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Research Paper

A Novel Method for Determination of Deltamethrin Residues in Aquatic Tox Medium followed by Gas Chromatography Mass Spectrometry Method

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Abstract: *A simple and sensitive validated GCMS-EI analytical method was developed for the determination of deltamethrin residues in different aquatic tox mediums. The tox mediums were those which provide nutrients and help the growth of different aquatic organisms for their survival and multiplication. The constituent of different mediums includes blended water for fish, M4 Medium for Daphnia magna and OECD TG 201 medium for Alga. The method was validated using in aquatic tox samples spiked with deltamethrin sample at different concentration levels (0.5 and 5.0 mg/L). Average recoveries (using each concentration six replicates) ranged 87-94%, with relative standard deviations less than 2%, calibration solutions concentration in the range 0.5-100 mg/L and limit of detection (LOD) and limit of quantification (LOQ) were 0.2 mg/L and 0.5 mg/L respectively. The proposed method can be applied successfully for the determination of deltamethrin residues in different aquatic solutions.*

Keywords: Deltamethrin, LOD, LOQ, Aquatic Tox medium and GC-MS-EI method.

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1. Introduction

Deltamethrin is an insecticide belonging to the pyrethroid family[1-3]. Pyrethroids are man- made versions of pyrethrins, natural insecticides from chrysanthemum flowers. Deltamethrin is used outdoors on lawns, ornamental gardens, golf courses, and indoors as a spot or crack and crevice treatment. In its purest form, deltamethrin is colorless or light beige crystals that have no odor. Deltamethrin was first described in 1974 and entered the market place in 1978.

Deltamethrin[4] is in a veriety of products used to kill a wide range of insects. Deltamethrin can be formulated in insecticide products as aerosols, sprays, dusts, granules and wettable powders. The illegal, unregistered product known as “Chinese Chalk” or “Miraculous Chalk” often contains deltamethrin as the active ingredient. “Chinese Chalk”, “Miraculous Chalk”, and products like them are not registered for use in the United States and illegal products such as these should be avoided at all times.When deltamethrin gets on the skin, it can cause skin sensations like tingling, itching, burning or numbness at that spot. These sensations usually go away within 48 hours. Deltamethrin can be mildly irritating if it gets in the eye. If enough deltamethrin is breathed in, it can cause headaches and dizziness. Although not common, individuals who have ingested large amounts of deltamethrin[5-8] have experienced nausea, vomiting, abdominal pain, and muscle twitches. Deltamethrin is low in toxicity when it is touched or breathed in and is low to moderately toxic if eaten.

Deltamethrin is moderately to highly toxic to fish under laboratory conditions. However, when products are used according to the label, deltamethrin is less likely to affect fish. This is because deltamethrin is practically non-toxic to birds when they eat it. Deltamethrin is practically non-toxic to birds when they eat it. Deltamethrin is highly toxic to honeybees under laboratory conditions. It did not harm bees in field studies, and formulated products actually had a repellant effect that lasted for 2-3 hours. Earthworms were not affected when soil was treated with deltamethrin. The current study explains about a suitable method for the determination of deltamethrin in aquatic tox mediums [Fish Medium (1:1.7 Reverse osmosis water and well water), Daphnia (M4 Medium)[11-12] and Algae medium (OECD – TG201 Medium)[13-14]. So, the present research deltamethrin which analysis by GC-MS-EI method.

2. Experimental Procedures

GC-MS Conditions for the Determination of Deltamethrin

The configuration of GC–MS system used includes a (Agilent/ 7890A) gas chromatograph coupled with 5975C Mass-Selective Detection (MSD) and Chemstation software, the detector was set in selective ion monitoring mode (EI) mode. The ions m/z 505, m/z 253 and m/z 181 were used as qualifier ions (**Figure 2**) and the target ion used for the measurement was the ion at m/z 181. The Deltamethrin peak separation was obtained on a DB-1 capillary column (30 m length, 0.25 mm internal diameter, 0.25µm film thickness). The injection system was operated in split mode with a split ratio of 20:1. The injector and the transfer line temperatures were 280ºC and 300ºC, respectively. The oven temperature program was 250ºC, held constant for 5 min and ramp at 20ºC /min raised the column temperature up to 300ºC, held constant for 10.0 min. The carrier gas used was helium (GC grade) at a flow rate of 2.0 ml /min and the sample volume injected onto the column was 2.0 µL. An Agilent Chemstation Software was used for acquisition of data and calculation of peak area. The carrier gas used was helium (GC grade) at a flow rate of 1.0 ml /min and the sample volume injected onto the column was 2.0 µL. An Agilent Chemstation Software Software was used for acquisition of data and calculation of peak areas. The retention time of deltamethrin was about 10.0 min and the total time of chromatographic analysis was 18 min.

