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THE BENZ[A]PYRENE MONITORING IN SUNFLOWER SEEDS AS THE WAY TO CANCEROGENIC SAFETY OF FOOD OILS AND OIL AND FAT CONTAINING PRODUCTS.

Показано актуальність проведення моніторингу насіння соняшнику на вміст поліциклічних ароматичних вуглеводнів, зокрема бенз(а)пірену. Обґрунтовано необхідність вирішення проблеми канцерогенної безпеки олієжирових та жировмісних харчових продуктів з надійним їх контролем за бенз(а)піреном.

Ключові слова: *канцерогенна безпека, соняшникове насіння, олія, жири, бенз(а)пірен, моніторинг.*

Показана актуальность проведения мониторинга семян подсолнечника на содержание полициклических ароматических углеводородов, а именно бенз(а)пирена. Обоснована необходимость решения проблемы канцерогенной безопасности масложировых и жиросодержащих пищевых продуктов с надежным их контролем по бенз(а)пирену.

Ключевые слова: *канцерогенная безопасность, семена подсолнечника, масло, жиры, бенз(а)пирен, моніторинг.*

The importance of monitoring the contents of polycyclic aromatic hydrocarbons (namely benz(a)pyrene) in sunflower seeds on is shown. The necessity of reliable monitoring the level of benz(a)pyrene in oil, fat and fat-containing food products for the sake of cancerogenic safety is substantiated.

Keywords: *cancerogenic safety, sunflower seeds, oil, fat, benz(a)pyrene, monitoring.*

The problem in general.

Polycyclic aromatic hydrocarbons (PAHs) are widespread contaminants of sunflower seeds, vegetable oils and foods based on them. To solve the problem of cancerogenic safety it is necessary to provide the control of PAHs in this group of foods because the above mentioned compounds have cancerogenic effect. [1- 4]. As it is known from the activity of oil and fat enterprises which export vegetable oil, the benz[a]pyrene amount is under special control among the organic ecotoxicants [5, 6].

Benz[a]pyrene is an oncogenic matter belonging to PAHs which are formed in some organic substances under high temperatures. Technologic and burnt gases, combustion products from the heating units, stove and smoke fumes contain PAHs [7-12]. The most important thing in PAHs spreading in the atmosphere is more than 90% amount of benz[a]pyrene from the total emissions of all the hydrocarbons. These compounds get to vegetable oils and other oil-and-fat products from the environment [13-15]. The most possible way of PAHs penetrating into oilseeds is drying with the heating unit which contains products of incomplete combustion including PAHs [16]. A significant amount of PAHs appears while burning rubbish, polymeric packages and oil derivatives. In modern conditions benz[a]pyrene is found in the products that

haven't been considered as those containing PAHs before. It is discovered that PAHs in oilseeds contain about 95% of benz[a]pyrene [17-21].

The presence of benz[a]pyrene in foods is considered as cancerogenic PAHs contamination marker. Nowadays in EU countries a lot of attention is paid to oil-and-fat products safety control as well as to the amount of benz[a]pyrene in vegetable oils. The EU Commission instruction 208/2005/EU strictly regulates the content of PAHs in foods. In particular, the content of benz[a]pyrene in fat must not exceed 0,002 mg/kg [17-21].

To protect consumers' health it is necessary to minimize the amount of benz[a]pyrene in particular foods and special products, especially in those with high concentration of vegetable oils, fats, modified fats as well as in products which can be highly contaminated while smoking or drying [23, 24]. The impact of technological treatment on the benz[a]pyrene amount in vegetable oils is known. Hydration and alkaline neutralization do not create conditions for benz[a]pyrene disposal. A number of adsorbents used while bleaching depending on their nature do not conduce entirely, partly or at all benz[a]pyrene disposal from vegetable oils. Hydration and deodorization process reduces the benz[a]pyrene level to 40%-80% in comparison with original oil and fat stock. PAHs disposal from vegetable oils is possible through complete refining including adsorptive purifying and deodorization at 210˚C [25 - 29].

The system of quality and safety monitoring is introduced at oil and fat enterprises. This system is based on international standards of hazards and critical control point's analysis. So there is an urgent need to create the system of receiving necessary information about technological processes specifically monitoring used to find critical points. This permits to reduce the amount of benz[a]pyrene in sunflower seeds, oils and oil and fat products.

Analysis of latest researches and publications.

Concentration, trends and distribution of PAH in industrial region's ground has been shown in the work [11]. Risk factors and total negative influence of ecotoxicants (pesticides and PAHs) on the people in Minnesota (USA) has been shown in [12]. The issue concerning the 3,4 benz[a]pyrene amount regulation in vegetable oils and fats has been highlighted in the work [27]. The problem of identifying the 3,4 benz[a]pyrene in vegetable oils and fats is urgent especially for oil-and-fat complex of Ukraine [28]. To solve the problem of cancerogenic safety it is necessary to provide the control of PAHs in foods [30].

