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RESEARCH ARTICLE

DISSIPATION RATE OF λ -CYHALOTHRIN, THE ACTIVE INGREDIENT OF THE PESTICIDE KARATE 2.5 EC IN GRAPE

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ABSTRACT

Implementation of Good Agricultural Practices, establishing MRL for each combination agricultural crop/pesticide and determination of PHI, is an extensive process involving a lot of interested parties, such as agriculture scientists, analytical chemists, farmers, representatives of legislative and executive bodies, etc. All countries should be responsible for implementation of this process in order to prevent agricultural products with pesticides residues content higher than established MRL enter in food chain guaranteeing that safety standards are met and GAP have been applied in using pesticide formulations in agricultural crops. This paper describes the determination of dissipation rate of λ-Cyhalothrin, the active ingredient of insecticide Karate 2.5EC, used in grapes. The field samples have been submitted to analytical procedure in order to determine PHI. Normal and double dose have been used and one treatment for each dose has been applied followed by sampling successive days after the application. The AOAC analytical method was used to determine first the recovery coefficients of λ-Cyhalothrin in grapes in three different concentration levels. Later, the samples of grapes sprayed with Karate 2.5EC have been submitted to analytical procedure of sample processing, extraction, selective partition and quantitative determination using a GC-μ/ECD. The results obtained were compared to the Maximum Residues Limit (MRL) for λ-Cyhalothrin in grapes and PHI was determined.

INTRODUCTION

The customers have become more conscious about the food they consume and the public attention has been drawn more and more to environmental concerns relating to pesticides and other chemicals used or derived from anthropogenic activities. The main reason of determination the stability of pesticides in field consists in the fact that because of different characteristics of pests, their different pertinence as well as different climatic and geographic condition and agricultural practices in crops cultivation, the pesticides residues in agricultural crops at the harvest time may vary considerably for each combination pesticide/agricultural crop. During recent years Albania has made efforts to be integrated in European family. Among a number of important economic and juridical obligation, it stands out even the food safety in order to enable their free and safe entrance to the European market, guaranteeing the European consumers and Albanian consumers' safety as well. So for years now the basis to carry out complex studies to make evident the residues level in our domestic food products in general and in agricultural crops in particular have been established. This paper describes the methodology attended for the determination of dissipation rate of Lambda Cyhalothrin, the active ingredient of insecticide Karate 2.5EC in grapes sprayed with this pesticide formulation. The used method is a multi residue one for the determination of synthetic pyrethroides in agricultural crops, described in detail in AOAC (AOAC, edition 16, Volume I, 2000).

MRL for Lambda Cyhalothrin and its PHI is different in various countries. The Codex Alimentarius Commission established a MRL of 0.2 mg kg^{-1} for Lambda Cyhalothrin in grapes with a pre harvest interval of 7 days. Even the European Regulation (EC) No 396/2006 MRL for Lambda Cyhalothrin is fixed in 0. 2 mg/ kg for grapes. The determination of the pesticide's fate on fruits and vegetables is very important since this will greatly affect the effectiveness of sprayed pesticides on plants, the preharvest interval and the amounts of residue on vegetables at the harvest time and up to the end of the consumers. The objectives of this paper is (*i*) the presentation of the method used for the determination of Lambda Cyhalothrin in grapes and (*ii*) the establishment of the dissipation rate of Lamba Cyhalothrin in grape to determine safe PHI (preharvest interval) that do not exceed MRL values at the harvesting time and during the whole distribution and consuming food chain until to the end of consumer.

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MATERIALS AND METHODS

Experimental setting up

Experimental trials were conducted at the experimental fields of the ex-Institute of Plant Protection, Durres. This experiment consists in Lambda Cyhalothrin application in grapes in normal and double dose. Lambda Cyhalothrin was used in one of its formulations Karate 2.5EC. After the last application (grape is only single sprayed at both doses) random sampling was made. Bulk sample was sent within the same day to laboratory where the analytical sample was obtained. Usually Lambda Cyhalothrin is applied very close to the harvest time, consequently the edible part of the already mature fruit is exposed to the pesticides and residues are expected to be detected and found quantitatively even days after application and harvest. That's why we took samples for a long period starting since the first day until 15 days after the application followed later by sample processing, Lambda Cyhalothrin residue extraction and gas chromatographic analysis in a GC-µ/ECD system. This paper shows the results obtained from this experiment aiming at studying the dissipation rate of Lambda Cyhalothrin applied to grapes as a function of the application dose and type of the crop, in order to determine its PHI (Pre Harvest Interval) for the respective pesticide/crop combination. The spraying procedure (dose applied, formulation type, phase of grape maturation when sprayed) was based on the agricultural practice for the selected crop and pesticide formulation. Grapes were sprayed with Karate 2.5EC at 30 g a.i/ha corresponding to normal recommended dose at 0.03 kg a.i/ hl and 60 g a.i/ha corresponding 0.06 kg a.i/ hl. Grapes was single sprayed at August at both doses. Weather condition during spraying and successive sampling were favorable for the experiment, high temperature and no rain. (Boci *et al.*, 2003)

