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TOXICOLOGICAL STUDIES ON FOOD PRODUCTS FROM BRASOV COUNTY

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Abstract: *Food quality is very well monitories by local and national Directions for Food Safety. The results of their analyze concerning the content of heavy metals (lead, cadmium) and the level of organophosphorus and organochlorine pesticides, during 2006 and 2007 were presented in this article. In all those cases the obtained values range are in the maximum allowed limits of the present legislation.*

Key words: *heavy metals, pesticides, toxicology, chromatography, food.*

1. Introduction

Foods may be contaminated by chemicals from many different sources (soil, sediment, water, air). Using different kinds of food (meat, dairy products, fish, vegetables, and fruits), animals and human may beings also contaminated with chemicals.

Heavy metals toxicology is an important problem of environmental pollution, together with still uncontrolled use of pesticide for crop protection. Most of heavy metals are harmful for human beings' health, animals and plants. All these contaminations with heavy metals determine important health hazards associated with the toxic effects of organochlorine pesticides, because of bioaccumulation in the bodies of wildlife and people [10]. Organophosphorus pesticides used in agriculture are highly toxic as acute exposure and sometimes, their metabolites indicate an increase in their toxicity during the microsomal oxidation.

Hexachlorocyclohexane (HCH), a synthetic organochlorine pesticide, commercially known only from four (α-HCH, β-HCH, γ-HCH, and δ-HCH) of its eight isomers. γ-HCH, commonly referred to as lindane, is used as seed treatment for barley, corn, oats, rye, sorghum, and wheat. Lindane is also used in very small quantities as prescription medication for the treatment of scabies and lice [7].

The FDA does not recommend the use of γ-HCH for infants, children and adults weighing less than 50 kg.

DDT (dichlorodiphenyltrichloroethane) is one of the most well-known synthetic pesticides, used with great effect among both military and civilian populations to control mosquitoes spreading malaria and lice transmitting typhus, resulting in dramatic reductions in the incidence of both diseases. Under the Stockholm Convention, DDT was subsequently banned for agricultural use worldwide [3].

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Actually, its controversial use is limited only to disease vector control (in certain parts of the world).

Organohosphorus pesticides (OP)/nerve agents are still considered important chemicals acting on living organisms and are widely used. They are characterized according to their action as compounds influencing cholinergic nerve transmission via acetylcholinesterase inhibition (AChE). The toxic effects of nerve agents are due primarily to their inhibition of AChE and the resulting accumulation of acetylcholine [1], [2], [9].

Pesticide analysis remains one of the leading qualitative and quantitative applications of TLC and HPTLC for analysis of foods and crops, environmental samples, forensic and medical samples, biological samples and commercial formulations [8].

To problems associated with a high content of heavy metal in food and feed are compared with the maximum allowed limits in several commodities recommended by European legislation, a.o. Commission Directive 2001/22/EC [4], Commission Directive 2002/32/EC [10] and Commission Regulation (EC) 466/2001 [5].

The aim of this study was the evaluation of the heavy metals (lead and cadmium) and pesticides (organophosphates -OP and organochlorines - OCl) contents in several food products from supermarkets of Brasov County. Monitoring these contaminants in food samples is of extreme importance considering the impact that such polluted matrices would have on our everyday lives.

2. Materials and Methods

The analyses were carried out in the D.S.V.S.A. - Brasov and Galati laboratories.

The samples were minced and homogenized with a mixer and measured with a weigh precision of 10^{-4} g.

The determinations were made using for the determinations class A glassware and high purity reagents for chromatography.

The residual analyses we made were:

Heavy metals: the heavy metals (Pb, Cd) were determined after the calcination of samples by means of atomic absorption spectrometry (AAS).

For determining Pb and Cd the homogenates samples were burned to ashes, purified in HCl solution (c = 6mol/L) - and diluted in HNO_3 solution (c = 0.1 mol/L). The results were read with the help of a spectrophotometer with atomic absorption capacity after a calibration curve had been made, for Pb, or Cd (Table 1), (according to SR-EN 14 082/2-2003.) in D.S.V.S.A. - Brasov laboratory.

Standard samples of lead and cadmium used for calibration curves in AAS Table 1

Standard solutions	Stock solution	Used solution no.1	Used solution no.2	Used solution no.3	Used solution no.4	Used solution no.5
Cd	100	0,1	0,3	0,5	0,7	1,0
Pb	100	0,2	0,4	0,6	0,8	1,0

Pesticides: by the extracted samples in a organic solvents, by means of the gas chromatography method (according to AOAC 970.52) in D.S.V.S.A.- Galati laboratory.

All used chemical reagents were certified with quality certificates by the supplying companies. The necessary equipment was validated and metrological labelled.

