DETERMINATION OF CD, PB, AS, ZN, CU IN VEGETABLES AND VEGETABLE PRODUCTS AND HERBS

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ABSTRACT

In order to control the hygienic and health conformity of vegetable food products from the consumer basket for the preparation of a full-day military meal, among other analyses, the maximum allowable quantities of the elements Cd, Pb, As, Zn, Cu are monitored. With the AAS technique, three samples each of twenty fresh vegetables, vegetable products and herbs were analyzed and the quantity of the elements of interest was examined. The results of the examination of three samples of: fresh beans, carrots, potatoes, onions, cabbage, spinach; canned vegetables: peas, green beans, peppers (glass and tin packaging), beets (glass and tin packaging), cucumbers (glass and tin packaging), tomato paste, mushrooms; herbs: ground paprika, black pepper, parsley and mixed seasoning are presented. The samples are from different producers from the Macedonian area. Using the method of comparative analysis, it was concluded that the obtained results are in accordance with the norms of the rulebook and those of the literature.

Key words: AAS, essential elements, food products, toxic elements, vegetables.

INTRODUCTION

Food contamination with toxic elements is a serious problem, starting from its production (contaminated soil, water and air), through processing, packaging and storage, to preparation for use. Metal salts from the soil normally enter the natural composition of vegetables and vegetable products. Those quantities are minimal and harmless. But industry, traffic, irrational use of artificial fertilizers and pesticides contaminate ecosystems with additional amounts of contaminants that, through products of plant origin, are introduced into the human body. They are resorbed in the digestive tract and cause damage in the body at organ and tissue level. Resorption through the digestive tract is from 5 to 10% of the concentration of those elements in food. On the other hand, some elements such as lead, cadmium and arsenic show toxic properties even in relatively low quantities and have the property to gradually accumulate in tissues (Beckett et al., 2007). The essential elements zinc and copper, taken in excessive amounts, can also cause health problems. In order to control hygienic and health conformity, the maximum allowable quantities of certain elements in food products are monitored. After examination with appropriate methods such as AAS, insight is gained about the hygienic and health conformity of those food products in relation to the toxic elements of interest.

MATERIAL AND METHODS

In the laboratory for toxicological examination of food at the Military Medical Center - Skopje from the consumer basket for the preparation of a full-day military meal a total of twenty foods from fresh vegetables, vegetable products and herbs were analyzed after each purchase and the quantities of the elements of interest was examined in them. All samples are from the Macedonian area. From each food product, three different units from different manufacturers were examined. The content of the elements arsenic, cadmium, lead, copper and zinc was determined by atomic absorption spectrometry.

Standard solutions of $As(NO_3)_3$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, $Cu(NO_3)_2$ and $Zn(NO_3)_2$ with a mass concentration of 1g/L of arsenic, cadmium, lead, copper and zinc, respectively, were used. The samples were decomposed with nitric acid, and the modifier hydrogen peroxide was used during the examination. Hydrochloric acid, sodium borohydride and potassium iodide were used for the determination of arsenic with a hydride system.

The detection limits of the techniques used are: for copper 0.4 μg/L and for zinc 0.5 μg/L (with flame AAS), for arsenic 0.5 μg/L (with hydride system), for cadmium 0.1 μg/L and for lead 0.6 μg/L (with electrothermal AAS). Quantities below the detection limit are marked with "nd" (not detected).

The obtained results are compared by a comparative analysis with the results of the literature and valid regulations.

RESULTS AND DISCUSSION

Fresh vegetables and herbs in the diet are used raw or thermally processed. These foods and their products are the greatest source of essential elements for the human body. Due to their high representation, but also different frequency of representation from meal to meal, they can also be a potential source of toxic elements originating from a contaminated environment where they were grown, especially polluted soil (root vegetables), air or irrigation water (leafy vegetables) or from contamination of vegetable products during the processing and canning process. (Davydova, 2005; Zaidi et al., 2005; IRAC, 2006; Hu et al., 2013) Of great importance for the content of elements in vegetables and vegetable products, in addition to the quality of the soil, water and air where they are grown, is the risk of contamination with the group of insecticides that contain salts of arsenic, lead, copper. The quality of the water used to irrigate vegetable crops also plays an important role. There is a large difference noted in the content of elements in each vegetable, respectively, but also within the same type of vegetable from different origins, although some papers also state general concentrations of elements in vegetables, for example for zinc 22.2 μg/g, for copper 5.8, for lead 10.2 and for cadmium 0.1 μg/g. (Mehari et al., 2015). Vegetables have a short shelf life, therefore their processing and canning is used. Modern technological processes of food packaging in cans (lead-free soldering of cans) contribute to reducing the content of lead in canned food. Of particular importance for low contents of toxic elements is the preparation of vegetables before canning: washing, chopping and packing.

Although used in small quantities, herbs should be taken into account in calculating the daily intake of toxic elements due to their relatively high content. The drying process is also a source of contamination for herbs. Spices serve to improve the taste of dishes, and due to the content of highly active pharmacological components, some of them are also used for medicinal purposes.