Data on the pesticide and other condition during the experiment

Pesticide preparation Karate 2.5 EC
Formulation TypeEC
Biological activity: Insecticide Sprayed area5x 6 m^2
Crop Grape Crop variety Cardinal
Weather condition during and after spraying: optimal
Temperature over 35°C
Active ingredient content: 2.5% Lambda Cyhalothrin
The condition of crop during treatment: Initial step of ripening

Pesticide formulation and its active ingredient

Cyhalothrin is a synthetic pyrethroid, active against a number of pests. Lambda Cyhalothrin, the active ingredient of the pesticide formulation KARATE 2.5 EC is a chlorofluoro compound of crisantemic acid. Lambda Cyhalothrin is the main residual component resulting from its degradation in the plant. It is the best of the pyrethroid insecticides controlling pests in cereals, grapes, vegetable brassicas, beans, onions, tomatoes, sweet corn, potatoes, grapes, white clover, seed crops, citrus and ornamentals. Although theoretically it can be a mixture of 16 enantiomers, this number is reduced practically in 4. Lambda Cyhalothrin is the most active pair of Cyhalothrin enantiomers (www.agchemaccess.com/Lambda_cyhalothrin). Lambda Cyhalothrin presents the same insecticide activity as Cyhalothrin but it is more active. It is a fast acting contact and stomach insecticide and is relatively stable in sunlight allowing longer persistence on the plant. Its chemical structure is as shown in the Fig.1

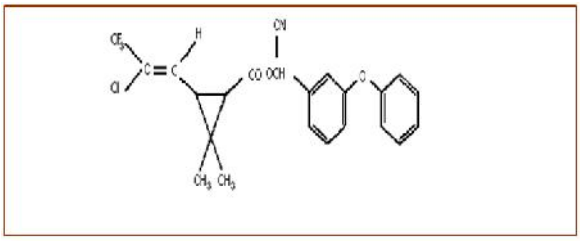

Fig.1. Chemical structure of λ-Cyhalothrin

The residues resulting from Lambda Cyhalothrin present in agricultural products are relatively low usually less than 0.2 mg/kg. Information and data gathered estimate ADI not more than 0.02 mg/ b.w (www.agchemaccess.com/Lambda_ cyhalothrin). In living organisms Lambda Cyhalothrin is metabolized very fast. In this case it happens the ester bond breakage which leads to more polar compounds which are less toxic and readily eliminated.[9] The main products of degradation are 3-(2-chloro-3,3-trifluoropropil-enil)-2-dimethylciklopropan carboxylic acid which in soil condition is further degraded in CO_2. Lambda Cyhalothrin is absorbed in soil particles and it is not mobile in the environment. In the plants it is moderately degraded and the main compound of the residues in plant is Lambda Cyhalothrin itself.

Gas chromatographic system, its operational parameters and calibration

Chemicals

A standard of 98,0 % purity, ICI Agrochemicals, ASJ 10012-015 was used to prepare stock standard solution of Lambda Cyhalothrin in hexane, stored in -5º C. Later intermediate and working standard solution were prepared by dilution. Three Lambda Cyhalothrin working standards solutions have been prepared at concentrations from 0.01 mg/kg up to 0.5 mg/kg in order to plot calibration curve (Fig. 2) showing the detector response in peak height versus to concentration levels, by manually injecting 1 µl working standard solutions in HP 6890 Series GK/µ-ECD. The detector showed linearity through entire this concentration zone (R^2=0.99932)

Table 1. Operational parameters of GC/µ-ECD system

Instrumental parameters	
Oven	50°C~2' 20˚C/min@160°C Ramp 1 6°C/min @260°C Ramp 2 10°C/min@300°C~10'
Injector	Splitless, T=280˚ Carrier gas: Hydrogen 1ml/min 1µl manual injection by syringe 10µl
Column	Fused silica capillary column HP HP-5 phenyl methyl siloxan 30m x 0.25mm x 0.25 µ
Detector	µ –ECD,T=300˚C, Make up gas: Nitrogen

The instrumental chromatographic conditions used are given in the Table 1

Under the chosen conditions, Lambda Cyhalothrin presented an average retention time of 21.94 min. Chemistation Software system was used for data acquisition and processing.

