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**MASS SPECTRAL CONFIRMATION OF THE  
ISOMERIC CONVERSION OF DELTAMETHRIN**

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NWRI CONTRIBUTION No. 86-198

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Mass Spectral Confirmation of the Isomeric Conversion of  
Deltamethrin

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Executive Summary:

One route of degradation of the pesticide deltamethrin is isomeric conversion. Field and laboratory prepared samples were analyzed by GC/MS to provide confirmation that this conversion had occurred.

Management Perspective:

Pyrethoid insecticides such as deltamethrin are very toxic to many forms of aquatic life. This investigation forms part of a comprehensive field study into the aquatic fate of deltamethrin. The results presented confirm one degradation pathway of deltamethrin. The importance of this pathway in controlling deltamethrin concentration levels in receiving waters will be evaluated when the remainder of the field samples are analyzed.

Confirmation par spectroscopie de masse de la conversion  
isométrique de la deltaméthrine

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Résumé :

La conversion isomérique est l'une des détériorations possibles de la deltaméthrine. Des échantillons préparés sur le terrain et en laboratoire ont été analysés par CG/SM afin de confirmer qu'il y a eu conversion.

Perspective-gestion :

Les insecticides à base de pyréthoïde comme la deltaméthrine sont très toxiques pour bien des formes d'organismes aquatiques. Cette étude fait partie d'une étude détaillée sur le terrain relativement aux transformations aquatiques de la deltaméthrine. Les résultats présentés confirment un mode de dégradation de la deltaméthrine dont l'importance, en ce qui a trait au contrôle des concentrations de deltaméthrine dans les eaux réceptrices, sera évaluée lorsque tous les autres échantillons auront été analysés.

## Introduction :

Les insecticides à base de pyréthroïde sont reconnus comme étant des pesticides très puissants. Le "Decis 2.5 E.C.", Hoechst Canada Inc., un pyréthroïde synthétique actif contre les parasites de nombreuses cultures, contient l'isomère d-cis de la deltaméthrine [(S)-alpha-cyano-3-phénoxybenzyle(1R)-cis-3(2,2-dibromovinyle)-2,2-diméthylcyclopropanecarboxylate]. L'isomérisation est un mode de dégradation de la deltaméthrine. Après application aérienne de la formulation de "Decis", un extrait d'un filtre de fibres de verre utilisé pour recueillir du produit pulvérisé a donné un pic inconnu au cours de l'analyse chromatographique en phase gazeuse. Les temps de rétention obtenus suggèrent que ce composé est un isomère de la deltaméthrine. Cet échantillon et un échantillon de la deltaméthrine isomérisée au laboratoire ont été utilisés pour étudier le spectre de la masse du composé inconnu.

### Introduction:

Pyrethroid insecticides are recognized as highly efficient pest control agents. "Decis 2.5 E.C.", "Hoechst Canada Inc.", a synthetic pyrethroid active against several crop pests, contains the d-cis isomer of deltamethrin [(S)-alpha-cyano-3-phenoxybenzyl (1R)-cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate]. One route of decomposition of deltamethrin is isomerization. Following aerial application of the "Decis" formulation, an extract from a glass fibre filter used to collect spray drift showed an unknown peak during gas chromatographic analysis. Retention times suggested this compound to be an isomer of deltamethrin. This sample and a sample of deltamethrin isomerized in the laboratory were used to investigate the mass spectra of the unknown compound.

### Methods:

Two samples were provided by Air and Water Branch, Conservation and Protection Service, Dartmouth, Nova Scotia. Sample A was a concentrated extract from a glass fibre filter which collected spray drift. Sample B was a reference standard of deltamethrin treated to produce isomeric conversion. Samples of "Decis" and deltamethrin were also prepared for analysis.

Each sample was analyzed by gas chromatography / mass spectrometry (GC/MS) using a Carlo-Erba 4160 gas chromatograph with an on-column injector and a Riber Nermag R1010 mass spectrometer. The gas chromatograph, containing a 30m. x 32mm. DB-5 fused silica column, after an initial hold of 2 minutes at 220°C. was programmed at 8°C. per minute to 290°C. and held at this final temperature for 25 minutes. Mass spectra were obtained in both electron ionization (E.I.) mode and negative chemical ionization (-ve. C.I.) mode.

In E.I. mode the ionization potential was 70 ev. with a filament current of 200 ma. and a source temperature of 280°C.

Using methane at a source pressure of  $2.0 \times 10^{-2}$  torr. in the negative chemical ionization mode, the ionization potential was 90 ev. with a filament current of 0.05 ma. and a source temperature of 100°C.

