STUDIES ON THE DYNAMICS OF PESTICIDE RESIDUES CONTENT DURING THE TECHNOLOGICAL PROCESS OF OBTAINING TOMATO JUICE AT SC CONTEC FOODS SRL TECUCI

STUDII ASUPRA DINAMICII CONȚINUTULUI UNOR REZIDUURI DE PESTICIDE PE PARCURSUL FLUXULUI TEHNOLOGIC DE OBȚINERE A SUCULUI DE TOMATE LA SC CONTEC FOODS SRL TECUCI

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Abstract. *The purpose of this study was to monitor residues of organochlorine pesticides (DDT and its metabolites, the total HCH and its metabolites) and residues of organophosphorus pesticide (ethyon, diazinon, methyl parathion) on tomatoes as raw materials for industrialization at SC Contec FOODS SRL Tecuci. The performed analyses were aimed at evaluating the dynamics of the level of pesticide residues in raw materials, the samples taken during the technological process and the finished good. Pesticide residues were quantified by using the gas-chromatographic method. In the skin of the seed produced according to the manufacturing process, the contents of the α-HCH was under the limit of detection. In the seed and skin residues were found the highest levels of (op'+pp') DDT namely 0,0056 mg/kg. The boil at 60-70^{0}C and the concentration process followed by pasteurization at 94-96^{0}C resulted in increased levels of pesticide residues in the finished good. Concentrations obtained were below the maximum limit admitted by law.*
Key words: residues, organochlorine pesticides, tomatoes

Rezumat. *Scopul acestui studiu a fost monitorizarea reziduurilor de pesticide organoclorurate (DDT-ul şi metaboliții săi, HCH-ul total şi metaboliții săi) şi al reziduurilor de pesticide organofosforice (etion, diazinon, paration metil) din tomatele materie primă pentru industrializare în cadrul SC Contec FOODS SRL Tecuci. Analizele efectuate au vizat evaluarea dinamicii nivelului reziduurilor de pesticide din materia primă, probele prelevate pe fluxul tehnologic şi produsul finit. Reziduurile de pesticide au fost cuantificate prin metoda gaz-cromatografică. În pielița și semințele obținute după procesul de prelucrare, conținutul în α-HCH a fost sub limita de detecției. În reziduu de sămânță şi pielița s-au găsit cele mai înalte niveluri de (op'+pp') DDT şi anume 0,0056 mg/kg. Fierberea la 60-70^{0}C precum şi procesul de concentrare urmat de pasteurizare la 94-96^{0}C au dus la creşterea nivelurilor de reziduuri de pesticide în produsul finit. Concentrațiile obținute au fost sub limitele maxime admise de legislația în vigoare.*
Cuvinte cheie: reziduuri, pesticide organoclorurate, tomate

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INTRODUCTION

Pesticides are an important tool in crop management practices and are widely used throughout the world. Although pesticides are deliberately added to improve the conditions for growth of tomatoes intended for processing, the excessive use of such abuse chemical compounds likely to constitute a danger to human health due to toxic residue ingested by eating food (Hura et al., 2011).

Pesticides organochorine (based on HCH hexachlorocyclohexane and DDT-pp-diclorfenil-trichloroethane) and the organophosphorus (methyl-, ethyl-parathion, malathion) have been replaced because of their high persistence and remanence in soils and crops, with other compounds - pyrethroids, which was considered for a time that would be less harmful to the environment and humans.

DDT is used as an insecticide for the control of insects in hygiene and agriculture. Commercial DDT is a mixture of several closely related compounds in which the balance is made up of dichloro-diphenyl dichloroethylene (DDE) and dichloro-diphenyl dichloroethane (DDD). DDE and DDD major metabolites are also and degradation in the environment.

Commercial DDT has been proven to be a mixture of 14 substances: DDT itself is 65-80%, op 'DDT 15-20% and DDD can be up to 14%.

Hexachlorocyclohexane (HCH) was marketed as a mixture of isomers, but mostly of β-isomer, and γ-HCH or lindane. HCH isomer has similar properties to other pesticides organochlorine, but is less polar and water-soluble (7 mg/l). Concentrates of HCH were used for controlling pests in agriculture.

Most of the organochlorine pesticides have high toxicity, because of this, in theory, they are not recommended for use.

Pesticides organophosphorus are more readily degradable than pesticides organochlorine, the presence of residues in tomatoes is largely accidental. Leading representatives of these groups are chemicals: parathion, malathion, ethion etc.

In terms of remanence, parathion and diazinon have the ability to persist longer into the ground than when it is applied directly on the tomatoes. On tomato and leaves, parathion remaining is between 7-21 days, depending on the meteorological factors and enzyme activity of plants (Rusu et al., 2005; Alloway and Ayres, 1997).

By industrial processing, the extent to which pesticides residues are removed depends on a variety of factors, such chemical properties of pesticides, nature of the product horticultural type of product processing stage and the length of time of contact of pesticides with horticultural products (Ma Jesús Chavarri, Antonio Herrera and Agustın Ariño, 2005).