As it can be clearly seen, the recovery level is good, taking into account the physical characteristics and structure of the product. During processing the blank samples spiked with

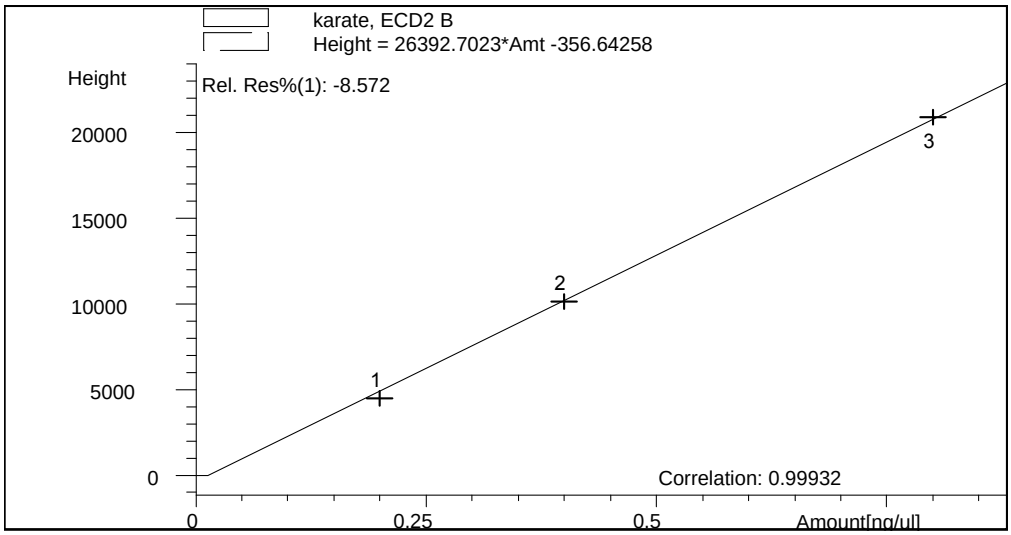

Fig. 2. Three level calibration curve of Lambda Cyhalothrin

Sample and its treatment

Samples were collected at random for each dose from 1 day until 15 days after the application. From the sprayed culture the bulk sample was obtained according to Codex Alimentarius recommendations (Pesticides Residues in Food. Methods of Analysis and Sampling). The sample was sent within the same day at the laboratory (1-2 hours after harvest) at fresh condition and packed to ensure its integrity and identity and to avoid any casual contamination or leaking. An amount of 2 kg (five units at minimum) of sample was taken. As soon as the samples had been picked up, they were transferred to the laboratory where they were chopped, blended and analyzed. The analytical portion was prepared in conformity to Codex Alimentarius recommendations taking into account that it should represent that crop part to which the MRL is applied. Grape is included in the *Group 12* of Codex Alimentarius*: Berries and Small fruit* (Pesticides Residues in Food. Methods of Analysis and Sampling) so the laboratory sample should represent all the product after stem cutting off. Almost all the samples were processed immediately at fresh condition without the need of deep freezing. The samples that we could not processed at the time of arriving at the lab were chopped, homogenized, taken the laboratory portion and put to deep frozen storage. From the sample two parallel subsamples each of 50 g were taken and further processed.

Lambda Cyhalothrin recovery in grape

Three different fortification levels were used 0.05 mg/kg, 0.1 mg/kg, and 0.2 mg/kg aiming at including the Lambda Cyhalothrin expected concentration levels within the linear working range. The lowest level was chosen to be 2-5 times more the Lambda Cyhalothrin detection level which for the analytical method used was 0.02 mg/kg. The recovery obtained for the three fortification levels are given in the Table 2 below:

Lambda Cyhalothrin, we didn't notice any particular condition which could have any impact on the expected results. This pesticide preparation presented a high stability against the work condition.

Table 2. Recovery of Lambda Cyhalothrin in grape

Grape	Level of fortification (mg/kg)		
	0.05 mg/kg	0.1 mg/kg	0.2 mg/kg
Recovery, in %	91	90	92

Analytical procedure

To quantitatively determine the Lambda Cyhalothrin in grape we used the official analytical procedure: Analysis of synthetic pyrethroides in agricultural products presented in AOAC. (AOAC, edition 16, Volume I, Cap.10, paragraph 998.01, pg.60)

Principle of the method

Fruits and vegetables are extracted with acetone. Residues are separated by using hexane the extract is evaporated until dryness and dissolved again in acetonitrile. Further it is cleaned up in deactivated Florisil column and then eluted by using 6% diethyl ether in hexane. The concentrated residue is later injected into GC/μ-ECD.