Results:

Deltamethrin

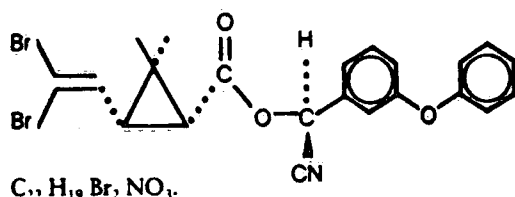


Figure 1 shows the spectra of deltamethrin in the E.I. mode. The prominent feature at  $m/z$  251, 253, 255 is due to simple cleavage of the C-C carboxylate carbon bond and the isotopic abundance of the two bromine atoms. In the negative C.I. mode, Figure 2, the prominent cluster at  $m/z$  295, 297, 299 is indicative of cleavage at the carbonyl group (C-O bond).

For stereoisomers the mass spectra of the two compounds should be the same and this is illustrated in Figures 3a,3b for sample A and Figures 4a,4b for sample B. The same fragmentation pattern is evident in the E.I. mode for the unknown and deltamethrin. The negative chemical ionization spectra of the two major components of sample A (Fig. 5a,5b) and sample B (Fig 6a,6b) provides additional confirmation that these compounds are deltamethrin and its isomer, suspected to be the stereoisomer alpha R deltamethrin.

The GC/MS spectra of the aerial spray "Decis", E.I. mode Fig. 7a,7b, shows the existence of the isomer in the product. From the reconstructed GC/MS chromatogram this commercial formulation was determined to contain approximately 5% of the isomer.

The results of the mass spectra investigation confirm the identity of the unknown in the field and laboratory samples to be the isomer of deltamethrin. Further, although the spray product contained a small amount of the isomer, the total ion chromatogram of the field sample showed the compounds to be of near equal concentration (Fig. 8) and thus significant isomerization had occurred in the field.

References:

B.D. Hill, 1983, Persistence of Deltamethrin in a Lethbridge Sandy Clay Loam, J. Environ. Sci. Health, B18(6), 691-703.

National Research Council of Canada, 1986, Pyrethroids: Their Effects on Aquatic and Terrestrial Ecosystems, NRCC NO. 24376

