ABSTRACT

Keywords: *nitrates/nitrites, heavy metals, pesticides, vegetable processing, Galaţi area*

The doctoral thesis bearing the title *„**Studies regarding some factors of pollution on horticultural raw materials as well as on the products resulting from the technological flow**”* aims at identifying and evaluating some products resulted after pollution, such as nitrates/nitrites, heavy metals and pesticides, in tomatoes, green peas and beetroot as well as in the finished products, due to the random factors, environmental and/or processing factors occurring in the transformation of such products.

The analysis of the chemical pollutants was continued with the investigation of the quality of auxiliary materials (technological water and the covering liquid) as potential polluting factors of the finished products with nitrates/nitrites and heavy metals.

The doctoral thesis is structured into two parts and contains 252 pages containing 39 tables, 134 colour figures and photos and the bibliography contains 188 titles. The first part of the paper related to the *current stage of research* of the problems approached contains the introduction and two chapters, and the second part represents our own *researches* presented in five chapters, including conclusions and recommendations.

In **Chapter I** entitled *Curent state of researches regarding factors of pollution* we present a synthesis of the bibliographic data related to the chemical pollution of the environmental components and the horticultural products.

Chapter II entitled *Pollution with nitrates/nitrites, heavy metals and pesticides of the horticultural raw materials* describes certain categories of pollutants (nitrites/nitrates, heavy metals – Pb, Cd, As, Hg, Cu, Zn, Cr and Sn, pesticides - organochlorine, organophosphorus, pyrethroids and fungicides) and their concentration in the environmental components and the horticultural products. In this chapter we also synthesize data related to the influence of the technological stages on the categories of pollutants under study from the processed products.

The part dedicated to our own researches starts with **chapter III** *Purpose and objectives of research,* where we describe a series of considerations regarding the purpose of the paper completed with the activities carried out within each objective envisaged.

In **chapter IV** we present the institutional framework for the carrying out of the research activity, the presentation of the vegetable and fruit processing unit from where we drew and analyzed the samples of horticultural products, their manner of drawing and preparation as well as the research methods used to attain the objectives proposed.

The research activity was carried out within the vegetable and fruit processing unit S.C. Contec Foods S.R.L. Tecuci, "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine of Iaşi (the *Horticultural product technology* Laboratory) and the Sanitary Veterinary and Food Safety Department of Iaşi (the Residue laboratory).

To determine the concentration of nitrates/nitrites, heavy metals and pesticides, we analysed samples drawn from the flow diagrams for the production of tomato broth, the canned green peas thermosterilized and the beetroot vinegar salad.

The work methodology complied with the following standards: *SR EN 26777/ ISO 6777/2002/C91/2006* for the determination of the nitrate content; *SR ISO 7890-3/2000* for the determination of the nitrite content*; SR EN 14082/2003* for the determination of Pb, Cd, Cu, Zn and Cr; *SR EN 13806:2003* for the determination of Hg; *SR EN 14546:2005* for the determination of total arsenic; *SR EN 15764:2010* for the determination of tin and *SR EN 12393-1,2,3:2009* for the determination of pesticides.

Chapters V, VI and VII contain the largest part of the doctoral thesis since they present the experimental results for each horticultural product under analysis, their presentation being accompanied by the statistic analysis of the results obtained.

A series of general conclusions are drawn from the three chapters related to the content of nitrates/nitrites, heavy metals and pesticides both in the horticultural and the finished products:

Results regarding the content of nitrates/nitrites, heavy metals and pesticides in tomatoes

- The nitrites/nitrates content in tomatoes decreased after processing thus obtaining a highly significant positive difference for nitrites between the tomatoes – raw material and the tomato broth (4.46 mg/L vs. 0.225 mg/L). The spectrometric analysis of the nitrate concentration in the tomato broth showed that the values obtained were under the detection limit of 2.21 mg/L.

- As for the heavy metal content, Pb and Cd in the raw material, the values obtained were under the LMA *(Reg. CE no. 1881/2006*). In case of Hg and As analysed by atomic absorption spectrometry, the values obtained for all the sample under analysis were under the detection limit of 0.01 mg/kg dry weight. The statistic analysis showed a significant positive difference for Pb (0.195 mg/kg dry weight vs. 0.135 mg/kg dry weight) and a distinctly significant positive difference for Cd (0.0155 mg/kg dry weight vs. 0.0028 mg/kg dry weight).

- The influence of the flow diagram over the concentration of Cu, Zn and Cr is high according to the statistic analysis performed, the differences being highly significant between the tomatoes-raw material and the tomato broth (12.565 mg/kg dry weight vs. 3.385 mg/kg dry weight - Cu; 4.142 mg/kg dry weight vs. 2.565 mg/kg dry weight - Zn; (0.0175 mg/kg dry weight vs. 0.0013 mg/kg dry weight - Cr).

- As for Sn, the values obtained in the finished products (0.2 mg/kg dry weight) are two times higher than for the raw material (0.1 mg/kg dry weight). Despite all these, the residue registered is much lower than the LMA imposed by the European Union for conserved food (200 mg/kg).

- For all pesticides analysed, the values obtained are below the MRL *(Reg. CE nr. 396/2005)* certifying first of all the quality of the raw material used and the food safety of the traded product, namely the tomato broth.