Selective partitioning and Lambda Cyhalothrin elution

50 g product is homogenized with 120 ml acetone in a high speed blender for 3 min. After sample homogenization and vacuum filtering, the solution together with the rinsing acetone are gathered in a separatory funnel. After adding 60 ml hexane and successive vigorous shaking, 200 ml aqueous solution of 4% NaCl (w/v) are added. The hexane layer passes through a glass funnel covered with glass wool and anhydrous

Na_2SO_4.After successive rinsing the content is evaporated until dryness by using a rotary evaporator at 40°C. The residue is dissolved in hexane and once again is poured into a separatory vessel where 30 ml acetonitrile saturated with hexane is added. After vigorous shaking the acetonitrile layer is separated into a conical flask where other rinsing portions of acetonitrile saturated with hexane are added. It is important the use of the exact amount of acetonitrile and hexane to have optimal results. Further acetonitrile is evaporated completely by rotary evaporator and the residue is dissolved in 5 ml hexane. The extract is further cleaned up in Florisil column freshly prepared, where the rinsing hexane of the conical flask is added as well. Lambda Cyhalothrin is eluted into a conical flask by using 120 ml eluting solvent of 6% diethyl ether in hexane. The eluted solution is further evaporated up to less than 5 ml, and the final volume is further adjusted according to the expected concentration of Lambda cyhalothrin.1µl extract is then injected into GC. Lambda Cyhalothrin is quantitatively determined by using the calibration plot. A chromatogram of sample sprayed with Karate 2.5EC is shown in the Fig.3

Data on residue and MRL of Lambda Cyhalothrin

Some MRL-s established in Regulation Pesticide EU-MRL (EC) No 396/2005 are presented in the Table 3. These values are obtained from extensive field experiment of Lambda Cyhalothrin applied on different agricultural crops. Depending of the legislation of different countries MRL are different and consequently even PHI which depends of the crop, number of applications as well as from the active ingredient in the pesticide formulation type.

Table 3. MRL-s of Lambda Cyhalothrin for some agricultural crops

Agricultural crop	MRL in mg/kg
Stone fruit	0.2
Grape	0.2
Leafy vegetables	0.5-1.0
Pome fruit	0.1