The aim of our researches is using modern analytical methods of PAHs identification, especially benz[a]pyrene in sunflower seed for 2011-2012 marketing year.

The basic research material presentation.

Identifying the benz[a]pyrene through HPLC method have been carried at Aglient 1200 liquid chromatograph with fluorescence detector according to ISO 22959 "Animal and vegetable fats and oils -- Determination of polycyclic aromatic hydrocarbons by on-line donor-acceptor complex chromatography and HPLC with fluorescence detection" [9-11].

For 2011-2012 marketing year more than 1000 samples of sunflower seeds have been investigated. As a result it has been established that the amount of benz[a]pyrene in sunflower seeds was anywhere from 0,9 to15,0 μg /kg, and in some cases reached 100 μg /kg. Images1-8 show the amount of benz[a]pyrene in oil samples in percentage points that does not exceed 2,0 μg /kg and exceeding the following standard for the period from September to April.

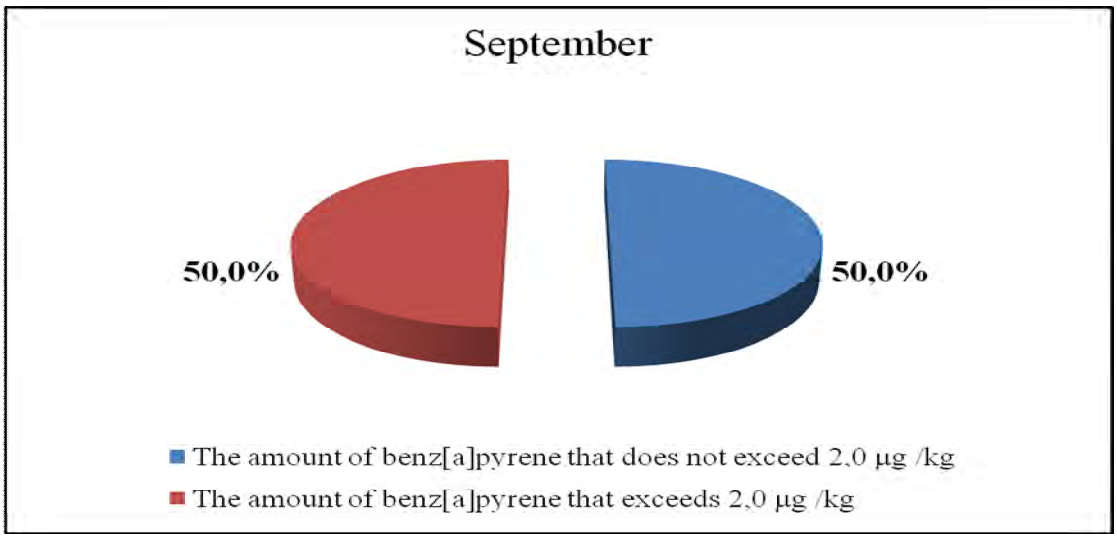

Image 1. The amount of benz[a]pyrene in oil samples for September.

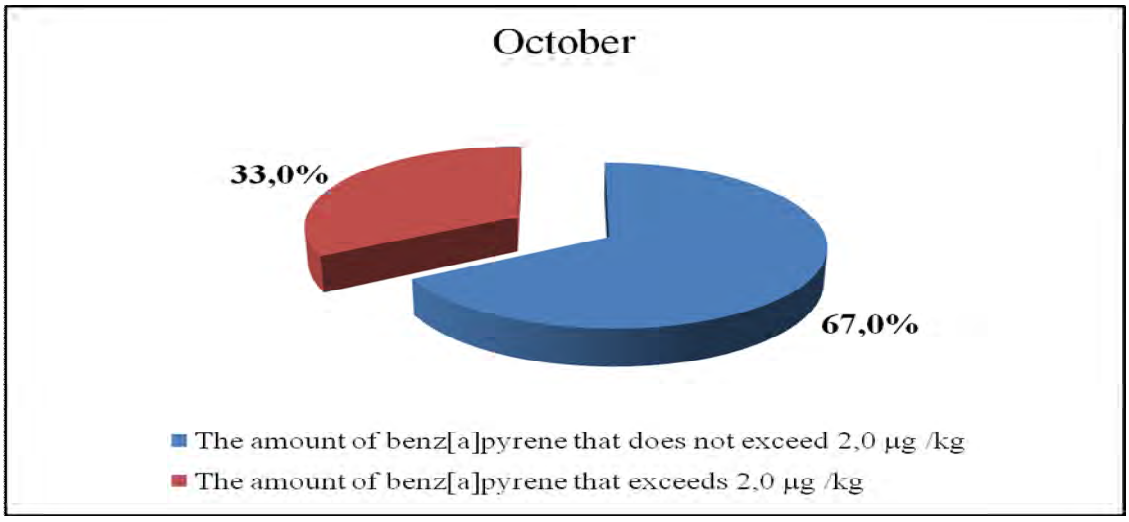

Image 2. The amount of benz[a]pyrene in oil samples for October.