Analytical Standards, Reagents and Solutions

The analytical standard of Deltamethrin was obtained from was purchased from sigma Aldrich.

The hydrochloric acid, ethylene diaminetetraacetic acid disodium salt (EDTA) used were AR grade, n- Hexane HPLC grade were purchased form rankem.

Standard Stock Solutions

The deltamethrin standard stock solution was individually prepared in n-Hexane at a concentration level 1000 mg/L and stored in a freezer at -18°C. The stock standard solution was used for up to 3 months. Suitable concentrations of working standards were prepared from the stock solutions by dilution using n-Hexane, immediately prior to sample preparation.

Sample Preparation

The samples were allowed to stand at room temperature for one hour, before it was kept at refrigerator condition, until analysis.

Test Medium

Test medium is a constitute of different macro nutrients, salts and vitamins. This helps in the survival of different organisms during exposure of different compounds.

Blended Water: A mixture of well water and reverse osmosis water in the ratio of 1:1.7 liters. This provides enough nutrients for the survival of fish during test item exposure.

M4 Medium: It is a combination of Trace elements, Marco nutrients and vitamins. The composition was given in **Table 1.**

OECD TG 201 Medium: This helps in the growth of green alga as it provides the required nutrients and useful salts which helps in their growth and multiplication. The composition was given in **Table 2.**

Table 1: Preparation of M4 Medium Nutrients (Daphnia Magna)

S. No.	Chemical Name	Formula	mg/l
Trace elements			
1	Boric acid	H_3BO_3	57190
2	Manganese chloride	$MnCl_2.4H_2O$	7210
3	Lithium chloride	LiCl	6120
4	Rubidium chloride	RbCl	1420
5	Strontium chloride	$SrCl_2.6H_2O$	3040
6	Sodium bromide	NaBr	320
7	Sodium molybdate	$Na_2MoO_4.2H_2O$	1230
8	Cupric chloride	$CuCl_2.2H_2O$	335
9	Zinc chloride	$ZnCl_2$	260
10	Cobalt chloride	$CoCl_2.6H_2O$	200
11	Potassium iodide	KI	65
12	Sodium selinite	Na_2SeO_3	43.8
13	Ammonium vanadate	NH_4VO_3	11.5
14	EDTA*	$Na_2EDTA.2H_2O$	5000
15	Ferrous sulphate*	$FeSO_4.7H_2O$	1991
Macro nutrients			
16	Calcium chloride	$CaCl_2.H_2O$	293800

17	Magnesium sulphate	$MgSO_4.7H_2O$	246600
18	Potassium chloride	KCl	58000
19	Sodium hydrogen carbonate	$NaHCO_3$	64800
20	Sodium silicate	$Na_2SiO_3.9H_2O$	50000
21	Sodium nitrate	$NaNO_3$	2740
22	Potassium phosphate monobasic	KH_2PO_4	1430
23	Potassium phosphate dibasic	K_2HPO_4	1840
Vitamin stock solutions			
24	Thiamine hydrochloride	--------	750
25	Cyanocobalamine (B12)	--------	10
26	Biotin	--------	7.5

* Both EDTA and Ferrous sulphate solution were prepared separately, poured together and autoclaved

Table 2: Preparation of OECD TG 201 Medium (green alga)

S. No.	Composition	mg/L
1.	$NaHCO_3$ (Sodium Hydrogen Carbonate)	50.0
2.	NH_4Cl (Ammonium Chloride)	15.0
3.	$MgCl_2.6H_2O$ (Magnesium Chloride)	12.0
4.	$CaCl_2.2H_2O$ (Calcium Chloride)	18.0
5.	$MgSO_4.7H_2O$ (Magnesium Sulphate)	15.0
6.	KH_2PO_4 (Potassium Dihydrogen Phosphate)	1.60
7.	$FeCl_3.6H_2O$ (Ferric Chloride)	0.064
8.	$Na_2EDTA.2H_2O$ (E.D.T.A. Disodium Salt)	0.100
9.	H_3BO_3 (Boric Acid)	0.185
10.	$MnCl_2.4H_2O$ (Manganese (II) Chloride)	0.415
11.	$ZnCl_2$ (Zinc Chloride)	0.0030
12.	$CoCl_2.6H_2O$ (Cobaltous Chloride)	0.0015
13.	$Na_2MoO_4.2H_2O$ (Sodium Molybdate)	0.0070
14.	$CuCl_2.2H_2O$ (Copper (II) Chloride)	0.00001

Extraction Procedure

The 100mL sample was shaken vigorously and transferred to a separating funnel. To this, 50 ml of n-hexane was added and shaken for 100 times for phase separation [9-10]. The separated organic layer was collected into a beaker and then again 50 mL of n-Hexane was added to the aqueous layer and shaken for 100 times and the separated organic layer was collected into the same beaker. The organic layer was filtered through sodium sulfate to remove excess moisture. The filtrate was injected into GC-MS.