The results of the examination of three samples each of: beans (table 1); root vegetables (table 2): carrot, potato, onion; leafy vegetables (table 3): cabbage, spinach; canned vegetables: peas and green beans (table 4), peppers (table 5), beets (table 6), cucumbers (table 7) in glass and tin packaging; tomato paste (table 8) and mushrooms (table 9) and herbs: ground paprika, black pepper and parsley (table 10); mixed seasoning (table 11) are presented in the following tables.

Table 1. Measured quantities of elements in legumes, beans

Beans	**As (μg/ kg)**	**Cd (μg/ kg)**	**Pb (μg/ kg)**	**Cu (μg/ kg)**	**Zn (μg/ kg)**
1	18	15	11	3680	**9700**
2	23	19	20	3706	**8405**
3	**20**	**16**	**15**	**3535**	**9663**

The content of elements in beans as a food, apart from the cultivation process (quality of soil, irrigation water and air), harvesting and storage, also varies depending on the moisture content of the grain. The obtained results are in accordance with the norms from the rulebook (Official Gazette of RM, 2013) and those from the literature (Onianawa et al., 2001), but somewhat higher than those stated in the work of (Ekholm et al., 2007).

Table 2. Measured quantities of elements in root vegetables

Carrot	**As (µg/ kg)**	**Cd (µg/ kg)**	**Pb (µg/ kg)**	**Cu (µg/ kg)**	**Zn (µg/ kg)**
1	nd	1	12	380	**630**
2	nd	1	16	445	**680**
3	nd	2	16	320	**580**
Potato	**As (µg/ kg)**	**Cd (µg/ kg)**	**Pb (µg/ kg)**	**Cu (µg/ kg)**	**Zn (µg/ kg)**
1	21	45	2	450	**800**
2	22	44	5	410	**815**
3	18	45	8	380	**845**
Onion	**As (µg/ kg)**	**Cd (µg/ kg)**	**Pb (µg/ kg)**	**Cu (µg/ kg)**	**Zn (µg/ kg)**
1	16	8	50	74	**540**
2	18	10	45	85	**550**
3	**15**	**8**	**40**	**80**	**465**

The measured contents of lead and cadmium in the group of foods from root vegetables are below the maximum allowable concentrations in the regulation (Official Gazette of RM, 2013) and are in accordance with those published in the paper of (Elbagermi et al., 2012), but higher than the results of (Ekholm et al., 2007).

Table 3. Measured quantities of elements in leafy vegetables

Cabbage	As (µg/ kg)	Cd (µg/ kg)	Pb (µg/ kg)	Cu (µg/ kg)	Zn (µg/ kg)
1	4	4	12	60	**870**
2	2	4	11	56	**890**
3	2	2	15	52	**865**
Spinach	**As (µg/ kg)**	**Cd (µg/ kg)**	**Pb (µg/ kg)**	**Cu (µg/ kg)**	Zn (µg/ kg)
1	2	5	240	820	**7400**
2	7	8	250	880	**6640**
3	**5**	**8**	**270**	**785**	**6820**

It is noted that the lead content in spinach as a leafy vegetable is expectedly higher than that of the root vegetables. The obtained results are in accordance with the norms of the rulebook (Official Gazette of RM, 2013).

Due to its short shelf life, fresh vegetable can be processed or canned. The procedure for processing and preserving vegetables and the type of packaging can also be a source of contamination.

Table 4. Measured quantities of elements in canned vegetables - legumes

Canned green beans (tin)	As (µg/ kg)	Cd (µg/ kg)	Pb (µg/ kg)	Cu (µg/ kg)	Zn (µg/ kg)
1	70	20	70	3680	**9700**
2	52	21	88	3706	**8405**
3	60	20	86	3535	**9663**
Canned peas (tin)	**As (µg/ kg)**	**Cd (µg/ kg)**	**Pb (µg/ kg)**	**Cu (µg/ kg)**	Zn (µg/ kg)
1	71	20	91	1210	**4610**
2	75	20	93	1605	**5605**
3	**70**	**25**	**82**	**1250**	**4560**

Table 5. Measured quantities of elements in pasteurized peppers in glass and tin packaging

Pasteurized peppers (glass packaging)	As (µg/ kg)	Cd (µg/ kg)	Pb (µg/ kg)	Cu (µg/ kg)	Zn (µg/ kg)
1	2	5	230	660	**1460**
2	8	10	220	680	**1530**
3	2	5	170	580	**1380**
Pasteurized peppers (tin)	**As (µg/ kg)**	**Cd (µg/ kg)**	**Pb (µg/ kg)**	**Cu (µg/ kg)**	Zn (µg/ kg)
1	nd	15	440	435	**1830**
2	2	15	405	450	**1870**
3	**6**	**10**	**390**	**485**	**1785**

The elevated content of lead in the case of pasteurized peppers (kapia) and pickled cucumbers (cornichons), pasteurized beets and pickled cucumbers in tin packaging compared to those in glass is an indicator of the importance of the type of packaging in terms of increasing the content of individual elements in packaged foods.