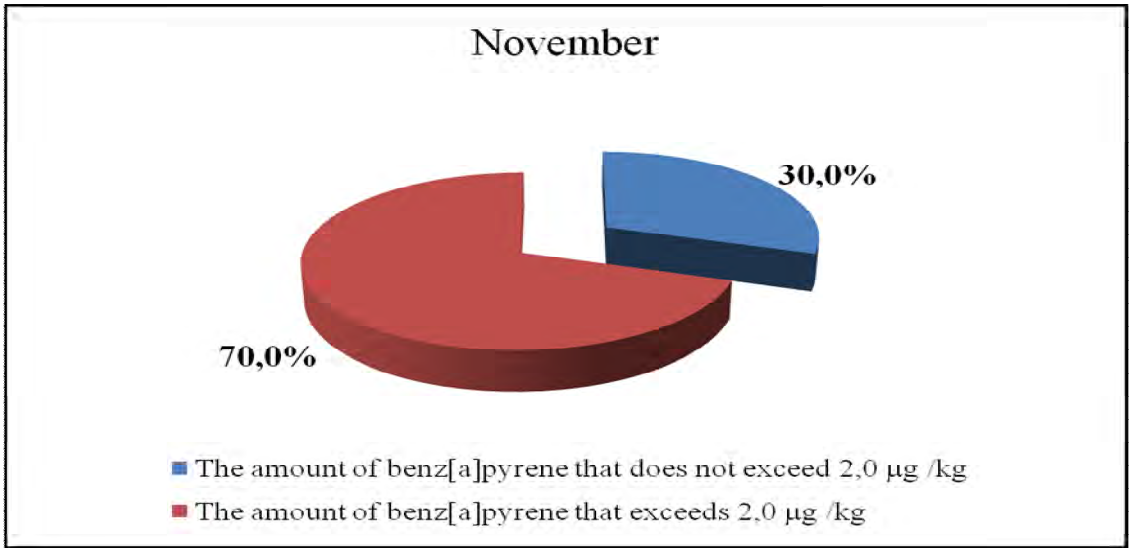

Image 3. The amount of benz[a]pyrene in oil samples for November.

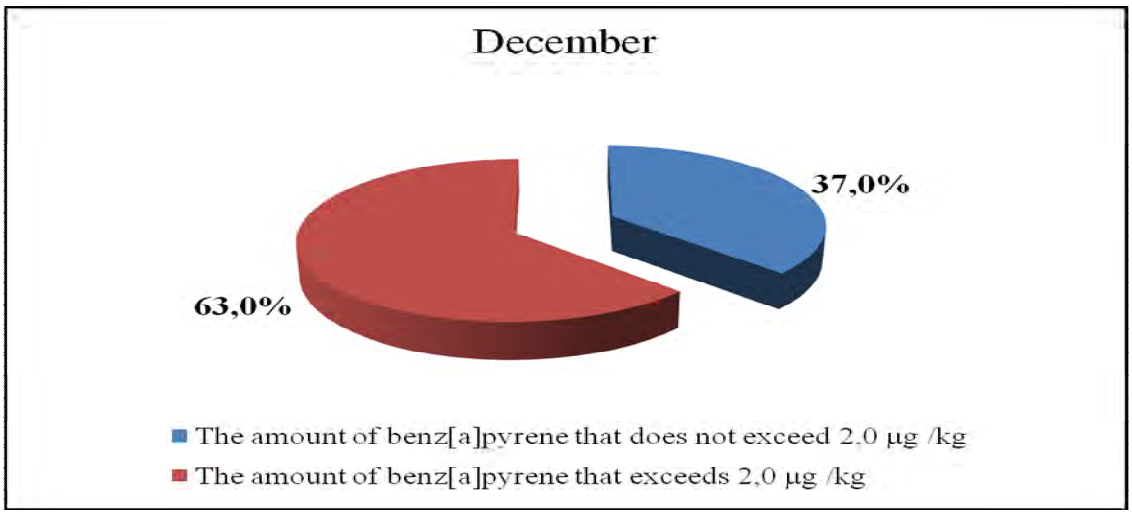

Image 4. The amount of benz[a]pyrene in oil samples for December.