The purpose was to assess the extent to which the various phases of the technological flow of tomato juice can influence both the upside and the decrease level of pesticides residues in the final product.

MATERIAL AND METHOD

Biological material used for the analyses was the tomatoes harvested at

maturity, in Tulcea County, and for recovery within the SC Contec FOODS SRL Tecuci. Samples were collected in October 2011. Immediately after sampling, the samples were put in polyethylene bags sealed with aluminium clips and stored at -20°C and liquid samples in glass containers, hermetically sealed and clean, stored at 4°C until extraction for pesticides residues.

In the study were determined organochlorine pesticides residues (10 active substances) and organophosphorus (3 active substances) from raw material, continuing with samples taken from the technological flow and reaching the final at the finished product.

Defining stages of processing as the tipping point for sampling in the analysis of the dynamics of content of pesticides residues are shown in fig. 1.

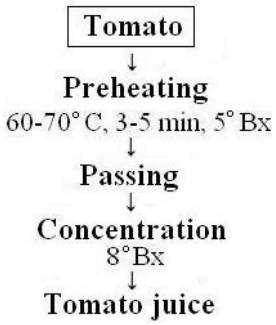

Fig. 1 - Stages of processing tomatoes for tomato juice

Determination of residues of pesticides has been carried out in accordance with the standards as follows: SR EN 12393-1, 2, 3: 2009-Food of plant origin. Multireziduu methods for the determination of pesticide residues by GC.

For the qualitative and quantitative determination of residues of POcl and POph study carried out within the same apparatus used as gas-chromatograph, Varian type 450, coupled with TSD detector, where they were injected automatically separated and purified samples after a preliminary processing of samples by extraction with organic solvents (acetonitrile, petroleum ether).

Following the results obtained, the correlations were calculated on the toxicity of pesticides on tomatoes, with their limits for admissibility laid down by the regulations of the European Commission. These limits are expressed in mg/kg, by Order No. 12 of January 23, 2006 are presented in table 1.

Table 1

Pesticide residues in tomatoes and maximum level (mg\/kg)

Pesticide	The maximum permitted level of pesticides (mg\/kg)
DDT (amount of pp'-DDT, op'-DDT, pp'-DDE, expressed as DDT)	0,05
HCH (alfa, gama, beta, delta)	0,01
Ethion	0,1
Diazinon	0,01
Methyl parathion	0,05

RESULTS AND DISCUSSION

The results for the contents in residues of DDT (op'+pp') and major metabolites in samples of different tomatoes collected after processing operations are shown in figure 2.

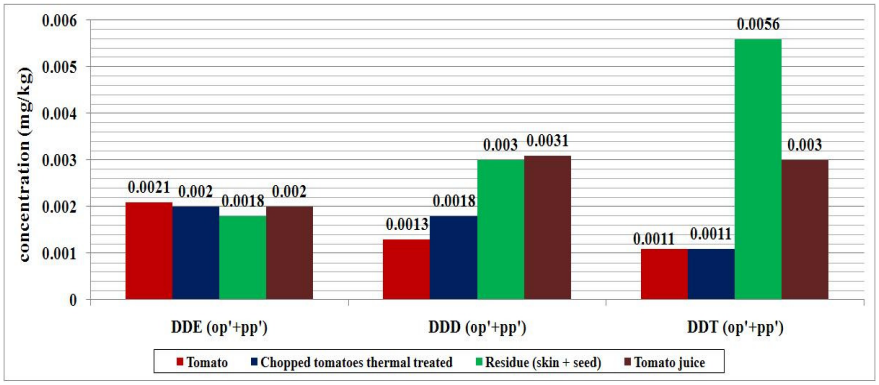

Fig. 2 - The effect of processing on the content of DDT and its metabolites, mg/kg

The level of residues of DDE (op'+pp') of tomatoes fell by 4.7% after washing and preheating at 60-70°C, the level remains constant and the juice of the tomatoes, finished product, due to its high stability to thermal processes (Abou-Arab, A. A. K., 1999).

Analysis on contents of DDD (op'+pp') of tomatoes highlight all samples of growth through their processing tomato with juicing. The level of residues after blanching increased by 38%, and between the tomatoes and the finished product has increased by approximately 2.5 times the original 0.0013 mg/kg.

Residues of DDT (op'+pp') of tomatoes and chop heat treated did not increase as a result of washing (2 washes and 2 showers with cold water) and chips, compared to the final product, where values have increased by 2.5 times, starting from a level of 0.0011 mg/kg. The highest content of DDT (op'+pp') are preserved in the seed produced cuticle, such as residues of processing tomatoes.

The levels of residues of tomato juice depend on the partitioning of their properties of peel/pulp and juice.

