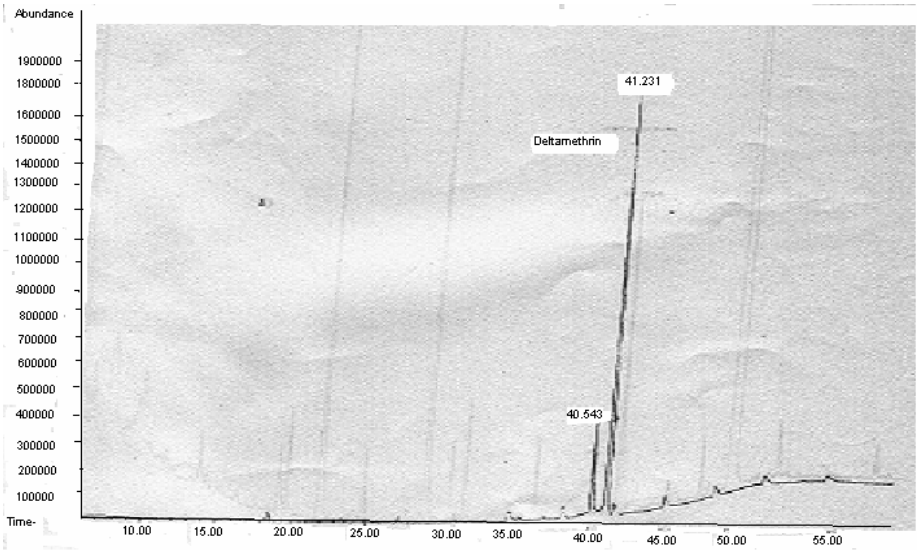


Figure 6. GC-MS chromatogram of standard deltamethrin (100 ppm)

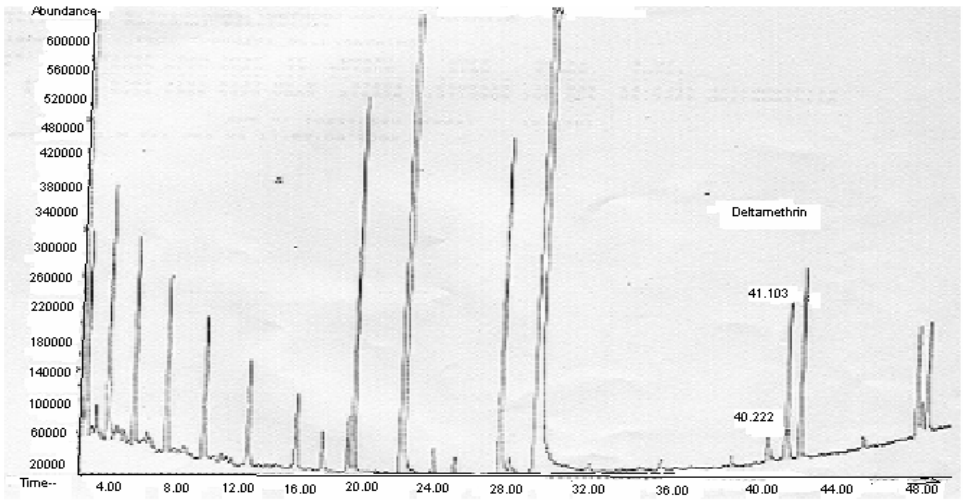


Figure 7. GC-MS chromatogram of deltamethrin extracted in acetone from the mosquito net

Hence, further GC-MS analysis was carried out with xylene solution, which is a common solvent for both deltamethrin and polyethylene. The results of GC-MS analysis of xylene solution of the previously acetone extracted net sample indicate that the net sample contains 1230 mg/kg of deltamethrin (Figure 8). Since the solubility of deltamethrin in xylene is reported to be 25 g/100 g, it is concluded that while dissolving the polymer in boiling xylene, all the deltamethrin was also dissolved in xylene. The polymer settled down on cooling, while the deltamethrin remained dissolved in xylene.

Since the acetone extract of the net sample contained 103 mg/kg of deltamethrin and the xylene extract of previously acetone extracted net sample contained 1230 mg/kg, the total amount of deltamethrin in the net sample is 1333 mg/kg.

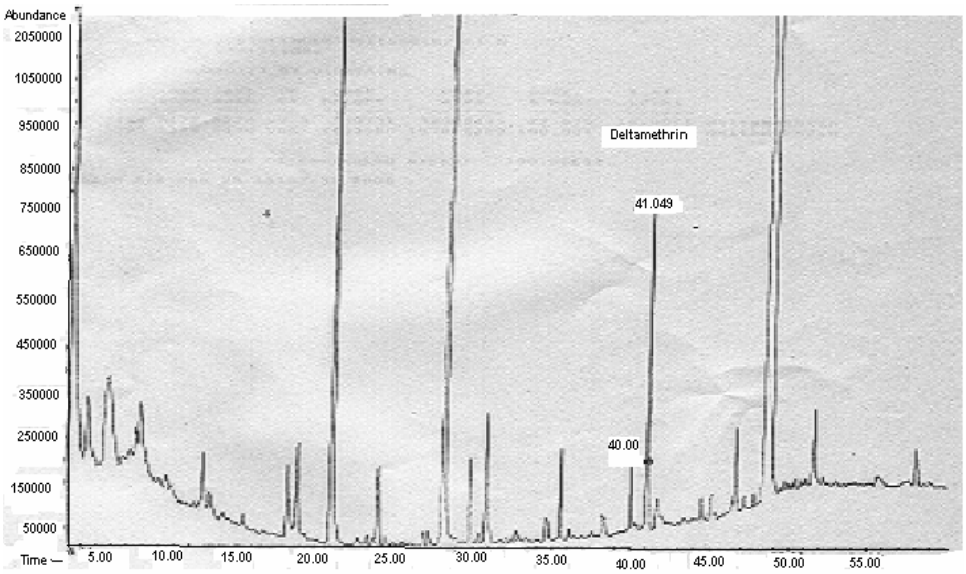


Figure 8. GC-MS chromatogram of deltamethrin extracted in xylene from the acetone extracted mosquito net

Since the content of deltamethrin reported in the xylene solution is greater than that extracted in acetone, it clearly indicates that deltamethrin is incorporated in the material of construction and is not merely coated on the surface. The results are summarized in Table 1.

Table 1. Deltamethrin content as determined by various experimental methods using GC-MS

S.No.	Sample preparation	Deltamethrin content, mg/kg
1.	Acetone extract of net sample	103
2.	Xylene solution of previously acetone extracted net sample	1230
3.	**Total Deltamethrin content**	**1333**

Hence, from the analysis of the sample of mosquito net, it is concluded that the material of construction of the net is polyethylene and total amount of 1333 mg/kg of deltamethrin is coated as well as incorporated in the matrix of polyethylene.

Conclusion

- The material of construction of mosquito net can be identified using DSC technique and it was found to be polyethylene.
- The qualitative and quantitative determination of insecticide present in the mosquito net can be carried out using HPLC and GC-MS techniques.
- The mode of incorporation of deltamethrin in the mosquito net can be assessed by selection of suitable solvent-non solvent systems and then conducting GC-MS.
- Total amount of deltamethrin in mosquito net was found to be 1333 mg/kg.
- Quality standards for mosquito nets should be developed.
- For effective and long-tem action of mosquito repellency, the mosquito repellent chemical should be incorporated in the bulk of the net material.

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