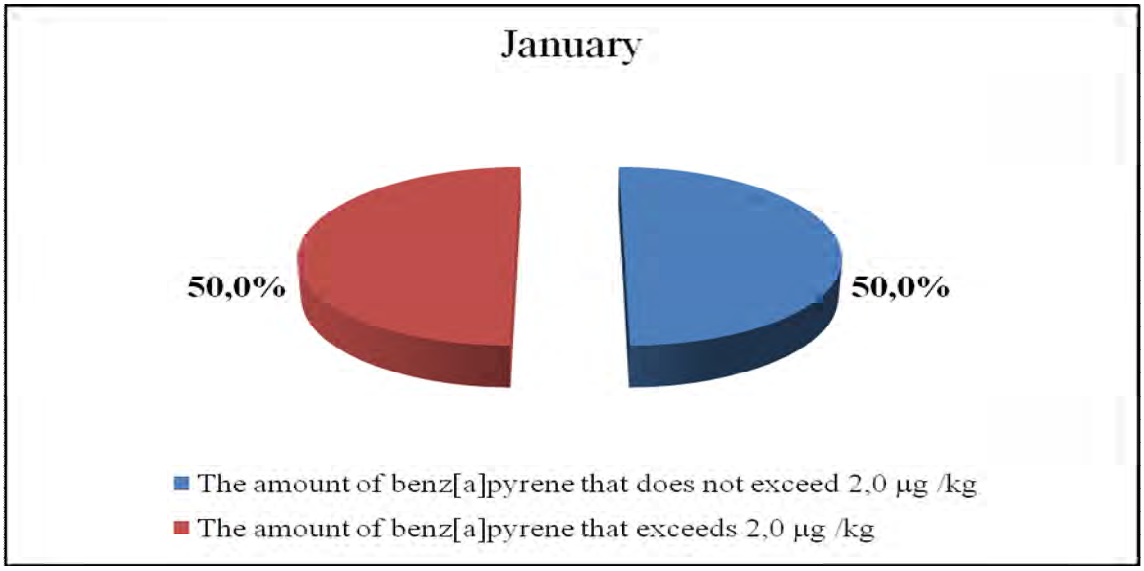

Image 5. The amount of benz[a]pyrene in oil samples for January.

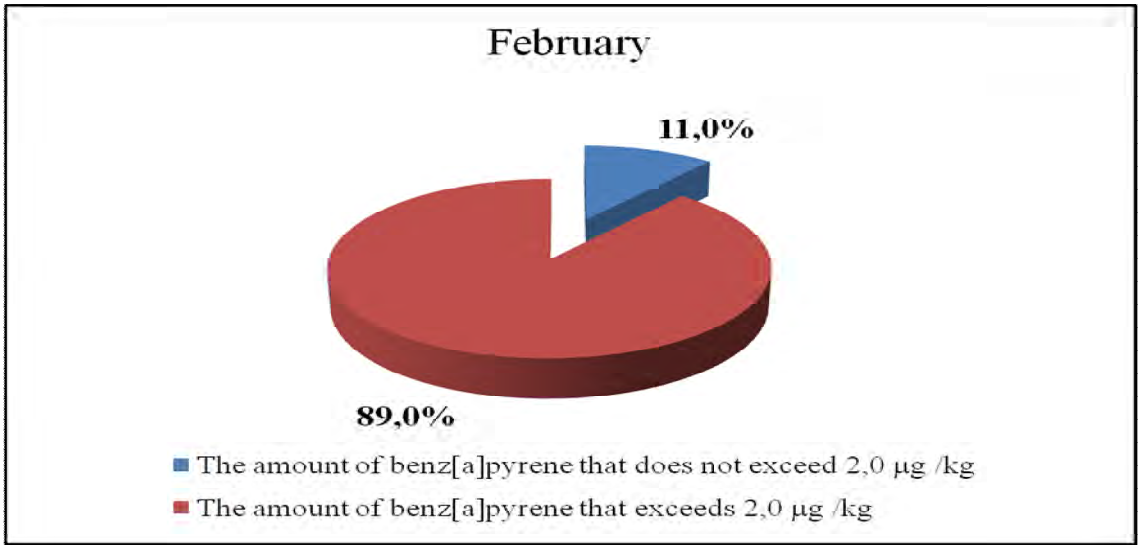

Image 6. The amount of benz[a]pyrene in oil samples for February.