Roussel Uclaf, 1982, Deltamethrin Monograph

Figure 1 Deltamethrin E.I. Mode

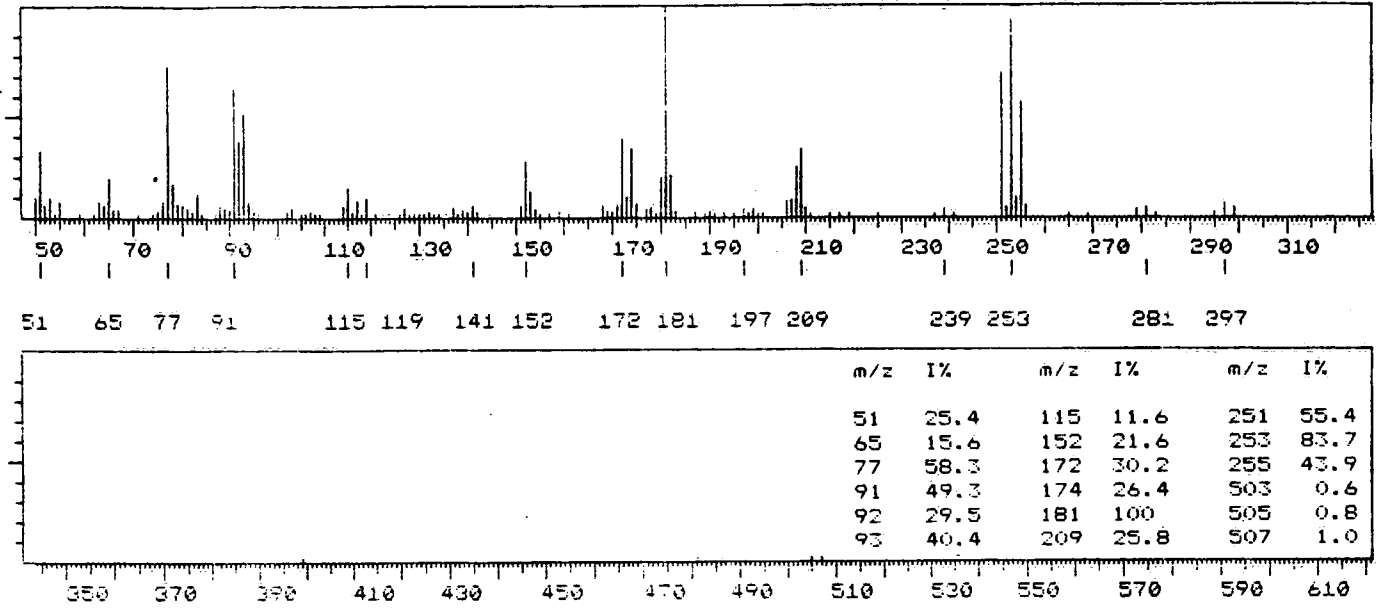


Figure 2 Deltamethrin Negative C.I. Mode

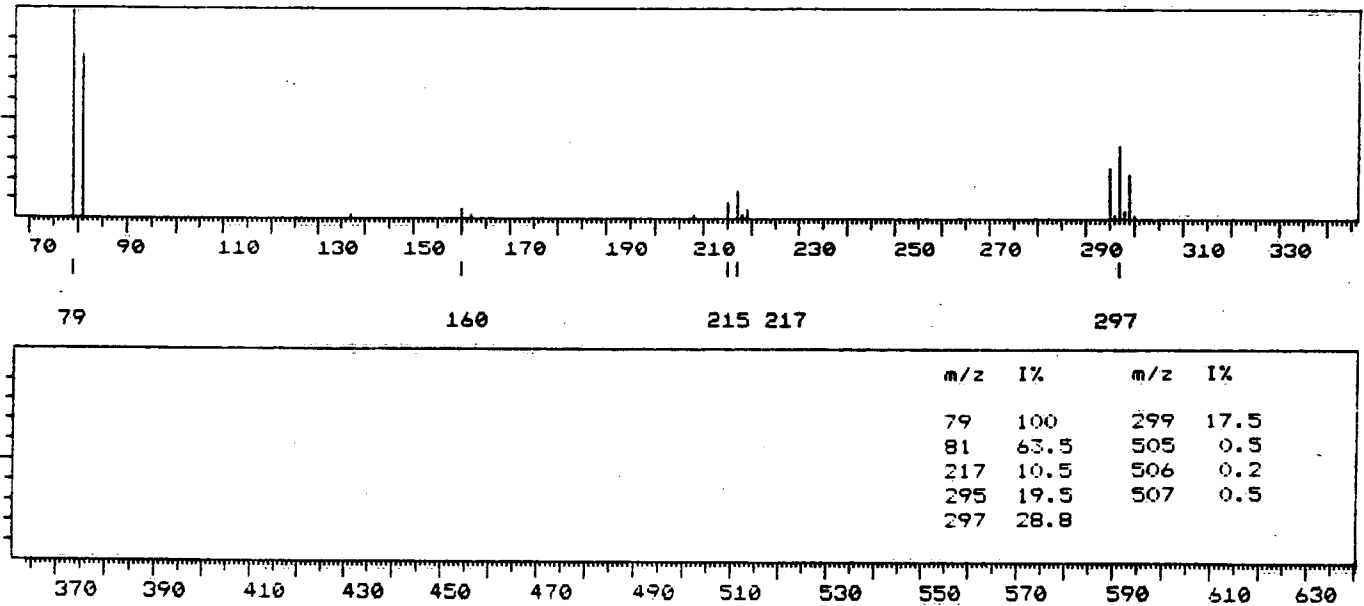




