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## **DETERMINATION OF AS, CD, PB, CU AND ZN IN MEAT, MEAT PRODUCTS AND FISH**

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### **ABSTRACT**

Meat, meat products and fish are significantly represented in a person's full-day meal and are an important source of proteins, essential amino acids, fats and mineral salts, enzymes, vitamins, etc. This paper shows the results of the examination of toxic elements with atomic absorption spectrometry: the essential elements Cu and Zn, as well as the toxic elements As, Cd and Pb in food products from the group of meat, meat products, and fish, that are part of a balanced full-day meal. A total of 36 samples were examined: three samples each of three types of fresh meat: beef, pork, and chicken, two semi-permanent sausages and a cooked sausage, canned meat cuts, two concentrates of chicken and beef soup from three producers from the Macedonian region and two types of frozen fish: hake and trout, and samples of canned sardine from the wider region. All results were compared by comparative analysis with results from the literature. In all the examined food products, the content of arsenic, cadmium, lead, copper, and zinc is below the maximum allowable and therefore they are considered safe for consumption.

**Key words:** arsenic, AAS, cadmium, copper, fish, lead, meat, zinc.

### **INTRODUCTION**

The quality of products intended for human consumption largely depends on their composition. Each product, according to relevant laws and regulations, must contain the prescribed quantity of constituents that are characteristic of that product, as well as values below the maximum allowable quantities of additives and trace elements. Food products that do not meet the prescribed norms are of poor quality; they are not allowed for use and are removed from circulation.

Meat, fish, and meat and fish products have a high nutritional value and are often included in a balanced all-day human meal. They represent a significant source of proteins, essential amino acids, fats and mineral salts, enzymes, vitamins, etc. as well as the non-metal arsenic (As), the metals cadmium (Cd) and lead (Pb), as well as the essential elements copper (Cu) and zinc (Zn).

The concern at the international level of pollution with toxic metals is due to their toxicity, characteristic persistence, non-biodegradability and accumulative tendencies. (Islam et al., 2018)

The aim of this paper is biomonitoring of these food products by atomic absorption spectrometry (AAS) to determine the content of toxic elements: the non-metal arsenic (As), the metals cadmium (Cd) and lead (Pb) that can accumulate in animal tissues, as well as the

essential elements copper (Cu) and zinc (Zn) which, in higher quantities than ones allowed, can have toxic effects on the human body.

## MATERIALS AND METHODS

In the laboratory for toxicological examination of food at the Military Medical Center a total of 36 samples from 12 types of food products from the consumer basket for the preparation of a full-day military meal were analyzed: three of fresh meat (beef, pork, and chicken), four of meat products, two concentrates of meat soups, and three foods of fish, after each purchase, and the amount of the elements of interest in them was examined. Three different units (samples) from different manufacturers or suppliers from the region and beyond were examined for each food product. Determination of the content of the elements arsenic, cadmium, lead, copper, and zinc was performed by atomic absorption spectrometry using flame atomic absorption spectrophotometry (FLAAS) and graphite furnace for atomic absorption spectrophotometry (GFAAS) by the wet digestion method.

In order to determine the content of arsenic, cadmium, lead, copper, and zinc, standard solutions of:  $\text{As}(\text{NO}_3)_3$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Zn}(\text{NO}_3)_2$  with a mass concentration of 1 g/L of arsenic, cadmium, lead, copper, and zinc respectively were used. Nitric acid was used as an oxidizing agent, and hydrochloric acid, sodium borohydride and potassium iodide were used for the analysis of arsenic with a hydride system. Hydrogen peroxide was used as a modifier.

The detection limits of the techniques used are: for copper 0.4  $\mu\text{g/L}$  and for zinc 0.5  $\mu\text{g/L}$  (with flame AAS), for arsenic 0.5  $\mu\text{g/L}$  (with hydride system), for cadmium 0.1  $\mu\text{g/L}$  and for lead 0.6  $\mu\text{g/L}$  (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

**Meat:** Meat comes into circulation as parts of slaughtered livestock in raw, frozen or processed state. It is an important source of trace elements and contributes greatly to the daily dietary intake of these micronutrients. Meat is one of the richest sources of zinc in the daily diet and also provides significant amounts of copper (Lombardi-Boccia et al, 2005). For the amount of essential, but also toxic elements, as well as possible contamination, proper nutrition, high-quality drinking water, health state and livestock breeding conditions are of great importance. The cumulative property of toxic elements results in their accumulation, depending on the age of the livestock, in the tissues of the organisms (Chan et al, 2021), and therefore also in pork and beef. In all of the food products, the content of the elements arsenic, cadmium, lead, copper, and zinc was examined and compared with the maximum allowable ones and the literature data.