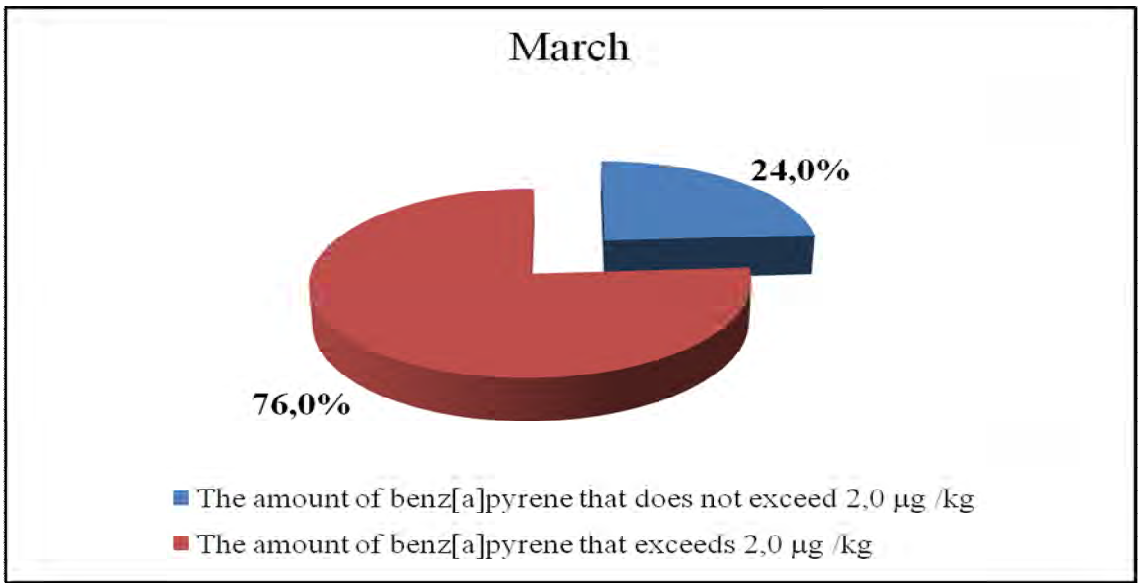

Image 7. The amount of benz[a]pyrene in oil samples for March.

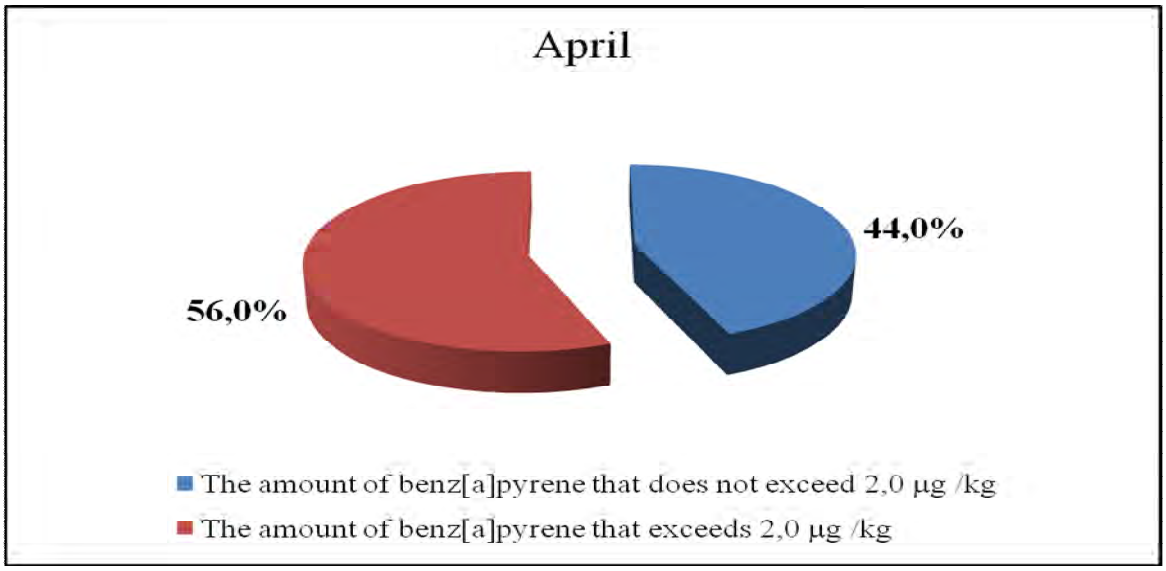

Image 8. The amount of benz[a]pyrene in oil samples for April.

The statistic data received for sunflower seeds (images 1-8) correlate well with the results of unrefined oils with excessive amount of benz[a]pyrene was 51% (image 9).

According to benz[a]pyrene monitoring data the necessity of techno chemical control of benz[a]pyrene amount in sunflower seeds, vegetable oils and their convertibles has been established to reduce the amount of benz[a]pyrene to 2 µg /kg.