Figure 3a Sample A Unknown E.I. Mode

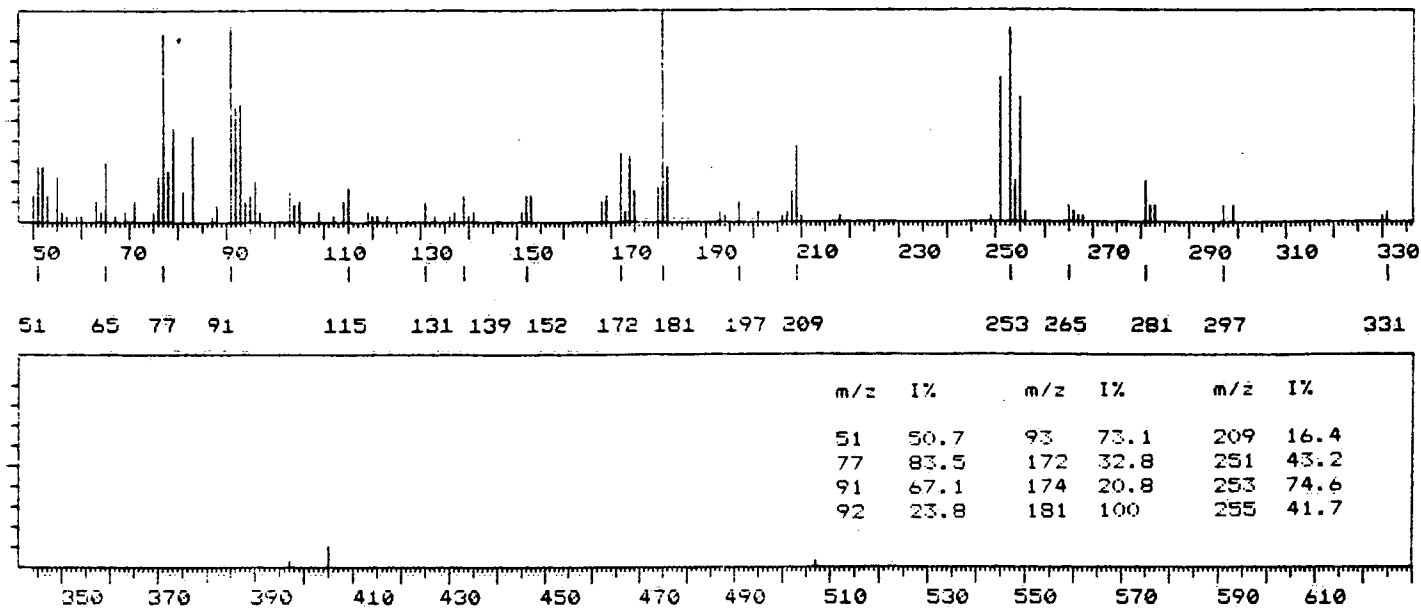


Figure 3b Sample A Deltamethrin E.I. Mode

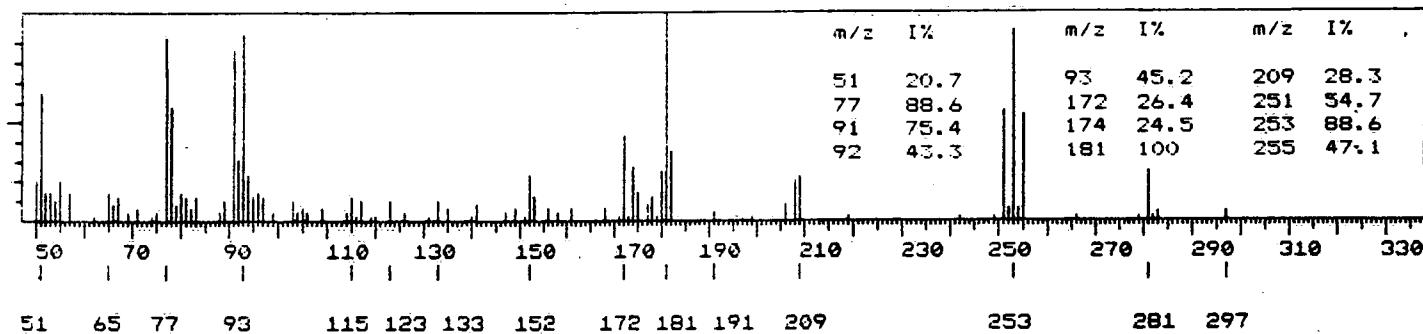


Figure 4a Sample B Unknown E.I. Mode

