CONSIDERATIONS ON THE CONTENT OF PESTICIDES RESIDUES IN VEGETABLES

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ABSTRACT

Pesticide contamination of vegetables, today, is more and more questionable. Biodegradability and molecular recalcitrance are two properties expressing the capacity of used substances in plant treatments. Therefore, it is preferred the use of those pesticides that decompose from a treatment to another without accumulating the pollutant residues. It is recommended that, when choosing a pesticide which is used in treatments, to keep in mind: no effect dose, tolerable daily intake, tolerable amount of residues, residues' limit, the maximum limit allowable, daily dose acceptable for the individual, level of tolerance, maximum limit of contamination allowed and the maximum daily intake acceptable for human. In the Laboratory of pesticide residues determination from plants and plant products in Târgu Mureş, pesticide residues were detected in some species of vegetables; methods of analysis used in the laboratory are multiresidual analysis methods developed in the laboratory (method GC x GC - TOF MS). To be mentioned that the pesticides detected values in vegetables have not exceeded the maximum permissible limits.

***Keywords**:* pesticide residues, chromatography, mass spectrometry, samples of plants, the active substance, the maximum limit admissible.

1. Introduction

In the pesticides category there are a number of natural or synthesized chemical compounds used in agriculture: herbicides, insecticides, fungicides, bactericides, rodenticides, nematocides, acaricides etc. The spread of pesticides(natural or synthesized chemical compounds used in agriculture) used for prevention or control, affect the environment(due to either actual use or accidental spread) and, as such, eventually reaching to food contamination, which affects human or animal's health and creates long term problems[6]. One of the pesticides was DDT, whose use was banned in the early 70's (U.S. 1972). It was subsequently banned the use of other pesticides (aldrin and dieldrin in 1983), which can persist in soil for long periods and, therefore, in plant products[1].

Nowadays over 6×10^6 chemical compounds are synthesized and over 60,000 are currently used. Beginning with 1950-1960, have started questions regarding their use, when it was noticed the negative effect, of some of them, on living organisms. Among the used pesticides, some are persistent, their residues accumulating in soils, water and plant products. The analysis of agricultural soils in our country showed the maximum concentrations of 9,543ppm and 9,113ppm HCH exceeding the allowable limit of 0.100ppm, influencing, of course, the amount of pesticide residues in vegetable products. The sizing of the residual amount and the persistence in time, in the soils depends on the chemical nature of the substance applied and the two properties that express its ability to be metabolized: biodegradability and molecular recalcitrance (chemical molecule resistance to metabolism).

It is preferred the use of pesticides containing active substance as effectively, but which will run out of control environment as soon as possible, respectively to decompose from a treatment to another without accumulating the pollutant residues[5].

The duration of active maintenance of a pesticide depends on a series of degradation factors: the presence of microorganisms, physical-chemical characteristics of the environment(pH, humidity)[3].

Uncontrolled application of fertilizers and pesticides or plant growing on soils contaminated above causes, determine the apparition both of nutritional disorders and of irreversible phenomena that affect quality, compromising crop production or cause the accumulation of substances above the permissible limits. When using a pesticide must be considered: no effect dose, tolerable daily intake, tolerable amount of residues, residues' limit, the maximum limit allowable, daily dose acceptable for the individual, level of tolerance, the maximum limit of contamination permissible and a maximum daily dose allowable for human[5].

In Romania, the Ministry of Agriculture and Rural Development, has the responsibility for monitoring national plans of pesticide residues in fruits, vegetables and grains. The Ministry of Agriculture and Rural Development, through the Laboratory for Pesticides Residues Control in Plants and Plant Products (LCRPPPV), as the national reference laboratory, is monitoring the pesticide residues in samples of fruits, vegetables and grains, according to the national monitoring plan, based on regulations (EC) 882/2004 and 396/2005.

2. Experimental procedure

In the Laboratory for the determination of pesticide residues from plants and plant products from Targu Mures, analyses have been made on 6 species of vegetables in order to find out the amount of pesticide residues in the fruit of the vegetables analyzed.

The laboratory for Mures area, tests the determination of pesticide residues in fruits, vegetables and cereals from producers in the counties: Mures, Alba, Bistrita Nasaud, Brasov, Cluj, Covasna, Harghita, Maramures, Satu Mare and Sibiu.

The Laboratory works in compliance with quality assurance requirements set forth in ISO 17025. The main activities that take place within this unit are:

- participation in monitoring programs for pesticide residues on agricultural products, classes of compounds and active substances;
- colaboration in establishing methods for the analysis of pesticide residues in plants and plant products compling with the requirements in EU directives;
- validation of the analysis on chemical classes of pesticides or active substances, namely on agricultural products.