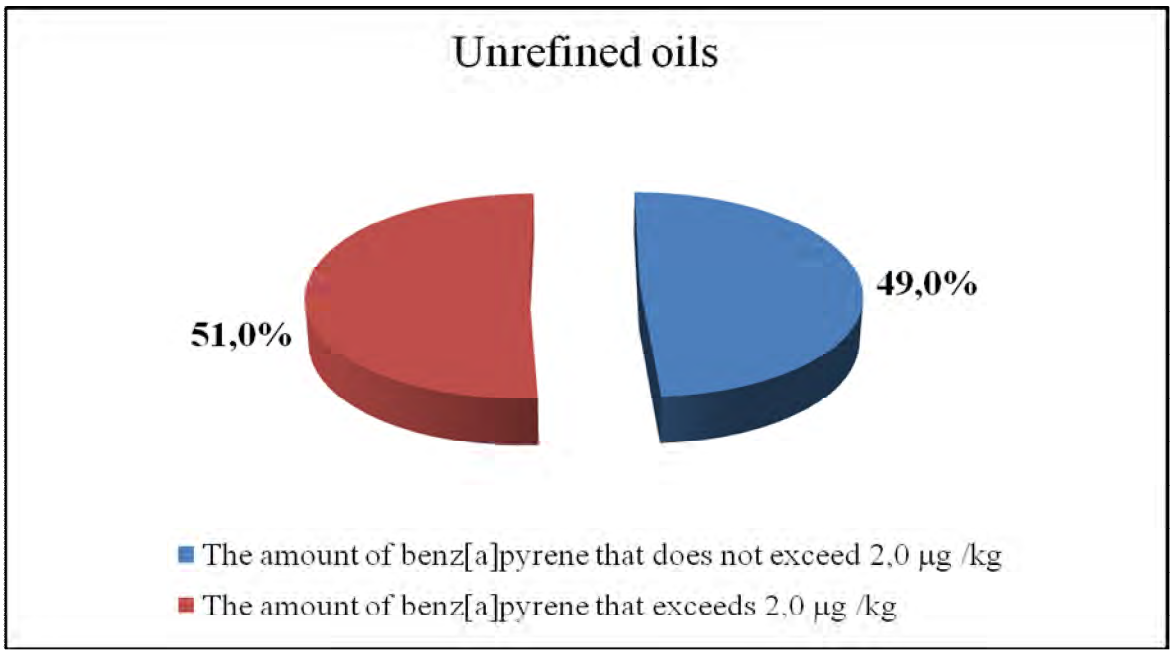

Image 9. Unrefined oils research data to identifying the amount of benz[a]pyrene.

The benz[a]pyrene monitoring in margarine products has been carried before and after its shipping for the long distance to the destination. While investigating margarine products (confectionery fats, margarines) to identify the benz[a]pyrene amount it has been established that when being transported the benz[a]pyrene amount was increasing and the benz[a]pyrene migration has been found at depths down to 8-12 mm [30]. On this showing the conclusion can be made that increasing of benz[a]pyrene amount on the surface of investigated products appears because it is adsorbed from gas emissions during shipment.

It has been also proved that the most likely way of benz[a]pyrene and other PAHs penetrating to oilseeds is drying with the heating unit which contains products of incomplete combustion and the storage the seeds on asphalt coating at grain storages. Analysis of sunflower seeds monitoring for 2011-2012 marketing year by the month (Images 1-8) shows technological process namely drying and predrying significantly influence the increase of benz[a]pyrene amount. Technologically drying at enterprises can be organized at different temperatures to reduce the humidity level in sunflower seeds. Depending on the humidity level in sunflower seeds the length and conditions of drying are changed and this impacts the adsorption of polycyclic aromatic hydrocarbons. Using active ventilation in the process of sunflower seeds drying reduces the benz[a]pyrene level (Image 10). It has been discovered that if sunflower seeds contain 0,5 µg /kg of benz[a]pyrene before drying, this level increases to 3,5 µg /kg after drying, but after active ventilation it reduces to 2,5 µg /kg. The data about reducing of benz[a]pyrene level (image 8) in comparison with the period from December 2011-March 2012 (images 3-7) can be explained by using drying and predrying technologies as well as active ventilation. By way of proof the data obtained we have investigated weedage seeds, petrol, flooring and furr. The data are shown in table 1.

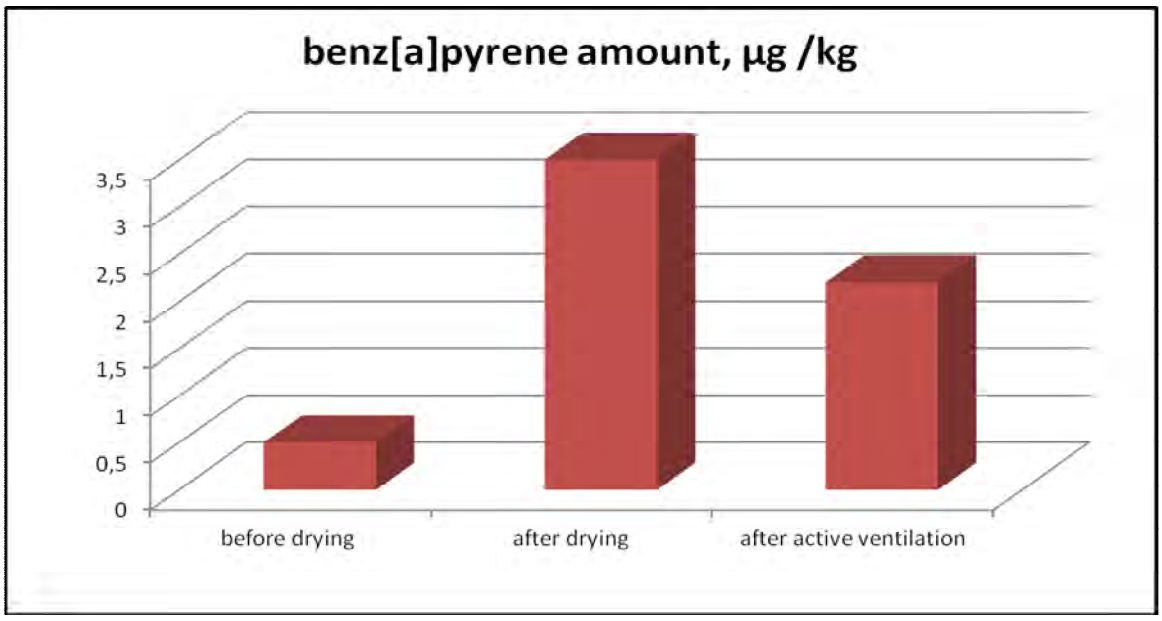

Image 10. The benz[a]pyrene amount in sunflower seeds while drying and after active ventilation.