The results of the examination of three samples of fresh meat: beef, pork, and chicken (table 1), two semi-permanent sausages and a cooked sausage (table 2), canned meat cuts (table 3) and two meat soups (table 4) from three producers from the Macedonian region are presented in the following tables.

The obtained results presented in Table 1. are in accordance with the regulations (Official Gazette of RM, 2013) and below the values published in the papers (Uluozlu et al., 2009; Demirezen and Uruc, 2006; Onianava et al., 2001; Gonzalez et al., 2015).

Table 1. Measured quantity of elements in fresh meat

<b>Beef</b>	<b>As (µg/kg)</b>	<b>Cd (µg/kg)</b>	<b>Pb (µg/kg)</b>	<b>Cu (µg/kg)</b>	<b>Zn (µg/kg)</b>
1	7	10	92	680	7020
2	4	47	96	655	6780
3	9	30	80	585	7210
<b>Pork</b>	<b>As (µg/kg)</b>	<b>Cd (µg/kg)</b>	<b>Pb (µg/kg)</b>	<b>Cu (µg/kg)</b>	<b>Zn (µg/kg)</b>
1	11	20	90	786	4320
2	15	43	92	720	3980
3	28	28	84	740	4120
<b>Chicken</b>	<b>As (µg/kg)</b>	<b>Cd (µg/kg)</b>	<b>Pb (µg/kg)</b>	<b>Cu (µg/kg)</b>	<b>Zn (µg/kg)</b>
1	24	12	42	347	2883
2	10	23	54	586	2350
3	20	14	80	460	2805

**Meat products:** Some of the meat products (cured meat products, sausages, hot dogs, meat cuts), besides meat, also contain amounts of fatty tissue, collagens, as well as substances added during production such as: starch, preservatives, nitrates, nitrites, and some also contain bicarbonates and polyphosphates, which reduces their biological value compared to fresh meat.

Sausages are products obtained by filling natural or artificial casings with a mixture of different types and quantities of minced meat, fatty tissues, skins, internal organs, the remains of connective tissue and, as in canned meat products, they contain added ingredients: spices and additives. Although meat soup concentrates are used in small amounts in the daily meal, they should be considered because of the relatively high quantity of the elements of interest. A source of contamination, apart from those already mentioned, is the production process as well.

Table 2. Measured quantity of elements in sausages

<b>Pork sausage</b>	<b>As (µg/kg)</b>	<b>Cd (µg/kg)</b>	<b>Pb (µg/kg)</b>	<b>Cu (µg/kg)</b>	<b>Zn (µg/kg)</b>
1	32	48	122	1180	6400
2	11	40	118	1040	5820
3	12	50	145	1260	6630
<b>Beef sausage</b>	<b>As (µg/kg)</b>	<b>Cd (µg/kg)</b>	<b>Pb (µg/kg)</b>	<b>Cu (µg/kg)</b>	<b>Zn (µg/kg)</b>
1	23	14	119	1015	5800
2	33	10	120	1580	6620
3	42	12	140	1210	5105
<b>Chicken hot dogs</b>	<b>As (µg/kg)</b>	<b>Cd (µg/kg)</b>	<b>Pb (µg/kg)</b>	<b>Cu (µg/kg)</b>	<b>Zn (µg/kg)</b>
1	nd	2	116	1020	1600
2	nd	2	114	658	1210
3	nd	4	82	420	895

Table 3. Measured quantity on elements in a canned meat cuts

<b>Canned meat cuts</b>	<b>As (µg/kg)</b>	<b>Cd (µg/kg)</b>	<b>Pb (µg/kg)</b>	<b>Cu (µg/kg)</b>	<b>Zn (µg/kg)</b>
1	50	52	508	750	7600
2	33	41	487	425	6850
3	12	26	4 40	655	7970

The results for the measured quantity of elements in meat products are below the maximum allowable concentrations and are in accordance with the cited literature (Lukacova et al., 2014; Mitic et al., 2012; Đogo Mračević et al., 2017), and are significantly lower than some quoted values in the paper of *Gonzalvez* (2015) .