- The statistic analysis showed that the flow diagram for the production of tomato broth influenced to a smaller extent the residue content of organochlorine pesticides, organophosphorus, pyrethroids and fungicides. The deltamethrin content decreased its values following the processing of tomatoes thus obtaining a distinctly significant positive difference (0.107 mg/kg dry weight vs. 0.0037 mg/kg dry weight). The technological process favored the increase of pp' DDE concentration, thus obtaining a significant negative difference between the raw material and the finished product (0.0023 mg/kg dry weight vs. 0.0047 mg/kg dry weight). The same technological process highlighted increased content of ethion and bifenthrin, registering a distinct significant negative difference (0.0013 mg/kg dry weight vs. 0.0037 mg/kg dry weight) and significant (0.018 mg/kg dry weight vs. 0.0207 mg kg dry weight).

Results regarding the content of nitrates/nitrites, heavy metals and pesticides in green peas

- The content of nitrites/nitrates of the raw material decreased under the influence of the flow diagram, the statistic analysis registering significant positive differences for nitrates (24.175 mg/L vs. 20.19 mg/L) and insignificant for nitrites (4.573 mg/L vs. 3.943 mg/L).

- The content of Pb and Cd in the green peas was under the LMA *(Reg. CE nr. 1881/2006).* In case of Hg and As analysed by atomic absorption spectrometry, the values obtained for all the sample under analysis were under the detection limit of 0.01 mg/kg dry weight. We did not identify statistic differences between the raw material and the finished product for Pb and Cd.

- As for the contents of Cu, Zn, Cr and Sn, the flow diagram has led to slight variations between the raw material and the finished product. The influence of the flow diagram applied

was statistically appreciated as being significant for Zn (14.24 mg/kg dry weight vs. 10.858 mg/kg dry weight) and distinctly significant for Sn (2.35 mg/kg dry weight vs. 2 mg/kg dry weight).

- As for pesticides, the values obtained for the raw material and the finished product were under the MRL *(Reg. CE no. 396/2005)*, values that influence negatively the quality of green peas canned for consumption.
- Following processing, the residue content of organochlorine pesticides, organophosphorus pesticides, pyrethroids and fungicides decreased in most cases (30 out of 35).
- The flow diagram applied had a very significant positive influence on the contents of cypermethrin 2, permethrin 1, permethrin 2, cyfluthrin 3, folpet and iprodione; distinctly significant for alpha HCH, gamma HCH, pp' DDE, dieldrin, diazinon and captan and significant beta HCH, pp' DDT, alpha endosulfan, heptachlor, parathion-methyl, cypermethrin 1, cypermethrin 4, fenvalerate, lamba-cihalothrin and clorothalonil. The flow diagram highlighted a distinctly significant increase for deltamethrin in the canned green peas as compared to the green peas-raw material (0.0103 mg/kg dry weight vs. 0.0163 mg/kg dry weight).
- As for the analysis of quality of the auxiliary materials, we noticed that the admixture of $CaCl_2$ and NaCl in the technological water leads to the increase of nitrate/nitrite content and heavy metals (Pb, Cu, Zn, Cr and Sn).

Results regarding the content of nitrates/nitrites, heavy metals and pesticides in the beetroot

- The nitrate/nitrite content in the beetroot decrease following the processing, the statistic analysis showing very significant positive differences between the raw material and the finished product (1047 mg/L vs. 412.50 mg/L - nitrates; 0.845 mg/L vs. 0.0045 mg/L - nitrites).
- The Pb content (0.063 mg/kg dry weight) and Cd (0.003 mg/kg dry weight) in the beetroot - raw material was much smaller than the LMA (0.2 mg/kg - Pb and 0.1 mg/kg - Cd). By processing it decreased a lot, the finished product registering values under the detection limit of the device (0.01 mg/kg dry weight for lead and 0.001 mg/kg dry weight for cadmium).
- The spectrophotometric analysis of Hg, As and Cu content in all the samples analysed from the flow diagram showed that the metal residues were under the detection limit of 0.1 mg/kg dry weight for mercury and arsenic and 1.5 mg/kg dry weight for copper.
- As for the Sn content, we noticed its appearance only in the beetroot vinegar salad, in very small quantities (0.011 mg/kg dry weight), a phenomenon that may be due to the contamination of the product with the water used in the preparation of the covering liquid. The tests carried out on the technological water sample confirm this hypothesis.

- The flow diagram had an insignificant influence on the Zn content (29.167 mg/kg dry weight vs. 24.057 mg/kg dry weight), and in case of Cr there was a very significant positive difference between the raw material and the finished product (0.803 mg/kg dry weight vs. 0.013 mg/kg dry weight).
- As for the pesticide content in the raw material and the finished product, the values obtained were within the MRL *(Reg. CE no. 396/2005).*
- The statistic analysis showed that the flow diagram influenced to a small extent the residue content of organochlorine pesticides, organophosphorus pesticides, pyrethroids and fungicides. The influence of the flow diagram was statistically appreciated as being significant in case of content of HCH – total, pp' DDT, permethrin 2, cyfluthrin 3, lambda-cyhalothrin, captan and chlorothalonil. As for the content of alpha endosulfan (0.0203 mg/kg dry weight vs. 0.0033 mg/kg dry weight), aldrin (0.0063 mg/kg dry weight vs. 0.0013 mg/kg dry weight) and deltamethrin (0.04 mg/kg dry weight vs. 0.0067 mg/kg dry weight) they registered very distinctly significant differences between the raw material and the finished product.
- The auxiliary materials used in the preparation of the covering liquid contributed to the increase of nitrite, zinc and tin contents in the technological water.

The analysis of nitrites/nitrates, heavy metals and pesticides shows that the tomato sauce, the green peas cans thermosterilized and the beetroot vinegar salad have a normal content of these compounds, so they have a good quality for human consumption and trading.