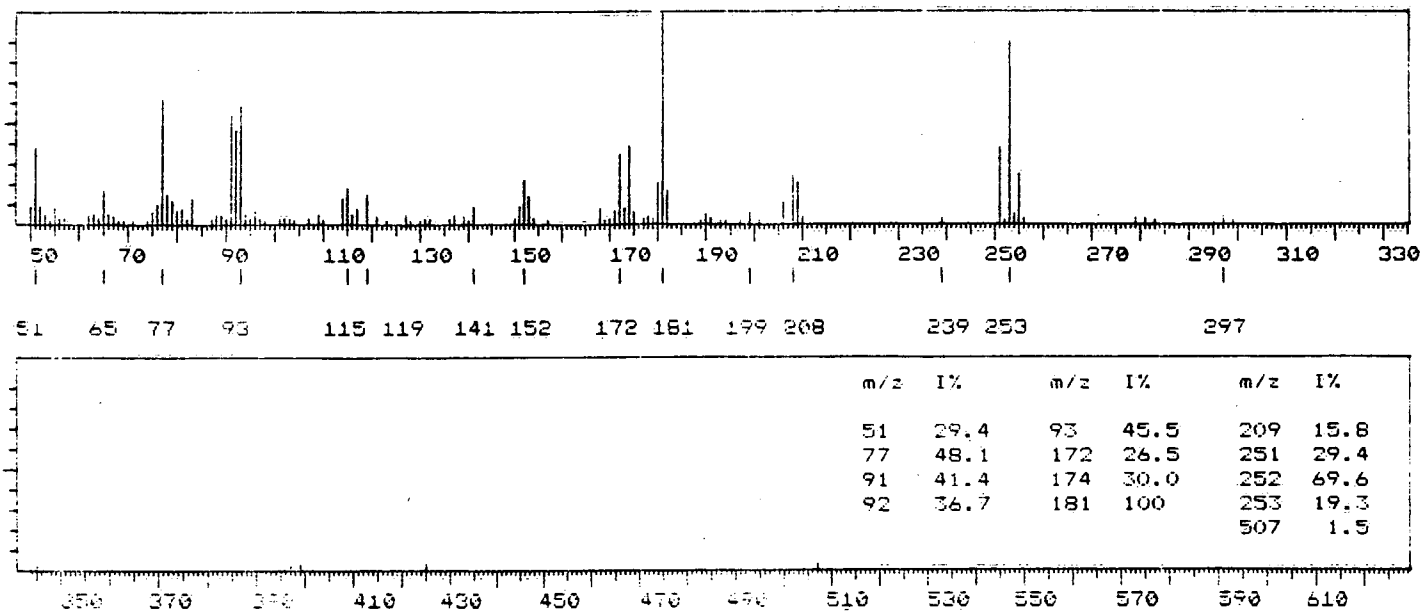


Figure 4b Sample B Deltamethrin E.I. Mode

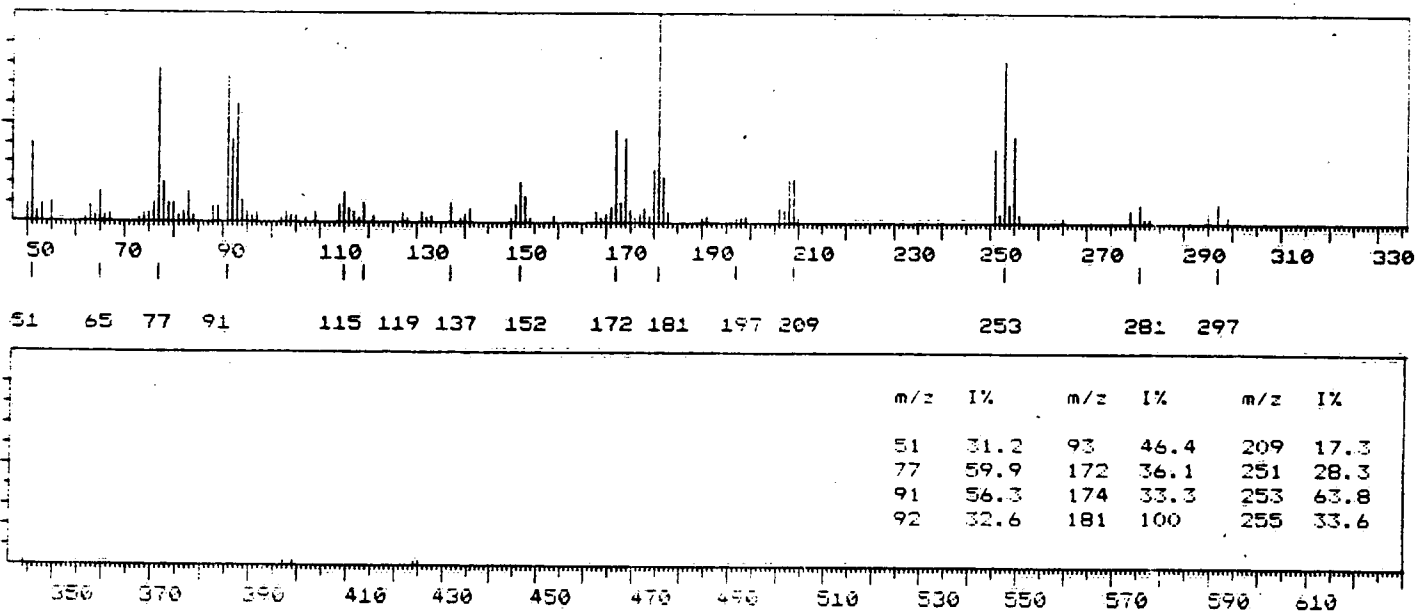


Figure 5a Sample A Unknown -ve. C.I. Mode

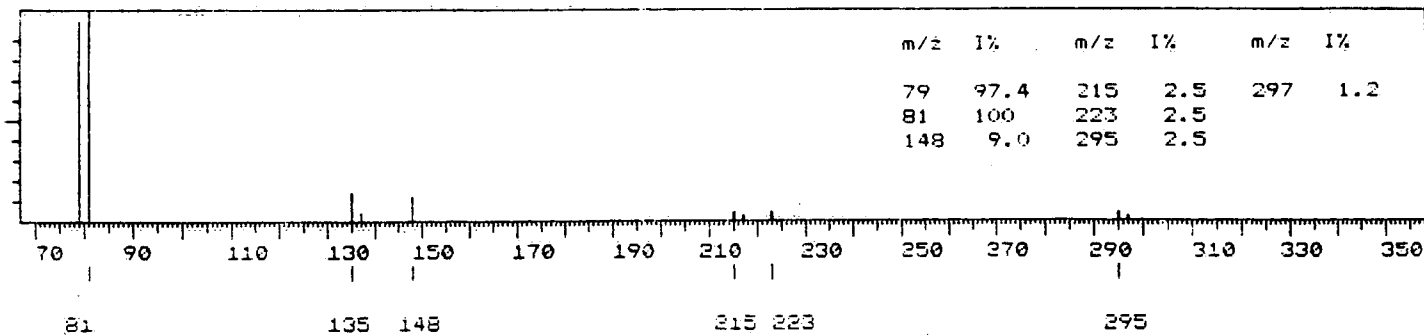


