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THE SCREENING OF CHROMIUM, LEAD, CADMIUM AND MERCURY IN YOGURTS

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ABSTRACT

In our study, we have focused on monitoring the content of cromium, lead, cadmium and mercury in the 11 samples of yogurt, available in the sales network of the Slovak Republic and comparing it with the Highest PermissibleQuantity (HPQ). Samples of yogurt were mineralized by microwave digestion unit MARS X-press. Heavy metals were determined by atomic absorption spectrometer VARIAN 240 FS and automatic mercury analyser AMA 254. On the basis of our findings it was shown that the content of Cr, Pb, Cd and Hg of the samples do not exceeded the HPQ, the content of cromium was in the range of 0.000 – 0.250 $mg.kg^{-1}$, lead content was 0.000 – 0.091 $mg.kg^{-1}$, cadmium content was 0.005 – 0.039 $mg.kg^{-1}$ and mercury content was 0.000144 – 0.003252 $mg.kg^{-1}$. The measured values were compared with the applicable legislative provisions for heavy metals maximum permissible levels of contaminants in yogurt by the food codex of Slovak Republic. During analysis, we found that none of the samples has exceeded the highest amount of all heavy metals in the food codex of the Slovak Republic.

Keywords: Heavy metals, chromium, lead, cadmium, mercury, yogurt

INTRODUCTION

People nowadays expect that the food was made from safe materials. Milk is among the basic foods that a person consumes just after birth as the mother's milk. Hygiene requirements for milk and milk products are laid down by legislation. Yoghurts are an important part of our food, they are fermented milk products and their composition contributes to the proper functioning of the digestive system. They are a source of calcium and vitamins of the B group.
Yoghurts are the most popular products fermented with two functional groups of microorganisms that are related metabiosis. Already in the 19th century in Paris Ilja Iljich Mečnikov Russian doctor and director of the Pasteur Institute cultivated lactic acid bacterium that is called *Lactobacillus bulgaricus*, for which subsequently received the Nobel Prize. The one of functional food in Germany were yogurts in 1996 because of their health benefits **(Zum Felde, 2004).** *Streptococcus thermophilus* at beginning of the fermentation and produces acidification causes growth substances having a stimulating effect on the growth of *Lactobacillus delbrueckii* subsp. *bulgaricus*. Second, *Lactobacillus delbrueckii* subsp. *bulgaricus* hydrolysed with some amino acids, and thus promotes growth *Streptococcus termophilus*. During symbiosis created unique aroma, which is caused by acetaldehyde of *Lactobacillus delbrueckii* subsp. *bulgaricus* **(Gallo *et al.*, 2013).** Such microorganisms must be live, in a 1 : 1 or 1 : 2 in favor of *Lactobacillus delbrueckii* subsp. *bulgaricus* **(Drábeková, Lengyelová, 2004).** The contamination of milk and products thereof constitutes a large risk to humans. Nowadays places great emphasis on food especially the presence of foreign and toxic substances. Highest risk group consists of just heavy metals that accumulate in the body and cause serious disease.
Milk is a secretion of the mammary gland, which is product of cows, sheep, goats or buffaloes. Raw milk must not be heated above 40 degrees Celsius. Milk comprises 86 -88% of water, dry mass contains 3-6% of fat, 3-4% of protein, 4-5% of lactose and 0.7-0.8% of minerals. Fat free dry mass consists of minerals and lactose **(Čuboň, 2012).** The most of important minerals are zinc, copper, magnesium and iron. Their deficiency can cause pathological changes in the human body. Heavy metals are brought into the milk of animals such contaminants from agriculture and industry **(Abou-Arab, 1997; Ebn *et al.*, 2009).** The yoghurt is often added a variety of fruit ingredients, which significantly affect the durability of the product **(Palo, 1983).** The heavy metal content in the fruit, that is used in the manufacture of yoghurt is a significant contaminant of these products **(Stefanut *et al.*, 2007).** Heavy metals also affect physiological processes of fruit such as photosynthesis, respiration, and transpiration **(Soceanu, 2009).** The consumption of milk in Slovakia has a long tradition. The development of consumption of milk can be divided into two stages. By the year 2000, milk consumption has declined by around 60 – 162.4 kg per person. In 2003 - 2004, consumption decreased by an average of 0.8 kg per person per year. The recommended dose of milk and milk products is 220 kg per person per year **(Kubicová, Dobák, 2012).**
The aim of our work was to assess the extent of yogurt contamination by heavy metals.