For pesticides analysis, the fats were obtained by extraction using petroleum ether from food matrices (32-35 ^{0}C), than from three times with acetonitril and petroleum ether. The etheric extract had been washed with sodium sulphate solution 4%. The following step was the purification with anhydrous sodium sulphate in columns, and florisil (60-100mesh). Elution solvents were concentrated at 5 mL, than petroleum ether was taken at 10 mL. This sample was injected in gas – chromatograph equipment.

During gas - chromatography specific work conditions were necessary:

- columns temperature = 200^{0}C;
- injector temperature = 225^{0}C -250^{0}C;
- gas phase: N_2 from 99,99%.

First, etalon solutions (1-2 µL) were injected in the column 2-3 times. Then had been injected 1-2 µL samples and their picks were compared with chromatogram picks of standard pesticides (OCl, OP).

The values of heavy metals content in analysed samples Table 2

Name product	**Pb, ppm**		**Cd, ppm**	
	2006	**2007**	**2006**	**2007**
Cereals	0,00..0,001	0,00..0,063	0,00	0,00..0,02
Meat (pork, beef, poultry)	0,00..0,001	0,00..0,0037	0,000	0,00..0,0001
Organs (pork, beef, poultry)	0,00..0,007	0,00..0,006	0,000	0,000
Salami	0,0026..0,0079	0,0015..0,0055	0,000	0,000
Milk	0,000	0,000	0,000	0,000
Cheese	0,000..0,0032	0,000..0,0042	0,000	0,000
Fish	0,00..0,026	0,00..0,076	0,000	0,000
Mushroom	0,02..0,05	0,04..0,09	0,00..0,05	0,000..0,07
Tea	0,00..4,23	0,29..4,49	0,00..0,84	0,039..1,05
Alcoholic drink	0,000	0,00..0,65	0,000	0,000
Sugar	0,000	0,000	0,000	0,000
Fruits	0,07..0,09	0,06..0,08	0,000..0,002	0,001..0,003
R^2	**0,996.....1,000**		**0,998…1,00**	

R^2 - The determination coefficient of Pb and Cd

3. Results and Discussion

The present study aims to prove the evidence of heavy metals and pesticides in food products in 2006 and 2007.

The samples gathered from food production units and supermarkets from the county of Brasov.

The values of heavy metals content in analysed samples are presented in the Table 2.

The values of the pesticides measurements in 2006 are shown in Table 3. The measurements from 2007 are present in Table 4.

The values for the pesticides measurements in 2006 Table 3

Name product	α HCH	Lindane	β HCH	DDT total	Other OCl	OP total
Eggs	0,003… 0,004	0,002…. 0,003	< 0,01	< 0,04	< 0,01	< 0,01
Row milk	0,005	0,005	< 0,01	< 0,01	< 0,01	< 0,01
Honey	< 0,005	0,001…. 0,004	< 0,01	< 0,01	< 0,01	< 0,01
Fat Meat (pork, beef, poultry)	0,004…0,005	0,005… 0,009	< 0,01	< 0,01	< 0,01	< 0,01
Cheese	0,004…0,016	0,005… 0,006	0,01... 0,013	0,08... 0,013	< 0,01	< 0,01
Fruits (pear, apple)	-	-	-	-	-	< 0,01

OCl – Organochlorine pesticides; OP- Organophosphorus pesticides

The values for the pesticides measurements in 2007 Table 4

Name product	α HCH	Lindane	β HCH	DDT total	Other OCl	OP total
Eggs	0,002… 0,004	0,001… 0,002	< 0,01	< 0,04	< 0,01	< 0,01
Row milk	< 0,005	< 0,005	< 0,01	< 0,01	< 0,01	< 0,01
Honey	< 0,005	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01
Fat Meat (pork, beef, poultry)	0,002… 0,006	0,004… 0,007	< 0,01	< 0,01	< 0,01	< 0,01
Cheese	0,004.. .0,016	0,005… 0,006	0,01…0,013	0,08… 0,013	< 0,01	< 0,01
Fruits (pear, apple)	-	-	-	-	-	< 0,01
Tomato	-	-	-	-	-	< 0,01

In all those cases the ranges of obtained values are in the maximum allowed limits of the present legislation:

- ANSVSA Ordonance 97 / 2005 for alimentary products;
- CE Ordnance 1881/2006.

These laboratories apply a GPL system and a quality system.

The final results were achieved by comparing the acquired values with the values imposed by the standards of producers' companies, the professional standards as well as the actual legislations.

4. Conclusion

The residual control of food products is an important element guarantee for quality and the consumer's safety.

The obtained values showed that none of the samples which had been tested were above the maximum allowed level.

Established supervision and control of heavy metals and pesticides in the present study proved that the above products were not a hazard for human health.

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