Figure 5b Sample A Deltamethrin -ve. C.I. Mode

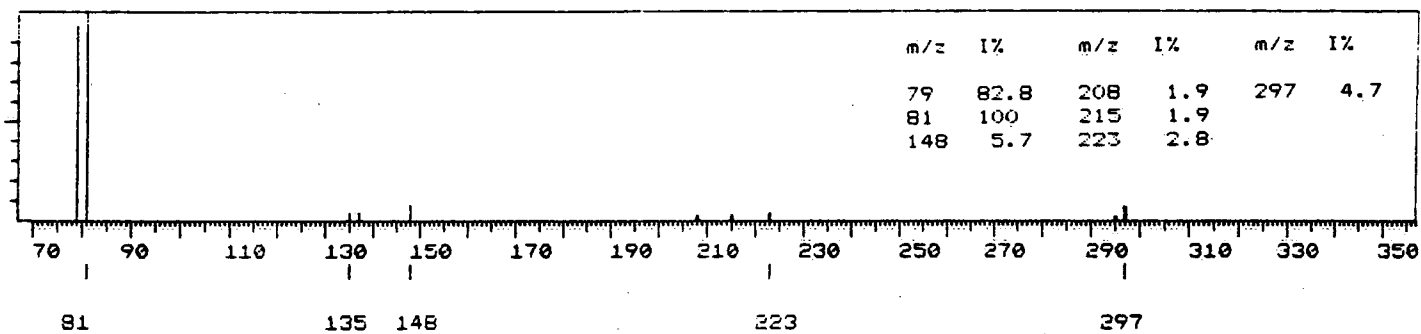


Figure 6a Sample B Unknown -ve. C.I. Mode

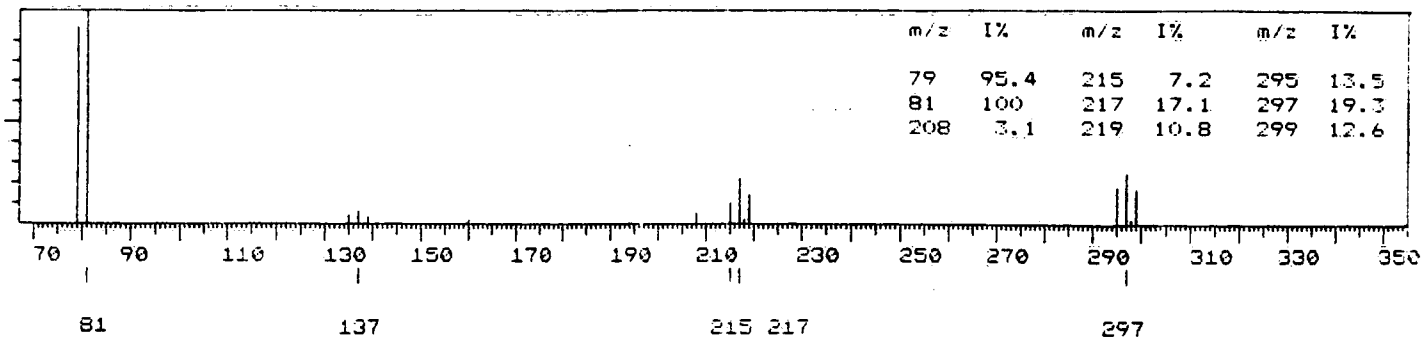


Figure 6b Sample B Deltamethrin -ve. C.I. Mode