Table 1

The weight part of benz[a]pyrene, µg /kg	
Weedage seeds	2,2
Asphalt flooring	29800
Furr	16,6
The weight part of benz[a]pyrene, µg /dm^3	
Petrol	5691

The obtained data prove that the most likely ways of cancerogenic PAHs penetrating to sunflower seeds, vegetable oil and foods through asphalt flooring, using petrol of poor quality, and growing sunflowers along the roads. Thus, there is an urgent need to identify the impact of sunflower cultivation technology, drying, predrying and converting to find the critical points. This allows reducing benz[a]pyrene amount in vegetable oils and oil and fat products. The benz[a]pyrene monitoring in oilseeds and oil and fat products is carried out under foods safety control and currently is under way.

Prospective of further investigations: carrying out the benz[a]pyrene monitoring in oilseeds, vegetable oils, oil and fat products under foods safety control.

REFERENCES

1. ***Falco G.*** Polycyclic aromatic hydrocarbons in foods: human exposure through the diet in Catalonia, Spain / G.Falco // J.Food Prot. —2003.—Vol. 66, N. 12.—P. 2325—2331.
2. ***Lu L.J., Wang M.Y.*** Modulation of benzo[a]pyrene—induced covalent DNA modifications in adult and fetal mouse tissues by gestation stage / Lu L.J., Wang M.Y. // Carcinogenesis.—1990.—Vol. 11, N 8.—P. 1367—1372.

3. ***Perera, F.*** 2005. "DNA damage from polycyclic aromatic hydrocarbons measured by benzo[a]pyrene—DNA adducts in mothers and newborns from Northern Manhattan, the World Trade Center Area, Poland, and China. / F.Perera // Cancer Epidemiol. Biomarkers Prev.—2005.—Vol. 14, N 3.—P. 709—714.
4. ***Zenzes M.T.*** 1998. Immunodetection of benzo[a]pyrene adducts in ovarian cells of women exposed to cigarette smoke / M.T. Zenzes // Mol.Hum.Reprod. — 1998.—Vol. 4, N 2.—P. 159—165.
5. New EU rules on PAH levels in food, mainly on benzo(a)pyrene: IP/04/1211.— Brussels, 2004. — 1 p..
6. ***Lacoste F.*** Undesirable Compounds And Contaminants In Fats And Oils In Fats And Oils Processing And Utilization / F. Lacoste // French Institute for Fats and Oils PESSAC: France AOCS / IUPAC Workshop, 6—8 December 2004.—Tunis, 2004. -P. 2.
7. Heavy metals and benzo(a)pyrene in ambient air in the Netherlands. A preliminary assessment in the framework of the 4th European Daughter Directive. RIVM rapport 680704001.—36 p.
8. ***Santodonato J., Howard P., Basu D.*** Health and ecological assessment of polynuclear aromatic hydrocarbons / J.Santodonato, P.Howard, D.Basu // J Environ Pathol Toxicol .—1981.—Vol. 5. N.1—P. 364.
9. ***W. Wilcke, M. Krauss, G.Safronov*** Poylcyclic aromatic hydrocarbons (pahs) in soils of the Moscow Region - concentrations, temporal trends, and small-scale distribution / W. Wilcke, M. Krauss, G.Safronov [et al.] // Journal of Environmental Quality.—2005.—Vol. 34.—P. 1581—1590.
10. ***Clayton C.A.*** Distributions, associations, and partial aggregate exposure of pesticides and polynuclear aromatic hydrocarbons in the Minnesota Children's Pesticide Exposure Study (MNCPES) / C.A.Clayton // J.Expo.Anal.Environ Epidemiol.—2003.—Vol. 13, N 2.—P. 100—111.
11. ***Lambert T.W., Lane S.*** Lead, arsenic, and polycyclic aromatic hydrocarbons in soil and house dust in the communities surrounding the Sydney, Nova Scotia, tar ponds / T.W.Lambert, S. Lane // Environ Health Perspect.—2004.—Vol. 112, N 1.—P. 35—41.
12. ***Howard J. W.*** Extraction and estimation of polycyclic aromatic hydrocarbons in smoked foods. I. General method / J. W. Howard, R. T. Teague, R. H. White Jr. [et al.] // J. AOAC. — 1996. — Vol. 49. — P. 595—611.
13. ***Lijinsky W, Ross AE.*** Production of carcinogenic polynuclear hydrocarbons in the cooking of food / W. Lijinsky, A.E. Ross // Food Cosmet Toxicol .—1967.—Vol. 5.—P. 343—347.
14. ***Lo M.T, Sandi E***. Polycyclic aromatic hydrocarbons (polynuclears) in foods./ M.T. Lo, E. Sandi // Residue Rev.—1978.—Vol. 69.—P. 35—86.
15. Dennis M. J. Factors affecting the polycyclic aromatic hydrocarbon content of cereals, fats and other food products / M. J. Dennis, R. C.Massey, G. Cripps [et al.] // Food Addit. Contam. — 1991. —Vol. 8. — P. 517—530.
16. ***Григоренко Л. Т.*** Исследование загрязнения пищевых растительных масел 3,4 бензпиреном и изыскание путей выведения из них: автореф. дис. на соискание науч. степени канд. техн. наук : спец. 05.02.08 «Химия» / Л. Т. Григоренко. — Л., 1973. — 20 с.
17. ***M. Lodovici, P. Dolara, C. Casalini [et al.]***Polycyclic aromatic hydrocarbon contamination in the Italian diet / M. Lodovici, P. Dolara, C. Casalini [et al.] // Food Addit Contam.— 1995.—Vol. 12.—P.703—713.
18. **M.J. Dennis, R.C. Massey, D.J. McWeeny** Analysis of polycyclic aromatic hydrocarbons in UK total diets / M.J. Dennis, R.C. Massey, D.J. McWeeny [et al] // Food Chem Toxicol.—1983.—Vol. 21.—P. 569—574.
19. ***Григоренко Л. Т., Дикун П. П., Калинина И. А*** Содержание 3,4-бензпирена в семенах подсолнечника и продуктах их переработки / [Григоренко Л. Т., Дикун П.

