

EFFECT OF INDUSTRIAL PROCESSING ON THE LEVEL OF PYRETHROIDS RESIDUES IN GREEN PEAS

EFFECTUL PRELUCRĂRII INDUSTRIALE ASUPRA NIVELULUI UNOR REZIDUURI DE PIRETROIZI DIN MAZĂREA VERDE

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Abstract. The main objective of this study was to quantify the effect of industrial processing, including washing, blanching, sorting, and sterilization, the level of pesticide residues in samples of green peas, which were analyzed for the content of cypermethrin (1, 2, 3 and 4), permethrin (1 and 2), cyfluthrin (1, 3 and 4), fenvalerate, esfenvalerat, lambda cyhalothrin and bifenthrin. Pesticide residues were quantified by gas-chromatographic method (GC - TSD). The results indicated that pyrethroids quantify the green peas bean were substantially reduced to canned green peas bean in brine (finished product). However, the residual cyfluthrin 1, did not change from the industrial processing of green peas bean. Pesticide concentrations detected in samples of green peas were below the MRL's.

Keywords: pyrethroids pesticides, industrial processing, green peas

Rezumat. Obiectivul principal al acestui studiu a fost de a cuantifica efectul de prelucrare industrială, incluzând, spălarea, blanșarea, sortarea și sterilizarea, ce au fost analizate pentru conținutul de cipermetrin (1, 2, 3 și 4), permetrin (1 și 2), ciflutrin (1, 3 și 4), fenvalerat, esfenvalerat, lambda cihalotrin și bifentrin. Reziduurile de pesticide au fost cuantificate cu ajutorul metodei gaz-cromatografice (GC - TSD). Rezultatele au indicat că, piretroizii evaluați cantitativ în mazărea verde boabe s-au redus substanțial până la conserva de mazăre verde boabe în saramură (produs finit). Cu toate acestea, nivelul rezidual de ciflutrin 1, nu s-a modificat în urma prelucrării industriale a mazării verzi boabe. Concentrațiile de pesticide detectate în eșantioanele de mazăre verde au fost sub LMR.

Cuvinte cheie: pesticide piretroide, prelucrare industrială, mazăre verde

INTRODUCTION

In Romania, the most widely used pesticides are fungicides followed by herbicides and insecticides.

Pyrethroid pesticides comprise an important group of insecticides, used as internal insecticides because of their toxicity is relatively low and the effect on insects is high, and are also used in agriculture, since the advantageous properties

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through short residence time in soil and the environment. In recent years, research has been directed towards obtaining synthetic pyrethroids, which are cheaper and more convenient than natural, and which are widely used to protect various crops (Beltran et al. 2003).

Among the most commonly used pyrethroid insecticides are cyhalothrin, cyfluthrin, cypermethrin, fenvalerate, esfenvalerate and bifenthrin. These six pyrethroids are moderately toxic to humans. Esfenvalerate can be mixed up with a wide variety of other types of pesticides, such as carbamates and organophosphates compounds.

Based on this information and given that there are few data on pyrethroid residues in vegetables, the aim of the present study was to determine the concentration of pyrethroids in green peas which was analyzed to quantify the effects of the washing, blanching, final sorting and sterilization of the technological process flow of canned green peas beans in brine.

Effects of industrial processing of vegetables and fruits on pyrethroids were analyzed by researchers such as Lin H. et al., (2005) and Rasmussen R.R. et al. (2003). These authors concluded that there was a reduction in the level of pesticide residues, due to techniques for processing, for the most part. It has been suggested that the effects of processing on the levels of cypermethrin residues may cause hydrolysis degradation during processing, thus reducing consumer exposure.

Maximum residue limits established by the European Union (Reg. (EC) No. 396/2005) for residues of peas (without pods) (Garden pea, green pea, chickpea) were 0.7 mg/kg for cypermethrin (cypermethrin including other mixtures of constituent isomers (sum of isomers)), 0.05 mg/kg cyfluthrin (cyfluthrin including other mixtures of constituent isomers (sum of isomers)) and bifenthrin, fenvalerate and esfenvalerate to 0.02 mg/kg and 0,2 mg/kg for λ cyhalothrin. Thus, the methods multireziduu used to determine the pyrethroid samples of green peas must be sensitive enough to reach the level of quantification.