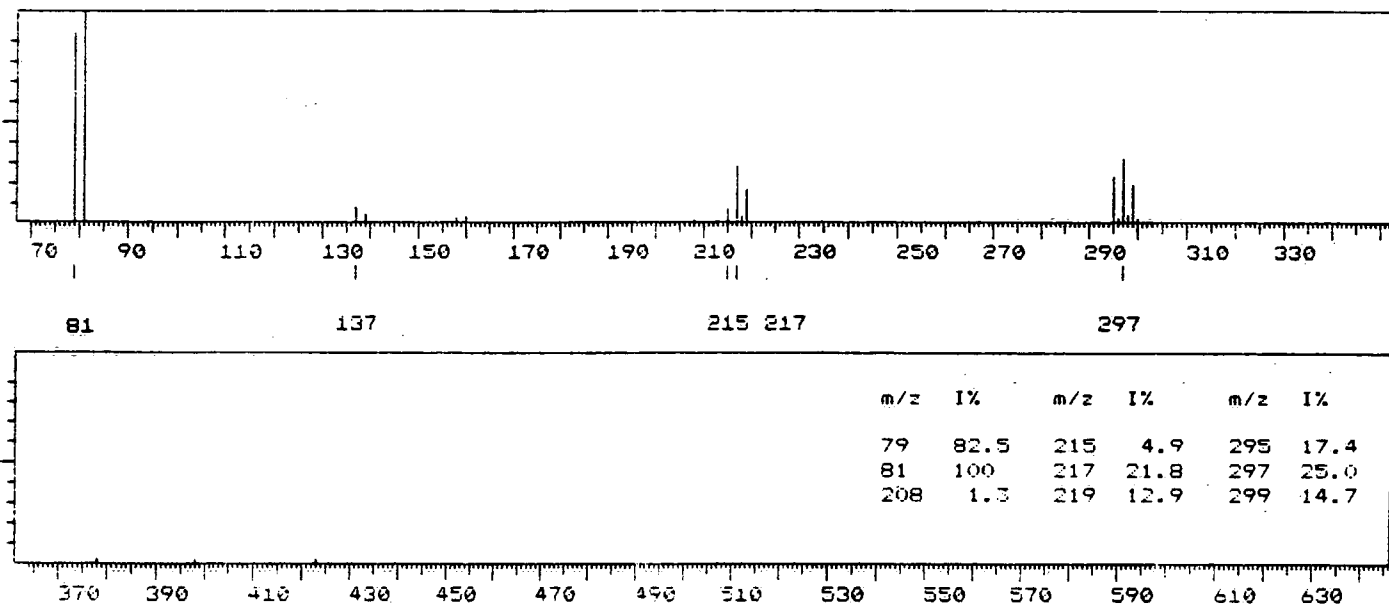


Figure 7a "Decis" Deltamethrin Isomer E.I. Mode

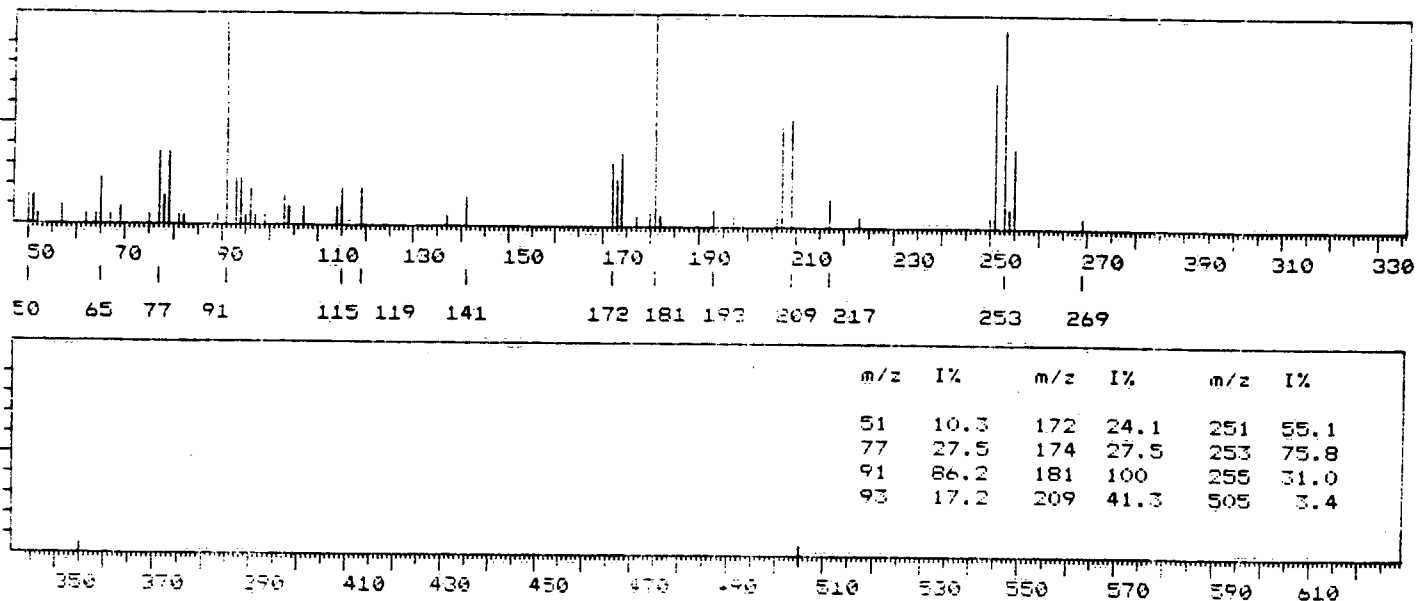
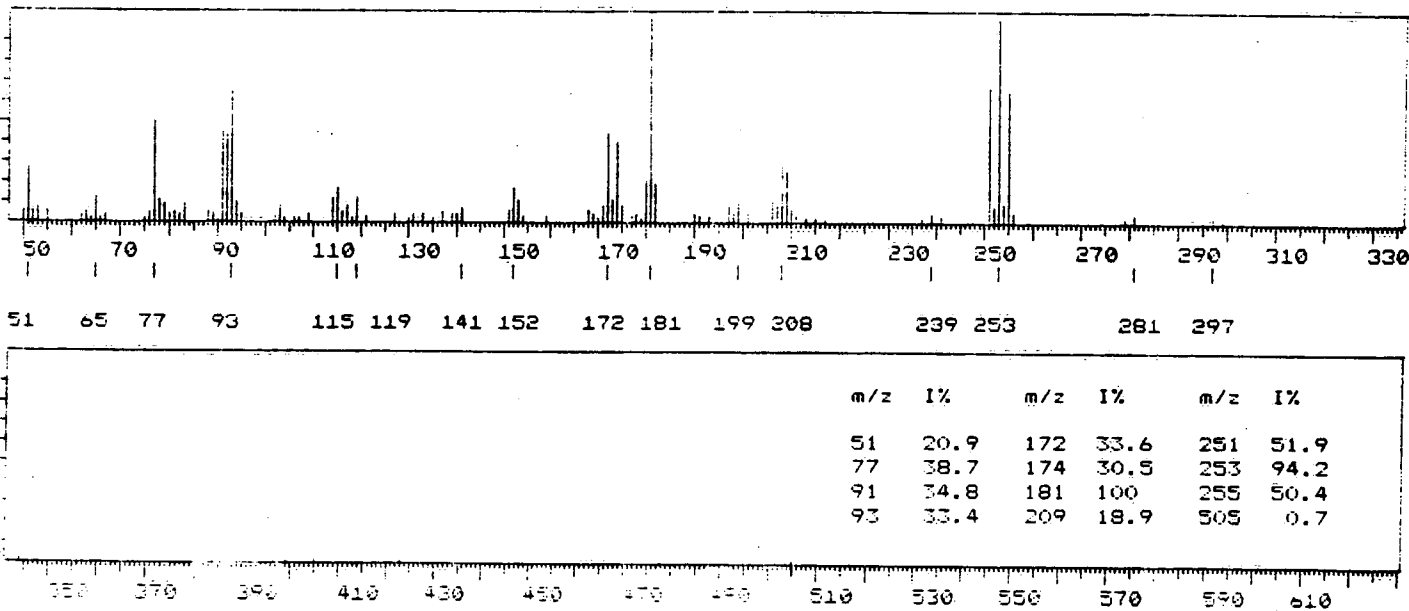
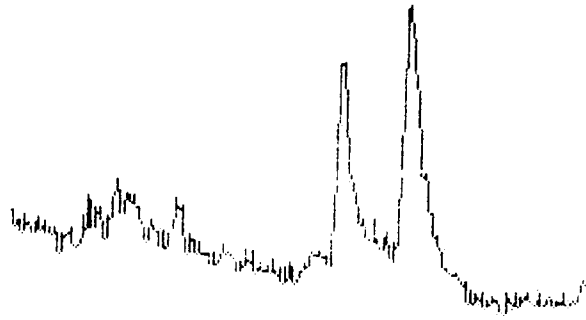