2.1. Analysis methods and quality assurance. The principle of the method.

Pesticide residues are extracted from plant samples with organic solvents, an aliquot of the extract is evaporated and reversed in the mixture isooctane/toluene(9:1) containing hexachlorobenzene (HCB) as internal standard. Qualitative and quantitative determination of pesticide residues are realized through gas chromatography coupled with mass spectrometry (GC-TOF MS x GC). Methods of analysis used in the laboratory are multiresidual methods of analysis, developed in the laboratory. GC x GC-TOF MS method was developed for 65 active substances including isomers.

3. Results and discussions

For determination of pesticide residues was used a GC x GC TOF MS equipment (gas chromatograph coupled mass spectrometer with time of flight). The method of analysis was as follows:

3.1. Operating Parameters Agilent Gas Chromatograph 7890: Carrier gas: Helium, 1 ml/min Temperature Program: Column 1: Rxi MS: 30 m x 0.25 mm x 0.25 um Column 2: BPX-50: 1.6m x 0.1mm x 0.1um Coloana1: 70°(1 min), 20°/min, 140°, 5°/min-310°(4 min) Column 2: 95°(1 min), 20°/min, 165°, 5°/min-330°(4 min)

Mass spectrometer: Leco Pegasus 4D GC x GC TOF MS Ionisation: EI, 70eV Source temperature: 220° C Mass range: 40-450u.

3.2. Processing and interpretation of data:

Chroma TOF Leco software with automatic identification of peaks and their deconvolution.

Vegetable species were subjected to determinations:

- pepper (Capsicum annuum L.ssp. macrocarpum P),
- cucumbers (Cucumis sativus L.),
- tomatoes (Lycopersiconesculentum Mill)
- mushrooms (Psalliota hortensis Cooke),
- cabbage (Brassica oleraceaL convar.capitata),
- potatoes (Solanum tuberosum).

Analyzed vegetables are of indigenous origin, except for a tomato sample from Turkey.

Table 1
Samples of vegetables subject determinations

Agricultural product	Analyzed samples				Samples without pesticide residues				Samples with pesticide residues			
	Total	Original	Import UE	Import non UE	Total	Original	Import UE	Import non UE	Total	Original	Import UE	Import non UE
Pepper	9	9	0	0	6	6	0	0	3	3	0	0
Potatoes	79	79	0	0	76	76	0	0	3	3	0	0
Cucumbers	14	14	0	0	9	9	0	0	5	5	0	0
Mashrooms	5	5	0	0	4	4	0	0	1	1	0	0
Tomatoes	14	13	0	1	10	10	0	0	4	3	0	1
Cabbage	12	12	0	0	12	12	0	0	0	0	0	0
Total	**133**	**132**	**0**	**1**	**117**	**117**	**0**	**0**	**16**	**15**	**0**	**1**

From Table 1 it is observed that it was analyzed a total of 133 samples, of total samples analyzed, in 16 samples (15 domestic and one imported) were detected pesticide residues. This is emphasized in Table 2.

The observations made show that in two of the samples (tomatoes imported and domestic potato sample submitted, each with two pesticides), other samples had only one pesticide (Table 2).

Table 2
Monitoring pesticide residues in samples analyzed

Agricultural product	Sample's origin	Nr. s.a.	s. a. 1	Result (mg/kg)	s.a. 2	Result (mg/kg)	Environment autorisation limit(mg/kg)
Potatoes	original	1	Lambda cihalotrin	0,01			0,1
Mushrooms	original	1	procloraz	0,36			0,5
Potatoes	Original	1	pirimicarb	0,01			2
Cucumbers	Original	1	spiroxamina	0,02			0,05
Tomatoes	Turcia	2	captan	0,08	triadimenol	0,07	3/0,2
Peppers	Original	1	propargite	0,10			3
Tomatoes	Original	1	vinclozolin	0,02			0,05
Peppers	Original	1	bromopropilat	0,03			2
Cucubers	Original	1	bifentrin	0,01			0,3
Cucumbers	Original	1	bifentrin	0,01			0,3
Peppers	Original	1	propargite	0,04			3
Cucumbers	**original**	**1**	**ciprodinil**	**0,11**			**1**
Cucumbers	Original	1	ciprodinil	0,04			1
Tomatoes	**Original**	**1**	**bifentrin**	**0,01**			**0,3**
Potatoes	original	1	clorpirifos	0,02	tebuconazol	0,14	0,5/1

Frequently detected pesticides in vegetable samples are: cyprodinil(C14 H15 N3), bifenthrin(C23 H22 Cl F3 O2), for which we present the chromatogram for cucumber and tomato samples, calibration curves and spectra of cyprodinil and bifenthrin.