MATERIAL AND METHOD

In general, production procedures canned green peas bean include four steps, washing, blanching, sorting and final sterilization. In the current study, green peas was analyzed in five stages (green peas - unprocessed, washing, blanching, sorting and final sterilization) and taken to determine and investigate the variation in the content of pesticide residues during processing.

Each processing step (see below) was considered a point of sampling for residue analysis.

(i) Washing: Green peas was subjected to washing steps (four washes) with sorting has been done in pre-sorted and hydraulic conveyor.

(ii) Blanching: Stage of scalding (blanching) was carried out in continuous scalding machine at a temperature of 98°C for 3 minutes.

(iii) Final sort: After blanching was carried out in a rapid cooling to a temperature of 30°C for 1 minute; at the same time there was a further washing. After cooling was achieved a final sorting conveyor belts.

(iv) Sterilization has been carried out in an autoclave at a temperature of 120°C for 15-35 minutes, followed by cooling of the vessels (jar) on the outside, cooling is provided at 40 minutes, during which time the product is brought to a temperature of 40°C.

Immediately after removal of the unit of processing fruit and vegetables, samples were placed in plastic bags and stored at -20°C until analysis, and analyzed as such.

Determination of pesticide residues was carried out according to standards: EN 12393-1, 2, 3:2009 - Foods of plant origin. Multiresiduu methods for determining pesticide residues GC.

For the quantitative determination of residues of POCl performed in this study was used as the gas chromatography apparatus of Varian 450 coupled to the detector TDS, where the samples were injected automatically separated and purified by a pre-processing thereof by solvent extraction organic (acetonitrile, petroleum ether).

To report levels of pesticide residues were using two parameters: mean value and standard deviation (s) from three identical samples for each sampling point, expressed in mg/kg. Data were subjected to analysis of variance (ANOVA).

RESULTS AND DISCUSSION

Study results concerning pyrethroid pesticide residues analyzed along four processing steps are shown in table 1.

The average concentration of cypermethrin 1 of the unprocessed green peas was 0.0047 mg/kg. The washing steps were led to increased of concentration up to the 0.0050 mg/kg, content what subsequently decreased after step of blanching by up to 46% to a value of 0.0027 mg/kg. Also, the reductions of the content in this isomer were recorded and after step of sorting up to 52%, from 0.0027 mg/kg to 0.0013 mg/kg. In samples of green peas collected to canned achieve an increase in the average level of cypermethrin 1 as against the peas which was sorted, by 31%, from 0.0013 mg/kg to 0.0017 mg/kg.

The analytical data obtained for cypermethrin 2, is characterized by a decrease in all the samples analyzed on the flow as follows: at unprocessed green peas, the concentration of cypermethrin 2 decreased by 27.8% after the washing; the decrease in the concentration of cypermethrin 2 were recorded and after blanching stage, with 21%; in samples of peas sorted by 38% from peas that was blanched; and by 53% after sterilization of canned green peas beans.

It notes that the average level of concentration of cypermethrin 3 was different from that of cypermethrin isomers 1, 2 and 4 by the content oscillations under the action of heat treatments. After the blanching step the average level of concentration of cypermethrin 3 increased by 13%, from 0.0213 mg/kg (value obtained after the washing step) to 0.0240 mg/kg. After the sorting stage, the content of the isomer has slightly decreased by 4.16% from 0.0240 mg/kg to 0.0230 mg/kg and after the sterilization phase, with 3%.

Own investigations on the behavior isomer, cypermethrin 4 the technological flow, showed an increase after stages of washing and blanching. Were decreased by 11.25% of the concentration of cypermethrin 4, after the step of sorting comparative with the values recorded after the blanching step, from 0.0240 mg/kg at 0.0213 mg/kg.