MATERIAL AND METHODS

We used yogurt samples, commonly available in commercial network in Slovak republic, to determine the contents of the risk elements (chromium, lead, cadmium, mercury).. We analysed 11 yogurt samples . Each sample an average of 1 gram was withdrawn from the commercial product. All of the samples were prior to the date of expiration. Description and characteristics of the analysed samples is given in table (Tab 1).

Determination of heavy metals in yogurt (excluding mercury)
Samples of yogurt were mineralized by wet road using microwave digestion unit MARS X-press. The end of determination was analysed by using atomic absorption spectrometer (VARIAN 240 FS, by Varian, Inc. USA**).**

Determination of mercury in yogurt
Mercury content was determined by automatic mercury analyzer AMA 254 (LECO Corporation), dedicated atomic absorption spectrophotometer for direct determination of mercury in solid and liquid samples.

The results of analyses were compared with the limit values that define the Food Code of the Slovak Republic No. 608/3/2004 – 100 setting maximum levels for contaminants in foods). For statistical evaluation of results was used the program STATGRAFICS Plus 5.1 to process gained data (LSD test).

Table 1 Description and characteristics of the analysed samples

Sample number	Product name	Packing/weight	Country of origin
1	TAMI – apricot	180 g	Slovak Republic
2	TESCO - currant	140 g	Slovak Republic
3	HOLLANDIA – BIO bananas	180 g	Czech Republic
4	UPDATE 1 - strawberry	150 g	Hungary
5	TAMI PROMINENT - pineapple	135 g	Slovak Republic
6	Goat´s and sheep´s milk yogurt - blueberry	145 g	Unknown
7	Sheep´s milk yogurt - blueberry	145 g	Unknown
8	ZVOLENSKY - cranberry	145 g	Slovak Republic
9	DANONE - strawberry	150 g	Czech Republic
10	ZOTT JOGOBELLA LIGHT – roasted apple	150 g	Germany
11	MADETA - blueberry	200 g	Czech Republic

RESULTS AND DISCUSSION

The lowest Cr content was measured in the sample No. 8 with a value of 0.000 $mg.kg^{-1}$ and the highest Cr content was measured in the sample No. 10 with a value of 0.250 $mg.kg^{-1}$, which was not exceeded the limit value 0.500 $mg.kg^{-1}$ **(**Codex Alimentarius of the Slovak Republic**)**. Results are shown in the figure 1.

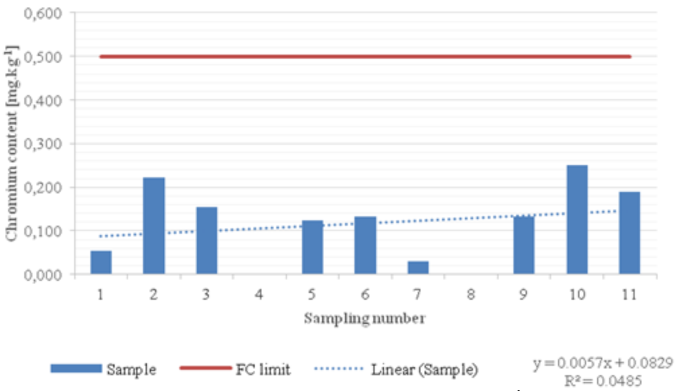

Figure 1 Chromium content in samples of yogurt ($mg.kg^{-1}$)

The lowest Pb content was measured in the sample No. 5 with a value of 0.000 $mg.kg^{-1}$ and the highest Pb content was measured in the sample No. 7 with a value of 0.091 $mg.kg^{-1}$, which was not exceeded the limit value 0.300 $mg.kg^{-1}$ (Codex Alimentarius of the Slovak Republic) Results are shown in the figure 2.