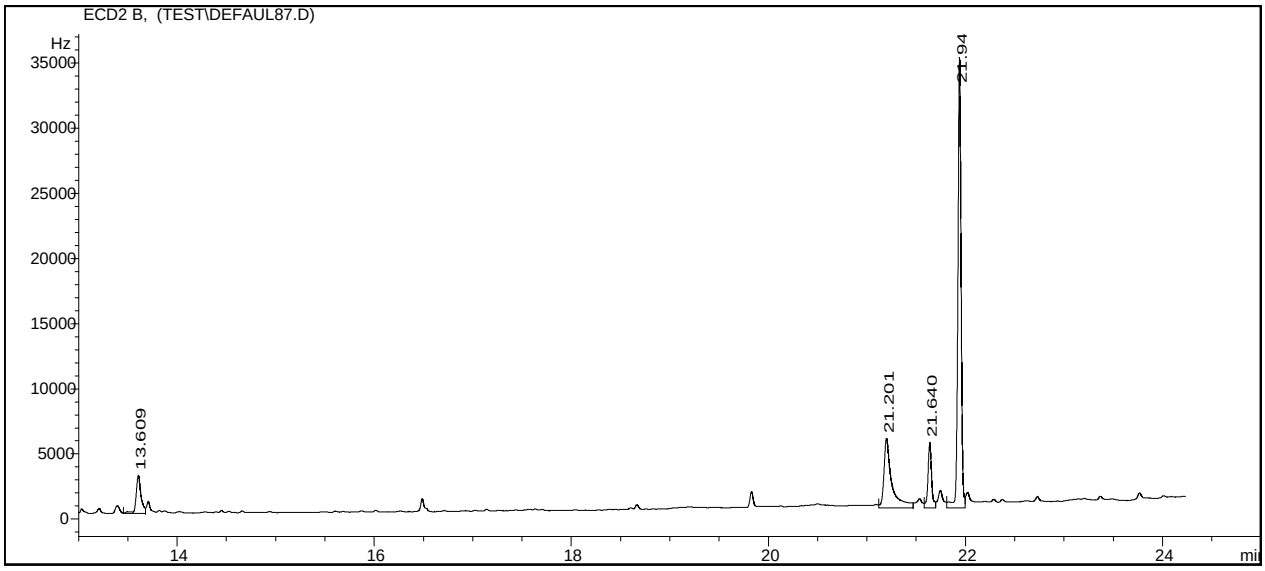

Fig.3. Chromatogram of a grape sample sprayed with Lambda Cyhalothrin RT =21.942

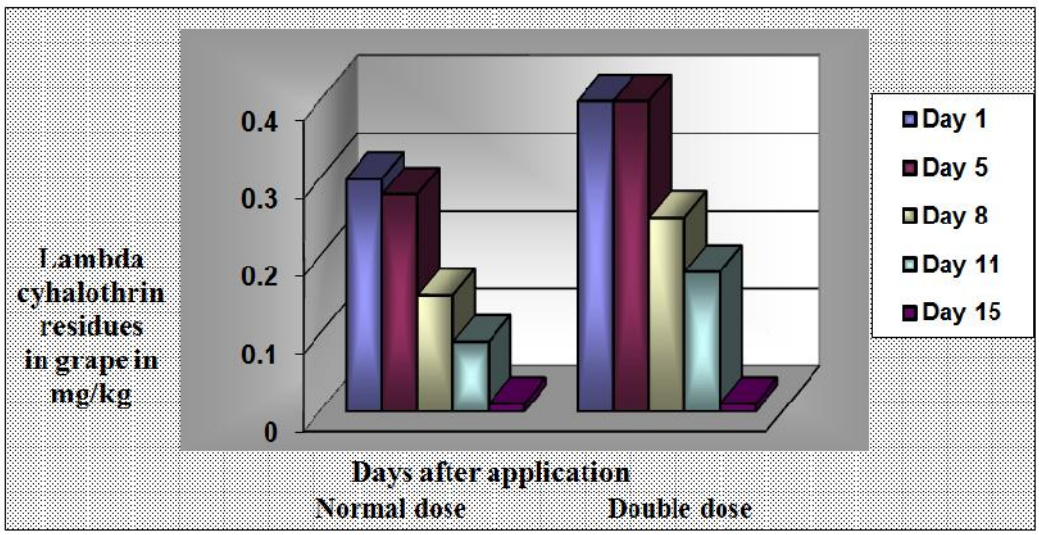

Fig. 4. Dissipation rate of Lambda Cyhalothrin in grape as a function of dose and time after application

Codex Alimentarius (Codex Alimentarius Vol.2B, Pesticides Residues in Food. Maximum Residue Limits 2000) and EC Directive (EC) No 396/2005) have established the value of 0.2 mg/kg as MRL for small berry fruit (grape for example). In drawing our conclusion we are referred to this value to determine the PHI for this active ingredient/commodity combination.

Lambda Cyhalothrin dissipation rate results

From the data obtained from field experiment and from the literature is confirmed that in most of the cases, it results very low or undetectable residues of Lambda Cyhalothrin after its application, because of the low concentration of the active ingredient (usually less than 50 g a.i/ha). The residues are low if we follow and use it in conformity to guidance and the manual accompanying the pesticide formulation and implementation of GAP. Codex Alimentarius has established a MRL of 0.2 mg/kg for Lambda Cyhalothrin which is the same with European MRL Figure 4 shows the Lambda Cyhalothrin dissipation rate in grape sprayed with Karate 2.5 EC at the recommended normal and double dose. If we consider its MRL of 0.2 mg/kg established by Codex Alimentarius and EC Regulations, the residue values fall below its MRL 8 days after its last and the only application, while if we consider the double dose its residues fall below its MRL only after 12 days after the last and only application. This study indicates that a pre harvest interval of 8 days (PHI) in the applied recommended dose is appropriate for the application of this pesticide formulation under the conditions studied so that the level of residues fall below the limits established by Codex Alimentarius and EC Regulation, while its PHI is 11 days if we use double dose of the formulation.

Conclusion

As it was expected the recovery of Lambda Cyhalothrin resulted satisfactory considering its stability against the working condition. It was consistent during all the tests performed. The quantitative determination of Lambda Cyhalothrin was not influenced from sample processing conditions. Lambda Cyhalothrin MRL in grape and its PHI are more or less the same for different countries legislation and agricultural crop applied.

If we base on MRL of 0.2 mg/kg established by Codex Alimentarius and EC Regulation it results a short PHI (Pre harvest interval) = 8 days for grape sprayed with Karate 2.5EC. Taking into consider the stable climacteric conditions during the experiment and the dissipation rate of Lambda Cyhalothrin we can say that its residues are low but detected during the first days after the last applications, leading to the fact that its residues are lower than respective MRL for the respective agricultural crop (grape) until 8 days after last application at a normal dose recommended applied and until 11 days last application for the double dose applied.

Acknowledgment

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