Tabel 1

Residue levels during processing in mg/kg of green peas (mean \pm SD) (n=3)

Pesticide	Unprocessed peas	Whasing	Blanching	Final sorting	Sterilization
Cypermethrin 1	0,0047 \pm 0,002	0,0050 \pm 0,002	0,0027 \pm 0,002	0,0013 \pm 0,001	0,0017 \pm 0,001
Cypermethrin 2	0,0110 \pm 0,001	0,0080 \pm 0,002	0,0063 \pm 0,002	0,0043 \pm 0,002	0,0020 \pm 0,001
Cypermethrin 3	0,0267 \pm 0,003	0,0213 \pm 0,001	0,0240 \pm 0,001	0,0230 \pm 0,001	0,0223 \pm 0,002
Cypermethrin 4	0,0227 \pm 0,002	0,0250 \pm 0,003	0,0240 \pm 0,004	0,0213 \pm 0,002	0,0173 \pm 0,002
Cyfluthrin 1	0,0013 \pm 0,001	0,0013 \pm 0,001	0,0017 \pm 0,001	0,0013 \pm 0,001	0,0013 \pm 0,001
Cyfluthrin 3	0,0180 \pm 0,001	0,0133 \pm 0,003	0,0090 \pm 0,002	0,0045 \pm 0,002	0,0050 \pm 0,001
Cyfluthrin 4	0,0030 \pm 0,001	0,002 \pm 0,002	0,0023 \pm 0,001	0,0033 \pm 0,002	0,0020 \pm 0,001
Fenvalerate	0,0040 \pm 0,001	0,0027 \pm 0,002	0,0010 \pm 0,001	0,0010 \pm 0,001	0,0013 \pm 0,001
Esfenvalerate	0,0020 \pm 0,001	0,0007 \pm 0,001	0,0010 \pm 0,001	0,0013 \pm 0,001	0,0013 \pm 0,001
λ cyhalothrin	0,0040 \pm 0,001	0,0030 \pm 0,001	0,0013 \pm 0,001	0,0013 \pm 0,001	0,0013 \pm 0,001
Bifenthrin	0,0190 \pm 0,002	0,0190 \pm 0,001	0,0180 \pm 0,002	0,0160 \pm 0,004	0,0137 \pm 0,004

Effect of industrial processing on the pyrethroid cyfluthrin was marked by fluctuations within each isomer studied (Table 2). The concentration by cyfluthrin 1 of 0.0013 mg/kg was recorded in samples of unprocessed green peas, and peas taken after the washing steps, value that which has increased to 31% after blanching step. Removal of vegetal remnants resulted from phase blanching, and sterilization ultimately leading at decreased concentrations of cyfluthrin 1 to the initial value by 0.0013 mg/kg.

The results obtained for cyfluthrin 3 are shown a concentration of 0.018 mg/kg for unprocessed green peas. The washing steps have reduced the level of residual cyfluthrin 3 to an average value of 0.0133 mg/kg. Blanching resulted in a decrease in the concentration of cyfluthrin 3 to 32%, from 0.0133 mg/kg at 0.0090 mg/kg. The sorting operations significantly influence the concentration of this isomer leading to reduced thereof by 50%.

The concentrations obtained for cyfluthrin 4, increased in the early stages of processing of green peas, 15%, after the step of blanching from 0.002 mg/kg (the washing step) at 0.0023 mg/kg and 43% from 0.0023 mg/kg (blanched green peas) at 0.0033 mg/kg, a level which corresponds to the samples of green peas collected by sorting step. Sterilization of canned green peas beans as compared to sorting phase, resulted in a reduction of 39% of the content in cyfluthrin 4 in the samples of green peas studied.

The analytical results of quantitative evaluation of the concentration of fenvalerate from green peas have indicated above average values before the

processing of 0.004 mg/kg, comparative with samples of the technological stages studied. The average concentration of fenvalerate has reduced after the steps of washing with 32.5%, up to a level of 0.0027 mg/kg. After the blanching step the content of fenvalerate was reduced by 63%, a percentage value which corresponds to 0.0010 mg/kg. After sterilization step, green peas taken canned green peas beans has registered a level of 0.0013 mg/kg.