We mention that the pesticides' values detected in vegetables have not exceeded the maximum permissible limits.

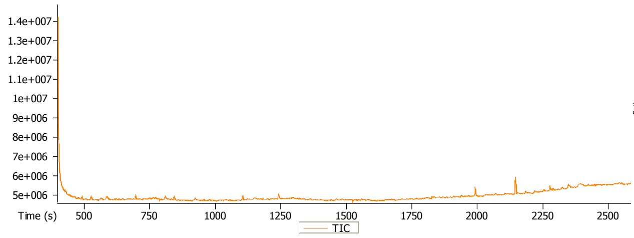

Fig 1. Cucumber sample chromatogram

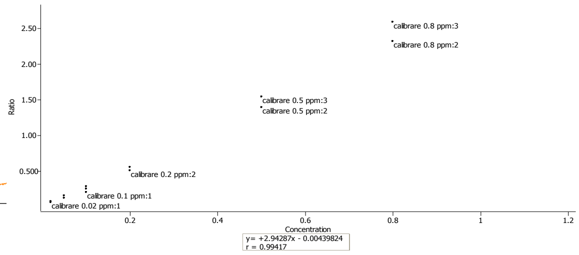

Fig.3. Cyprodinil calibration curve

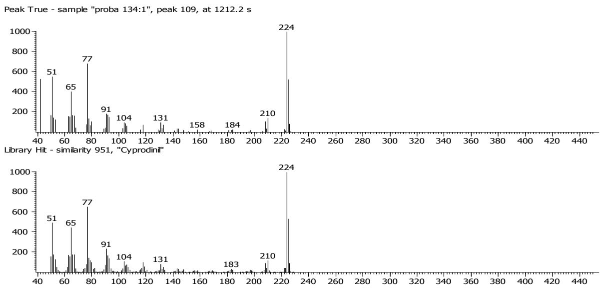

Fig. 2. Cyprodinil spectrum

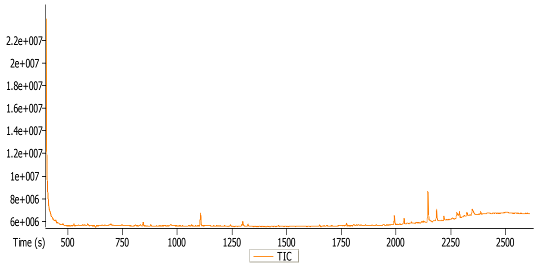

Fig. 4. Tomatoes samples chromatogram

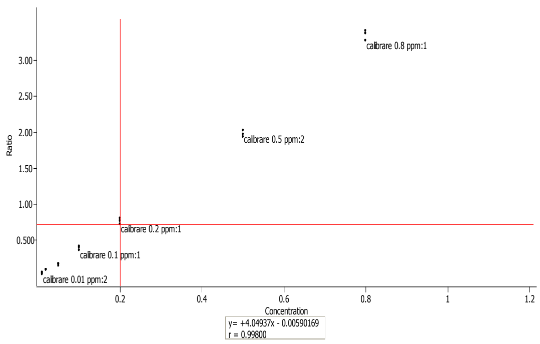

Fig 5 Bifethrin calibration curve

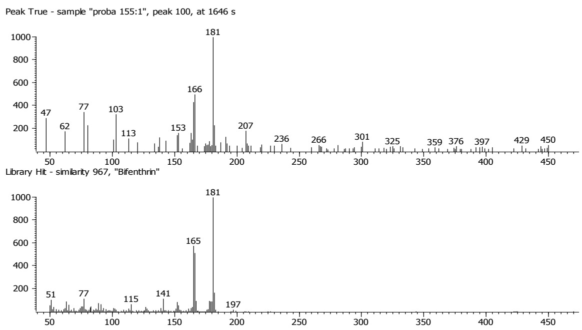

Fig. 6. Bifethrin spectrum

4. Conclusions

Following the observations made, we can mention:

- 133 samples were analyzed;
- All samples analyzed and found with pesticide residues and had lower values than the maximum limits allowed (MRL);
- The most common pesticide detected in samples are: cyprodinil, bifenthrin, propargite;
- Products that contained residues of pesticides in higher proportion were mushrooms.

References

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*** Regulation (EC) No 396/2005 of the European Parliament and Council, 23 February2005 on maximum residue levels of pesticides in or on food and feed of plant origin.