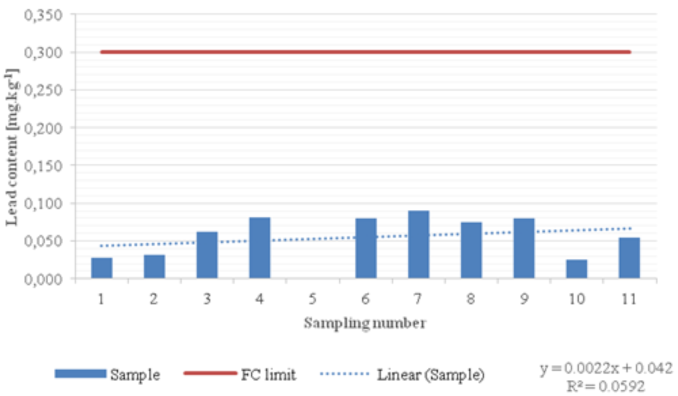

Figure 2 Lead content in samples of yogurt ($mg.kg^{-1}$)

The lowest Cd content was measured in the sample No. 8 with a value of 0.005 $mg.kg^{-1}$ and the highest Cd content was measured in the sample No. 7 with a value of 0.039 $mg.kg^{-1}$, which was not exceeded the limit value 0.050 $mg.kg^{-1}$ (Codex Alimentarius of the Slovak Republic). Results are shown in the figure 3.

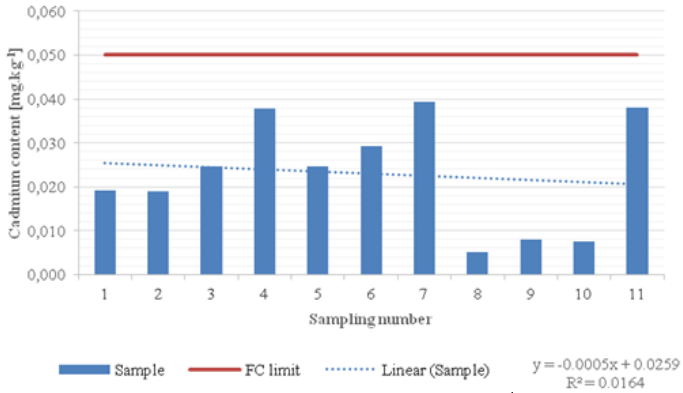

Figure 3 Cadmium content in samples of yogurt ($mg.kg^{-1}$)

The lowest Hg content was measured in the sample No. 5 with a value of 0.000144 $mg.kg^{-1}$ and the highest Hg content was measured in the sample No. 3 with a value of 0.003252 $mg.kg^{-1}$, which was not exceeded the limit value 0.020 $mg.kg^{-1}$ (Codex Alimentarius of the Slovak Republic). Results are shown in the figure 4.

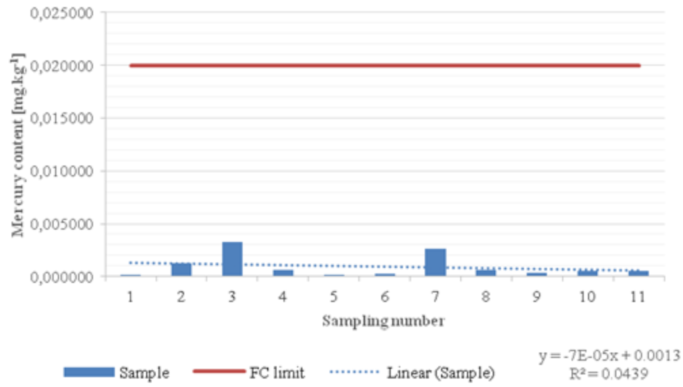

Figure 4 Mercury content in samples of yogurt ($mg.kg^{-1}$)