The washing steps reduced the content of esfenvalerate, with 65%, from 0.0020 mg/kg to 0.0007 mg/kg. The data obtained for the level of esfenvalerate after the step of blanching showed a high level of concentration of peas compared to samples taken after the washing steps, on average by 43%; sorting process has resulted to increased by 30% to 0.0013 mg/kg, a value that was recorded to samples taken after the sterilization phase.

Analytical results of the quantitative evaluation of λ cyhalothrin concentration of green peas have indicated the highest average value for green peas before processing of 0.0040 mg/kg. The washing steps followed by blanching step reduced content of the chemical compound with 25% and 57%. After stages of blanching, sorting and sterilization green peas has registered a content by 0.0013 mg/kg.

Influence of technological process on the content of bifenthrin decreased the concentration of green peas to the finished product. Decreases were recorded after blanching stage, by 6.8% from 0.0190 mg/kg to 0.0180 mg/kg; sorting stage for the removal of vegetal remnants results after blanching at 98°C, reduced content of 11%, from 0.0180 mg/kg to 0.0160 mg/kg. The stage sterilization reduced the average concentration of bifenthrin, with 14.3% from 0.0160 mg/kg to 0.0137 mg/kg.

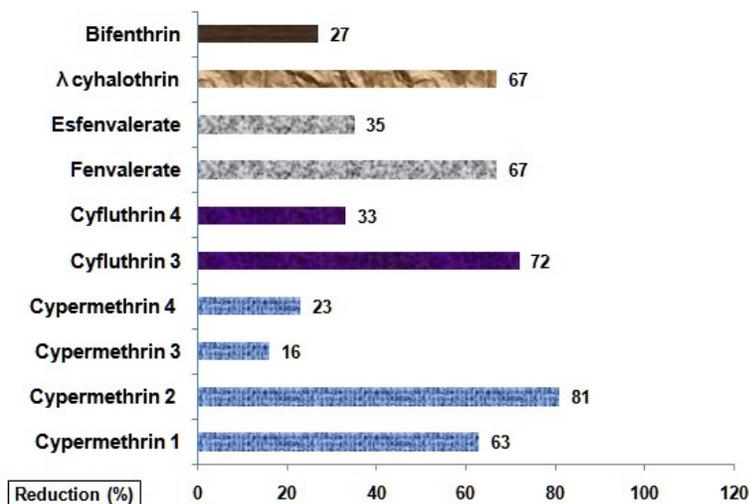


Fig. 1 - Decreased percentage (%) of pyrethroid residues of canned green peas beans in brine

The total amount of pesticides removed through processing steps for each pyrethroid compound (with the exception of isomer cyfluthrin 1, to effect processing did not change the content of green peas) is shown in Fig. 1.

In general, removal of residues was more effective (<70%) in the case of cypermethrin 2 and cyfluthrin 3.

Canned green peas and beans were reduced by up to 67% of the residue of λ cyhalothrin and fenvalerate, while bifenthrin, esfenvalerate, cyfluthrin 4, cypermethrin 4 and cypermethrin 3 showed a lower reduction of about 30% by processing green peas.

CONCLUSIONS

1. Samples of green peas taken from canned green peas beans in brine and analyzed to the average content of pyrethroids, have resulted through in values significantly decreased after processing.

2. The isomer cyfluthrin 1 did not change concentration after processing green peas.

3. The research results confirms the presence of pesticides in green peas, quantity these being well below maximum limits admissible (MRL's) (EC, 2005).

***Acknowledgements.** This work was carried out with the financial support of the Sectoral Operational Programme Human Resources Development 2007 - 2013 under the project, POSDRU/CPP107/DM1.5/S/77222, „Improvement and Development of Human Resources for Research and Innovation in Graduate School”*

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