Figure 7b "Decis" Deltamethrin E.I. Mode

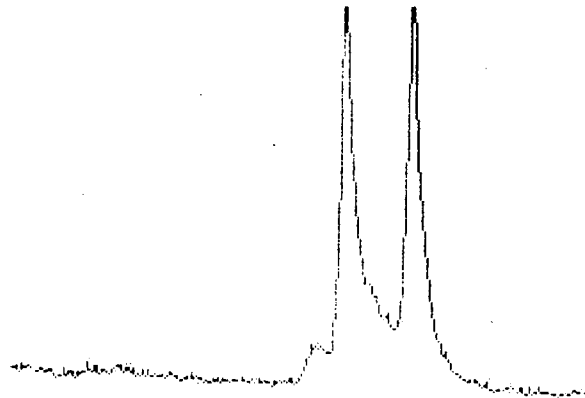


Sample A Total Ion Chromatogram E.I. Mode

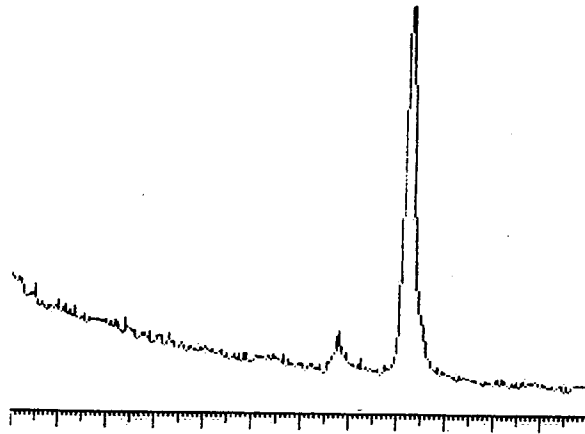
Figure 8



Sample B Total Ion Chromatogram E.I. Mode



"Decis" Total Ion Chromatogram E.I. Mode



Deltamethrin Total Ion Chromatogram E.I. Mode

