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Determination of Resmethrin in Corn Silk Matrix by Gas Chromatography-Flame Ionization Detector (GC-FID)

Hakan SERBEST*[1]

Abstract

The use of pesticides provides benefits such as growing food products necessary for life, sustainability of production efficiency and prevention of diseases caused by pests. However, these benefits can turn into negative effects for humans and other living organisms with the use of pesticides in inappropriate doses and application methods. In this study, it was aimed to determine resmethrin, which belongs to the insecticide class, by gas chromatography-flame ionization detector (GC-FID) method. Hence, a suitable temperature program was utilized to determine resmethrin at a certain retention time. Limit of detection (LOD) and limit of quantification (LOQ) values were recorded as 0.02 and 0.08 mg/L under the proposed conditions, respectively. After corn silk sample was extracted using acetonitrile, analytical measurements were carried out to investigate the presence of resmethrin. There was no analytical signal detected that belonged to resmethrin in the analyzed sample. Recovery experiments were performed using external calibration method with spiked samples at three different concentrations and good percent recovery results were obtained between 93 and 97%.

Keywords: Resmethrin, insecticide, pesticide, GC-FID, corn silk

1. INTRODUCTION

The use of pesticides is quite common in agriculture to preserve crop quality and yield, and in public health to prevent various diseases. Consumption of chemical pesticides helps to increase the yield at harvest time by protecting the crops, but it causes negative effects on species other than target organisms [1, 2]. The production rate of pesticides increased considerably in the 1940’s as dichlorodiphenyltrichloroethane (DDT) showed good results against insects that cause diseases such as typhus and malaria [3]. Over time, after understanding the toxic effects of DDT on living organisms, synthetic pyrethroids compounds were developed by British and Japanese chemists in the 1970s to meet the demand for a pesticide with better environmental properties and safer than DDT [1, 4]. Pesticides can be grouped into different classes based on the chemical type, target organisms, mechanism of action and type of application. According to their chemical types, they are categorized into four main groups

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known as organochlorine pesticides, carbamate pesticides, pyrethroid pesticides and organophosphate pesticides [5-7]. Among the pesticides used for a variety of purposes, such as the protection of crops, fields, and trees, and the control of mosquitoes and other pests, pyrethroids insecticides are synthetic analogs of pyrethrin. The use of pyrethroids has gradually increased over the years with their prominent features such as low toxicity, resistance to environmental conditions and high insecticide activity [8]. Resmethrin, one of the first members of the synthetic pyrethroids, was synthesized as a mixture of four stereoisomers [9]. Resmethrin, which belongs to the Type 1 pyrethroid insecticide group for the control of insects, is generally used against mosquitoes and certain arthropods and whiteflies in agricultural activities [9, 10]. In addition, resmethrin plays an active role as a preventative against insects, especially in products such as flour, wheat, corn and cornmeal [11]. Like all pyrethroids, resmethrin causes changes in the electrical properties of insect neurosecretory neurons. When the insect is exposed to a pyrethroid member, neurons are rapidly and continuously stimulated and trembling begins, then this event ends in paralysis [12, 13]. According to USEPA, resmethrin is currently registered for use in vector control and public health studies to control pests such as mosquitoes, houseflies, and midges [14]. Considering the health effects of Resmethrin, it has been reported that it can cause toxic effects by inhalation, ingestion, and dermal contact [9]. In terms of aquatic organisms, resmethrin and its metabolites may pose an acute risk, as well as adversely affecting the reproductive and developmental activities of living things. Although terrestrial animals have low exposure rate to resmethrin, the risk is increased for non-target species such as honeybees [14]. Therefore, the qualitative/quantitative determination of resmethrin and other pesticide residues in food and environmental samples has a critical importance in preventing their effects on humans and other living organisms.

Chromatography is a frequently used technique for the separation and determination of pesticides and other pollutants and is classified into liquid chromatography (LC) [15] and gas chromatography (GC) [16] according to the physical properties of the mobile phase used [17]. GC which is used as an effective separation of volatile organic compounds, is combined with different detectors such as thermal conductivity detector (TCD) [18], mass spectrometry (MS) [19], electron capture detector (ECD) [20], flame photometric detector (PID) [21], nitrogen phosphorus detector (NPD) [22] and flame ionization detector (FID) [18] for the determination of compounds with high accuracy and precision. A hydrogen flow mixed with carrier gas is used in the FID system. After the mixture is ignited, ionization occurs by burning the analytes. The ions formed are converted into current by the voltage between the flame jet and collector electrodes, and the signal is amplified and detected [23].

In this study, it was aimed to determine resmethrin by GC-FID in cornsilk matrix with high accuracy and precision.

2. MATERIALS AND METHODS

2.1. Instrumentation

Separation and qualitative/quantitative determination of resmethrin was performed using an Agilent 6890N model gas chromatography (GC) system and a flame ionizer detector (FID). A Domnick Hunter model 40H hydrogen generator was employed to produce hydrogen gas, which was delivered to the system at a flow rate of 35 mL/min. Before detection of resmethrin, it was eluted through an HP-5MS column with a length of 30 m, a film thickness of 0.25 μm, and an inner diameter of 250 μm. The total run time was 5.7 min and it was achieved by employing the following oven temperature ramp program: 45 °C/min from 100 °C (initial temperature) to 200 °C and 55 °C/min to 280 °C (2.0 min hold time). The temperature of inlet port was set at 250 °C and 1.0 μL of solutions were injected in splitless mode. Nitrogen was used as carrier gas at a flow rate of 2.2 mL/min. The retention time of resmethrin was determined by injecting different concentrations of standards into the GC-FID system. An ultrasonic bath (Alex Machine) and a vortex (ISOLAB) were used to mix the corn silk sample with acetonitrile. A centrifuge (Hettich) was used for easy separation of the liquid phase.