In samples was not exceed the total content limit values of monitored heavy metals. Between samples number 4 and 8, then 6 and 9 were not significant differences (P> 0.05) in the concentration of chromium. Between samples number 1, 2 and 10, then 3 and 11 and finally 4, 6, 8 and 9 were not significant differences (P> 0.05) in the concentration of lead, between samples number 8, 9 and 10, then 1 and 2, after then 3, 5 and 6 and finally 4, 7 and 11 were not significant differences (P> 0.0)5 in the concentration of cadmium and in the case of the concentration of mercury between samples number 1 and 5 were not significant differences (Tab 2).

Table 2 Level of the concentration significance of Cr, Pb, Cd and Hg in yogurt

Sample	Heavy metal content			
	Cr [mg.kg^{-1}]	Pb [mg.kg^{-1}]	Cd [mg.kg^{-1}]	Hg [mg.kg^{-1}]
1	0,055 c	0,027 b	0,019 b	0,000148 a
2	0,222 h	0,032 b	0,019 b	0,001267 h
3	0,154 f	0,062 c	0,025 c	0,003252 j
4	0,000 a	0,081 d	0,038 d	0,000655 g
5	0,123 d	0,000 a	0,025 c	0,000144 a
6	0,133 e	0,080 d	0,029 c	0,000264 b
7	0,030 b	0,091 e	0,039 d	0,002666 i
8	0,000 a	0,075 d	0,005 a	0,000646 f
9	0,133 e	0,080 d	0,008 a	0,000348 c
10	0,250 i	0,025 b	0,008 a	0,000520 d
11	0,190 g	0,054 c	0,038 d	0,000529 e
Mean	0,117 ±0,086	0,055 ±0,030	0,023±0,013	0,000949±0,001049
$HD_{0,05}$	0,0063563	0,0074745	0,0045379	0,0000043

$HD_{0,05}$ – marginal difference at 95% level of significance (LSD - test)

We cannot observe statistical significant of the correlations. Chromium, lead, cadmium either mercury content were not influenced by particular samples (Tab 3). Cr content was strong statistically significant influenced by Pb content. Cr content was not statistically significant influenced by Cd and Hg content. With increasing Cr content, the content of Pb decrease (Tab 4). Cd content was not statistically significant influenced by Cr, Pb either Hg content (Tab 4). Hg content was not statistically significant influenced by Cr, Pb either Cd content (Tab 4).

Table 3 Pearson correlation coefficient between samples and heavy metal content

Parameter		Correlation coefficient (r)
Dependent variable	**Independent variable**	
Sample	Cr	0,2199
	Pb	0,2510
	Cd	-0,1236
	Hg	-0,2095

Table 4 Pearson correlation coefficient between Cr,Cd, Pb, Hg and other heavy metal content

Cr	Pb	-0,4900**
	Cd	-0,2012
	Hg	-0,0269
Pb	Cr	-0,4900**
	Cd	0,2423
	Hg	0,3081
Cd	Cr	-0,2012
	Pb	0,1744
	Hg	0,2891
Hg	Cr	-0,0269
	Pb	0,3081
	Cd	0,2891

**strong statistical significant of the correlations, *statistical significant of the correlations

Analyses of literature showed that the published studies on migration of heavy metals in the system soil and fruits are up to date. The increased soil acidity, depressed topography, overgrown agricultural fields, decline in the level of farming practices, and inefficient use of chemical agents protecting plants from pests, diseases, and rodents promote a greater accumulation of heavy metals in fruits (**Dubovik, 2009**). Authors showed that consumption of milk products is nearly free of risks, but bioaccumulation of heavy metal through the food chain and intake from other food stuff should also be of concern (**Arafa M. S. Meshref *et al.*, 2014**).

CONCLUSION

The research was carried out by analyzing samples of yogurt available in commercial networks in Slovakia. Sampling was random and was tasked with the most different representation of products. The tested samples of yogurt do not pose a risk of heavy metal entry as a part of nutrition and thus a threat for human health.

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