Method Validation

Method validation ensures analysis credibility. In this study, the parameters accuracy, precision, linearity and limits of detection (LOD) and quantification (LOQ) were considered. The accuracy of

the method was determined by recovery tests, using samples spiked at concentration levels of 0.2 and 0.5 mg/L. Linearity was determined by different known concentrations (0.5, 1.0, 5.0, 10.0, 50.0 and 100.0 mg/L) were prepared by diluting the stock solution. The limit of detection (LOD, mg/L) was determined as the lowest concentration giving a response of 3 times the baseline noise defined from the analysis of control (untreated) sample. The limit of quantification (LOQ, mg/L) was determined as the lowest concentration of a given fungicide giving a response of 10 times the baseline noise.

3. Results and Discussion

Specificity

Specificity of the method was checked by injecting n- Hexane, standard, and extracts of media control. From the specificity of the method, it was concluded that there was no significant interference observed. To interfere with the analysis of deltamethrin residues shown in **Fig.2 and 3.** Furthermore, the retention time of deltamethrin was about 10.0 min.

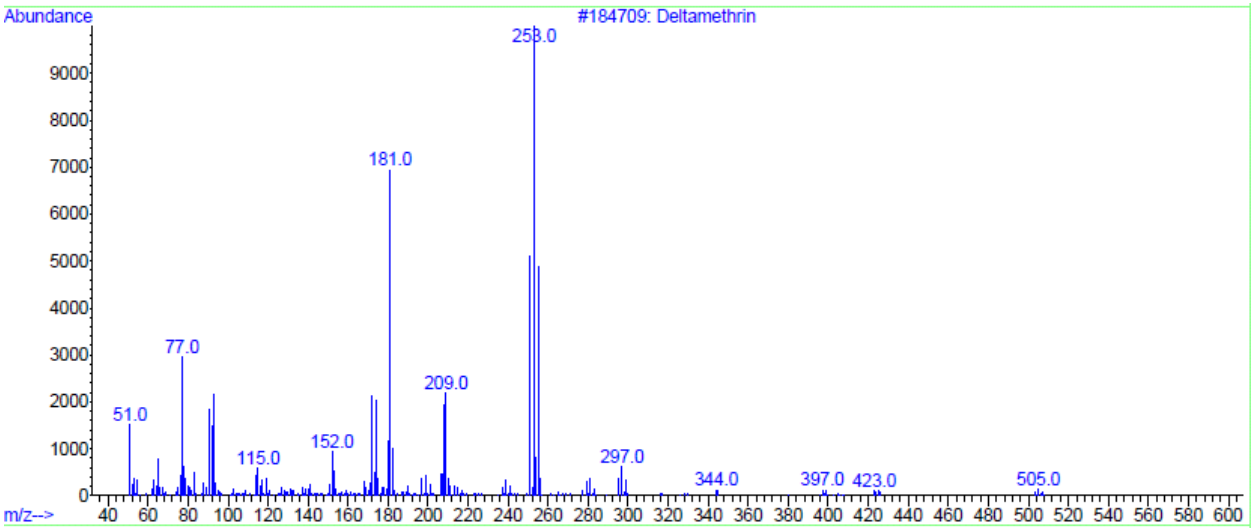

Figure 2: Representative GC-MS scanned spectrum of deltamethrin tested from fortified medium