2.2. Reagents

High purity standard of resmethrin (10453-86-8) was supplied from Dr. Erhrenstorfer (Augsburg – Germany) and dissolved in acetonitrile (Merck – Germany) to prepare a 1000 mg/L stock solution. Standard solutions of resmethrin at different concentrations were prepared by gravimetrically diluting the stock solution in a vial with acetonitrile. Before and after injection, analytical grade ethanol (Merck – Germany) was used to wash the 10 μL GC syringe.

2.3. Samples

Corn silk sample was purchased from an herbal market in İstanbul, Türkiye. Firstly, the corn silks were cut into very small pieces with a sterile cutter to increase surface area. Then, 0.50 g of the cut sample was weighed on a precision scale into a sample tube and acetonitrile was added so that the final weight was 5.0 g. Effective mixing was achieved by successively applying vortex mixing and sonication for 60 seconds. Then, the liquid phase was easily removed from the corn silk by centrifugation and filtration through a 0.45 μm syringe filter. Spiked samples were prepared from extracted corn silk matrix at 8.1, 16.2 and 40.2 mg/L concentrations.

3. RESULTS AND DISCUSSION

All standard solutions and samples were measured for triplicate to determine the precision and repeatability of the method. The average of peak areas of each measurement was used to get calibration plot. Percent recoveries of resmethrin were calculated from spiked samples to determine accuracy of the method.

3.1. Qualitative / quantitative determination of resmethrin

The operating conditions and temperature ramp program mentioned in Section 2.1 were used, and a total run time of 5.7 minutes was obtained for the elution of resmethrin. Measurements were performed for the calibration standard solutions prepared in the linear dynamic range of 0.10 – 163 mg/L. After the resulting peaks were integrated, the peak area values were used to develop a calibration plot that produced a coefficient of determination value equal to 1.000. The ChemStation software was used for data acquisition and evaluation of the signals and retention time of the analyte. The retention time for resmethrin was 4.8 min. The lowest concentration of the calibration plot of resmethrin (0.10 mg/L) was measured seven times to obtain the standard deviation values used to calculate the limit of detection (LOD), limit of quantification (LOQ) and percent relative standard deviation (%RSD) using the following formulas below:

$$\text{LOD} = 3 \times \text{Std Dev} / \text{Slope} \quad (1)$$

$$\text{LOQ} = 10 \times \text{Std Dev} / \text{Slope} \quad (2)$$

System analytical performance values calculated for resmethrin are presented in

Table 1. The calibration plot had linearity over a wide concentration range for the determination of resmethrin. The low %RSD values obtained in each measurement indicated that the repeatability was satisfactory. All chromatograms obtained for the measurements are shown in Figure 1.

Table 1 System analytical performances of GC-FID

Analyte	Resmethrin
LOD, mg/L	0.02
LOQ, mg/L	0.08
Linear Range, mg/L	0.10 - 163
Regression Coefficient	1.0000
Intra-day, %RSD	1.8
Inter-day, %RSD	7.7

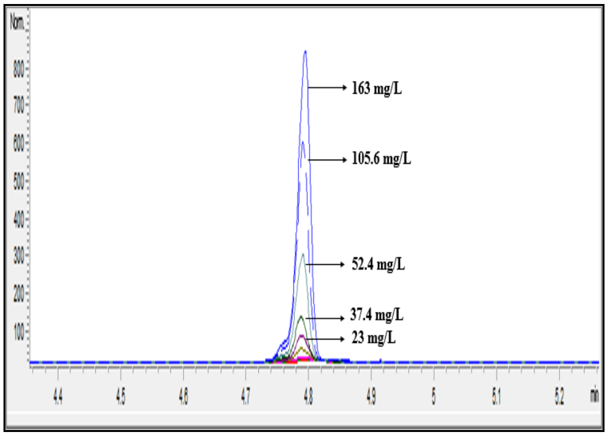

Figure 1 Overlay chromatograms of resmethrin calibration standards

3.2. Recovery experiments

The constant use of pesticides to control pests on farmlands and protect/increase the yield of farm products increases the risk of exposure to humans and other living organisms. After harvest, it is possible to encounter pesticide residues in products offered for human consumption. The aim of the recovery tests was to determine the amount of resmethrin that can be accurately and precisely quantified when present in corn silk samples. Since resmethrin showed high solubility in acetonitrile, the extraction process was performed as described in Section 2.3. Firstly, the blank extract of the sample was analyzed by the GC-FID system to determine the presence of resmethrin, but no analytical signal was observed at the retention time. Then, the corn silk sample was spiked at 0.31, 0.61, 8.1, 16.2 and 40.2 mg/L final concentrations. The percent recoveries calculated with the external calibration method under the proposed conditions are summarized in Table 2.

Table 2 Percent recoveries for corn silk sample spiked at different concentrations

Analyte	Spiked Concentration, mg/L	External Calibration Recovery ± Standard Deviation, %
Resmethrin	0.31	94.6 ± 3.3
	0.61	92.1 ± 2.3
	8.1	96.3 ± 2.5
	16.2	93.6 ± 1.8
	40.2	96.9 ± 2.0

4. CONCLUSION

In this study, a GC-FID analysis method was presented for the direct determination of resmethrin in corn silk samples. A suitable temperature program was used to elute the target analyte through the column within a short run time of 5.7 min. Percent recovery results calculated for the samples spiked at three different concentrations were in the range of 93.6 – 96.9%, and the relative standard deviation values recorded below 2.5% certified good repeatability for the method. Compared to the limit values of a study reported in the literature, the proposed method may be a good alternative for the determination of resmethrin with high accuracy [24].

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Authors' Contribution

The author contributed solely to the study.

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the author.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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