Table 6. Measured quantities of elements in pasteurized beets

Pasteurized beets (glass packaging)	As (µg/ kg)	Cd (µg/ kg)	Pb (µg/ kg)	Cu (µg/ kg)	Zn (µg/ kg)
1	2	10	280	860	**1720**
2	4	8	270	880	**1760**
3	2	8	255	855	**1645**
Pasteurized beets (tin)	**As (µg/ kg)**	**Cd (µg/ kg)**	**Pb (µg/ kg)**	**Cu (µg/ kg)**	Zn (µg/ kg)
1	8	10	310	560	**2830**
2	8	10	310	440	**3690**
3	**4**	**12**	**340**	**680**	**2580**

Table 7. Measured quantities of elements in canned cucumbers – pickles

Pickles (glass packaging)	As (µg/ kg)	Cd (µg/ kg)	Pb (µg/ kg)	Cu (µg/ kg)	Zn (µg/ kg)
1	12	10	310	450	**765**
2	14	10	320	410	**740**
3	12	15	355	405	**740**
Pickles (tin)	**As (µg/ kg)**	**Cd (µg/ kg)**	**Pb (µg/ kg)**	**Cu (µg/ kg)**	Zn (µg/ kg)
1	12	15	430	450	**850**
2	13	20	450	425	**840**
3	**14**	**20**	**425**	**440**	**840**

Table 8. Measured quantities of elements in tomato paste

Tomato paste	As (µg/ kg)	Cd (µg/ kg)	Pb (µg/ kg)	Cu (µg/ kg)	Zn (µg/ kg)
1	10	50	660	1450	**6815**
2	5	45	680	1520	**5780**
3	**5**	**35**	**750**	**1510**	**6760**

Table 9. Measured quantities of elements in canned mushrooms

Champignon mushrooms (glass packaging)	**As (µg/ kg)**	**Cd (µg/ kg)**	**Pb (µg/ kg)**	**Cu (µg/ kg)**	**Zn (µg/ kg)**
1	nd	4	121	855	**3190**
2	nd	3	125	925	**3220**
3	**nd**	**1**	**99**	**830**	**4255**

The obtained results for canned vegetables are in accordance with the norms (WHO, 2005), and lower than those published in the paper of Soylak et al. (2005).

Table 10. Measured quantities of elements in herbs

Ground paprika	**As (μg/ kg)**	**Cd (μg/ kg)**	**Pb (μg/ kg)**	**Cu (μg/ kg)**	**Zn (μg/ kg)**
1	nd	23	490	10400	**15650**
2	nd	28	505	9100	**15200**
3	nd	nd	405	10870	**16110**
Black pepper	**As (μg/ kg)**	**Cd (μg/ kg)**	**Pb (μg/ kg)**	**Cu (μg/ kg)**	Zn (μg/ kg)
1	8	nd	210	6450	**11 700**
2	5	nd	87	6520	**11 450**
3	nd	nd	148	6510	**11 660**
Parsley	**As (μg/ kg)**	**Cd (μg/ kg)**	**Pb (μg/ kg)**	**Cu (μg/ kg)**	Zn (μg/ kg)
1	5	21	270	250	**8500**
2	8	22	280	380	**7850**
3	**8**	**23**	**310**	**452**	**7760**

Table 11. Measured quantities of elements in mixed seasoning

Mixed seasoning	As (μg/ kg)	Cd (μg/ kg)	Pb (μg/ kg)	Cu (μg/ kg)	Zn (μg/ kg)
1	10	50	660	450	**815**
2	5	45	680	520	**780**
3	**5**	**35**	**750**	**510**	**760**

The obtained results are in accordance with the norms of the rulebook (Official Gazette of RM, 2013). The quantity of the examined elements in the herbs is below the ones predicted by WHO (2005). The results in the cited papers are in accordance with the measured quantities (Abou-Arab and Abou Donia, 2000; Gonzalvez et al., 2008; Dghaim et al., 2015).

CONCLUSION

Food of plant origin is a rich source of nutrients, as well as mineral substances, including the essential elements needed for normal development of the body and maintenance of overall health. The determination of toxic elements is of great importance, because as their content increases, the quality of these food products decreases (Milacic and Kralj, 2003).

In the modern lifestyle, we are witnessing an increasing consumption of fast food, but at the same time, a need for nutritional diets in which certain groups of products are more represented than others. A balanced full-day meal should include a greater intake of plant-based foods, especially vegetables. The use of food products with hygienic and health conformity such as vegetables and herbs is a significant prerequisite for proper nutrition, and thus a good health of the body.

From the results obtained by comparative analysis, it was found that in all the analyzed food samples from the consumer basket for the preparation of a full-day military meal, the measured presence of arsenic, cadmium, lead, copper and zinc are in accordance with the results in the literature and below the limits of the maximum allowable concentration MAC. These products are considered safe to use.

In order to reduce the risk of contamination of vegetables, in addition to the conditions in which they are grown (air quality, soil, irrigation water, use of protective means, pesticides, etc.), storage conditions after harvesting, transportation and sanitary conditions on the market should be controlled as well, and for vegetable products also the conditions during industrial processing and canning.

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