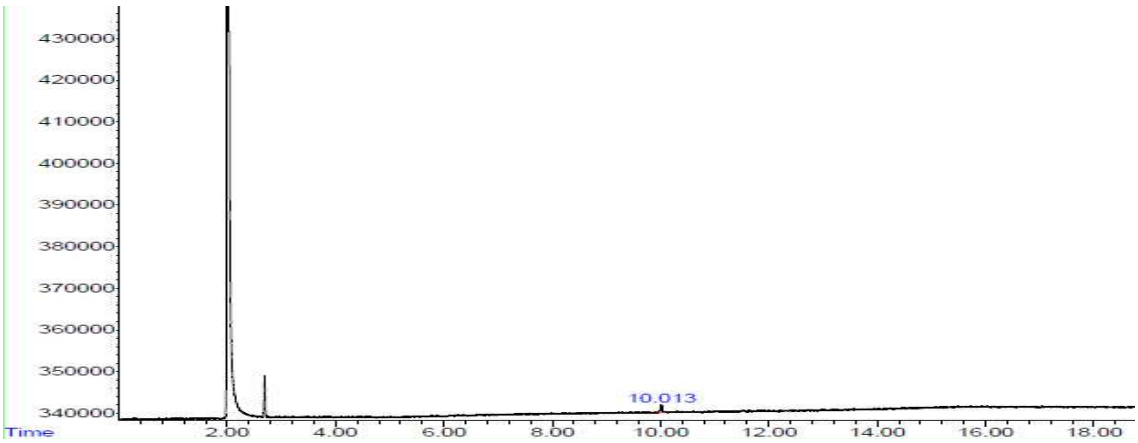

Figure 3: Representative GC-MS Chromatogram at fortification level of 0.5 mg/L

Linearity

Different known concentrations of deltamethrin standard (0.5, 1.0, 5.0, 10.0, 50.0 and 100.0 mg/L) were prepared in n- Hexane by diluting the stock solution. Each solution was prepared in triplicate. Injected the standard solutions and measured the peak area. A calibration curve has been plotted of concentration of the standards injected versus area observed and the linearity of method was evaluated by analyzing six solutions. The peak areas obtained from different concentrations of deltamethrin were used to calculate linear regression equation. This was Y=2150.15X + 62.57, with correlation coefficient of 0.9999. A calibration curve showed in **Fig. 1.**

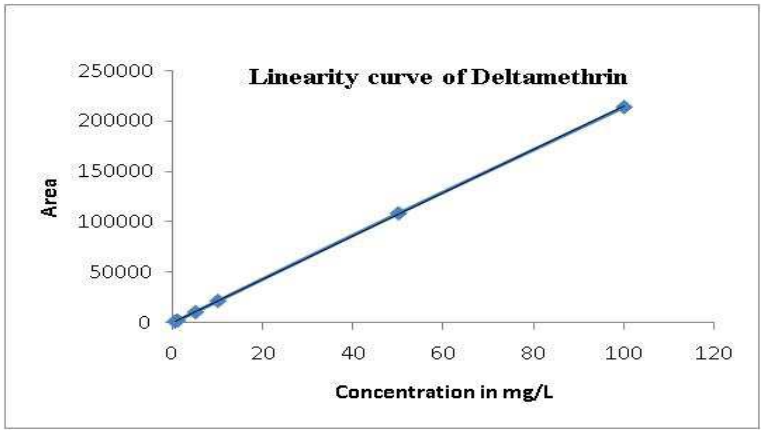

Fig.1: Representative Calibration curve of Deltamethrin

Accuracy and Precision

Recovery studies were carried out at 0.5 and 5.0 mg/L fortification levels for deltamethrin in different tox medium. The recovery data and relative standard deviation values obtained by this method are summarized in **Table 3.**

These numbers were calculated from four (6) replicate analyses of given sample made by a single analyst on one day. The repeatability of method satisfactory (RSDs<2 %).

Table 3: Recoveries of deltamethrin sample in different mediums

Medium	Fortification level (mg/L)	Deltamethrin	
		*Mean Recovery (%)	% RSD
Blended water	0.5	88.71	1.98
	5.0	93.25	1.36
OECD TG 201	0.5	88.25	1.92
	5.0	94.01	1.28
M4	0.5	87.28	1.87

	5.0	92.79	1.19

*Average of five replications

Detection and Quantification Limits

The limit of quantification was determined to be 0.5 mg/L. The quantitation limit was defined as the lowest fortification level evaluated at which acceptable average recoveries (87-94%, RSD<2%) were achieved. This quantitation limit also reflects the fortification level at which an analyte peak is consistently generated at approximately 10 times the baseline noise in the chromatogram. The limit of detection was determined to be 0. 2 mg/L at a level of approximately three times the back ground of control injection around the retention time of the peak of interest.

4. Conclusion

Appropriate analytical methodology for the determination of deltamethrin residues in aquatic tox medium (meant for fish, Daphnia, Algae and lemna) has been established and validated. Satisfactory validation parameters such as linearity, recovery, precision and very low limits were obtained and according to the SANCO guidelines. The proposed analytical procedure could satisfactorily be useful for regular monitoring of deltamethrin residues in different tox medium samples (meant for fish, Daphnia and Algae).

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