The effectiveness of the processing steps for decreasing concentrations of DDT and its metabolites also depends on their remanence in plant products. It is characterised by an extremely high persistence (after 17 years finding himself still 39% of the initial quantity), so that the amount of residue that can be removed by working decreases and residues tend to move into bloom or into deeper layers (often tomatoes pulp includes part of penetrating the skin, while retaining a substantial proportion of residues lipofile) (Ma Jesús Chavarri et al., 2005; Holland et al., 1994). This category of chemical contaminants has a reduced tendency to move from waxy layers.

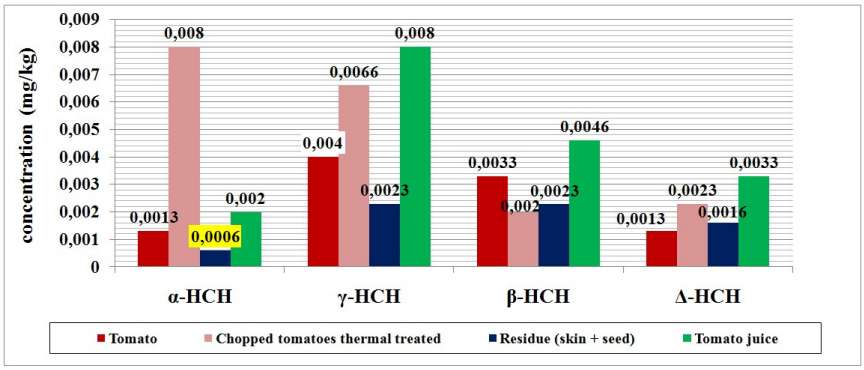

Fig. 3 - The effect of processing on the levels of HCH isomers, mg/kg

The effect of processing on the HCH isomers in tomatoes is shown in fig. 3.

Concentration of α, β, γ, δ-HCH has not been removed by processing tomatoes, this leads to an increase in concentration in the finished product. Effect of washing and thermal treatments, led to the concentration of pesticides in the tomato juice. This could be due to the strong absorption of plant tissues and/or low water solubility in this category of appropriate pesticides.

The contents of the isomer α-HCH, was below the limit of detection in the residue of hang and seed.

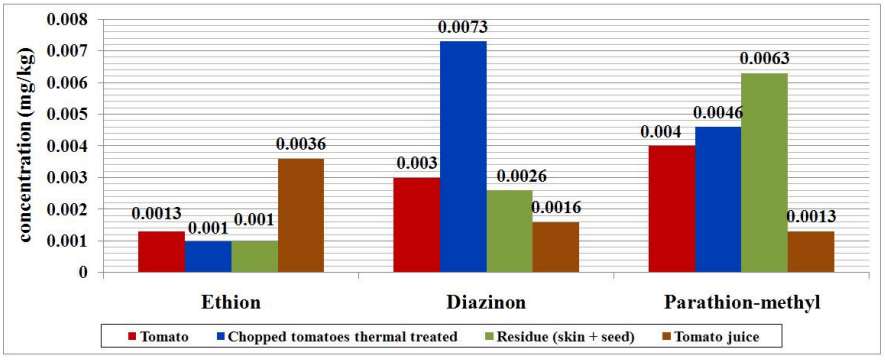

Fig. 4 - The effect of processing on the content of diazinon, ethion, parathion-methyl, mg/kg

The level of reduction of concentrations of diazinon and parathion-methyl on the stages of processing tomatoes, was higher due to the low stability to heat treatment and properties of water soluble to the values recorded for concentrations of ethion (fig. 4).

Residue level for ethion not dropped by the working class of the finished product, although after washing and thermal treatment of chop registered a decrease in apparent with only 23%. The sequence of heat treatments on the raw juice has led to an increase in concentration level for ethion 2.7 times, starting from a level originally 0.0013 mg/kg in tomatoes.

Influence of washing over the tomatoes, followed by heat treatment of chop on residues of diazinon has increased 2.5 times from an initial level of 0.003 mg/kg of tomatoes, which subsequently decreased by 46% in tomato juice.

Analysis of content of tomatoes on residues of parathion-methyl, led to an increase in heat treated chop with 15%, and then decreased to 32% by removing the residue of seed and hang and focus the raw juice followed by concentrated juice pasteurisation for packaging.

CONCLUSIONS

1. Influence of heat treatment processing through chop of 60-70°C, the phase of raw juice concentration at 8.5° Bx followed by pasteurization, resulted in increased concentrations of DDT and its metabolites and HCH's total, due to the high stability at high temperatures;

2. Because tomatoes are rich in vegetable waxes, pesticides are organochlorine and solvate in shell removal efficiency greatly decreased their (often tomatoes pulp including part of the reconstructed), contributing to the high content of the finished product;

3. Processing technological content in parathion-methyl and diazinon has been reduced, but did not place their total removal;

4. In all samples analysed, the levels of pesticides residues organochlorine and organophosphorus have been subject to the maximum extent permitted by applicable law.

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