П., Калинина И. А. и др.] ; под ред. В. П. Ржехина // Труды ВНИИЖ, 1970. — вып. 27. — с. 32—41.
20. ***М. Кобервейн, Л. А. Кошеватская, А. А. Иванова***. К вопросу о накоплении 3,4—бензпирена в семенах подсолнечника при сушке / Ю. М. Кобервейн, Л. А. Кошеватская, А. А. Иванова [и др.] // Масложировая промышленность. — 1976. — № 3. — С. 17—19.
21. ***Grimmer G.*** Content of polycyclic hydrocarbons in crude vegetable oils / G. Grimmer, A. Hilderbrandt // Chem. and Ind., 1967. — № 47. — P. 2000—2002.
22. Setting maximum levels contaminants in foodstaffs: Commission Regulation (EC) No 466/2001. — [of 8 March 2001]. — OJ L 77, 16.3.2001. — P. 109
23. ***Голодняк В., Н. Граница Н., Григорова Л.*** К вопросу о регламентации содержания 3,4 бензпирена в растительном масле и жирах / В. Голодняк, Н. Граница, Л. Григорова [и др.] // Збірник праць УкрНДІОЖ УААН. — 2007. — випуск 1. — С. 107.
24. ***Голодняк, Н. Граница, Л. Григорова*** О проблеме содержание 3,4 бензпирена в растительном масле и жирах / В. Голодняк, Н. Граница, Л. Григорова [и др.] // Олійно—жировий комплекс. — 2007. — № 3. — С. 55.
25. ***Григоренко Л.Т. , Дикун П.П, Калинина И.А.*** Исследование влияния производственной гидратации и щелочной нейтрализации пищевых растительных масел на содержание в них 3,4-бензпирена / Л. Т. Григоренко, П. П. Дикун, И. А. Калинина [и др.] // Труды ВНИИЖ, 1971. — вып. 28. — С. 243—247.
26. ***Григоренко Л.Т., Миронова А.Н.,. Дикун П П*** Влияние дезодорации растительных масел на содержание в них 3,4-бензпирена / Л. Т. Григоренко, А. Н. Миронова, П. П. Дикун // Масложировая промышленность, 1972. — №7. — С. 14—15.
27. ***Фальк Е. Ю.*** Влияние гидрирования подсолнечного масла на содержание в нем 3,4-бензпирена / Е. Ю. Фальк // Труды ВНИИЖ, 1973. —вып. 30. — С. 33—36.
28. ***Прохорова Л. Т., Миронова А.Н.*** О наличии 3,4 бензпирена в маргарине / Л. Т. Прохорова, А. Н. Миронова // Труды ВНИИЖ, 1971. —Вып. 28. — С. 37—38.
29. ***Левчук И.В., Кищенко В.А., Семенович В.К.*** Аналитическое определение бенз(а)пирена в маслах и масложиросодержащих продуктах / И. В. Левчук, В. А. Кищенко, В. К. Семенович [и др.] // Масложировая индустрия—2007 : VII—я междунар. конф., 3—5 окт. 2007 г. : материалы конференции. — К., 2007. — С. 33.
30. ***Левчук І.В.*** Удосконалення методів контролю показників безпеки у технології олієжирових виробництв⁄ Левчук І.В⁄⁄ Автореферат, Харків, 2011.

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