Table 4. Measured quantity of elements in soup concentrate

<b>Beef soup concentrate</b>	<b>As (<math>\mu\text{g/kg}</math>)</b>	<b>Cd (<math>\mu\text{g/kg}</math>)</b>	<b>Pb (<math>\mu\text{g/kg}</math>)</b>	<b>Cu (<math>\mu\text{g/kg}</math>)</b>	<b>Zn (<math>\mu\text{g/kg}</math>)</b>
1	10	1	240	85	350
2	8	nd	220	80	360
3	8	nd	220	85	330
<b>Chicken soup concentrate</b>	<b>As (<math>\mu\text{g/kg}</math>)</b>	<b>Cd (<math>\mu\text{g/kg}</math>)</b>	<b>Pb (<math>\mu\text{g/kg}</math>)</b>	<b>Cu (<math>\mu\text{g/kg}</math>)</b>	<b>Zn (<math>\mu\text{g/kg}</math>)</b>
1	12	10	140	140	425
2	10	8	180	110	390
3	12	6	155	110	405

The results obtained for chicken and beef soup concentrates are consistent with those of the cited literature (Soylak et al., 2006).

**Fish and products:** In continental countries like ours, fish and seafood diet is less represented than in the coastal ones. Fish is a food with a high nutritional value, but a low satiating power. It does not lag behind the best quality meat, because it contains many important ingredients such as essential amino acids, unsaturated fats and vitamins, which have an even better use. Fish also accumulate toxic metals as well as elevated levels of essential elements (Burger and Gochfeld, 2005). Contamination of freshwater and marine fish species is conditioned by the presence of pollutants in their environment. It is characteristic for some elements (As, Pb, Cd) to accumulate in the tissues of fish and seafood, and therefore eating contaminated fish can lead to an increase in the amounts of those elements in the human body. Arsenic in fish meat is organically bound, non-toxic and does not pose a great danger to human health. During the temperature conservation process, it is significantly transferred to the liquid (Amyot et al., 2023). Canned fish is a product that is easily available, and therefore often used in the daily diet. It is therefore also subject to regular quality controls, especially due to the additional risk of contamination during the canning process.

Three samples of frozen fish hake and trout (table 5) and canned sardine (table 6) from three producers from the wider region were examined.

Table 5. Measured quantity of elements in fish

<b>Hake</b>	<b>As (<math>\mu\text{g/kg}</math>)</b>	<b>Cd (<math>\mu\text{g/kg}</math>)</b>	<b>Pb (<math>\mu\text{g/kg}</math>)</b>	<b>Cu (<math>\mu\text{g/kg}</math>)</b>	<b>Zn (<math>\mu\text{g/kg}</math>)</b>
1	542	10	151	250	3405
2	644	20	130	305	2930
3	726	10	110	220	1890
<b>Trout</b>	<b>As (<math>\mu\text{g/kg}</math>)</b>	<b>Cd (<math>\mu\text{g/kg}</math>)</b>	<b>Pb (<math>\mu\text{g/kg}</math>)</b>	<b>Cu (<math>\mu\text{g/kg}</math>)</b>	<b>Zn (<math>\mu\text{g/kg}</math>)</b>
1	125	10	186	460	3020
2	98	5	108	320	2010
3	76	8	104	330	2430

Table 6. Measured quantity of elements in canned sardine

<b>Canned sardine</b>	<b>As (<math>\mu\text{g/kg}</math>)</b>	<b>Cd (<math>\mu\text{g/kg}</math>)</b>	<b>Pb (<math>\mu\text{g/kg}</math>)</b>	<b>Cu (<math>\mu\text{g/kg}</math>)</b>	<b>Zn (<math>\mu\text{g/kg}</math>)</b>
1	120	5	134	780	5055
2	140	4	152	1125	7840
3	210	8	108	902	8120

The obtained results presented in Tables 5 and 6 are in accordance with the prescribed norms from the rulebook (Official Gazette of RM, 2013) and the cited literature (Demirezen and Uruc, 2006; Stancheva et al., 2013; Novakov et al., 2017).

## CONCLUSIONS

The use of food products that are safe for consumption is of great importance for a well-balanced full-day meal. It is a prerequisite for proper nutrition that leads to a good health state of the consumers. Meat, meat products, and fish are products that are significantly represented in the daily meal of our population as an important source of proteins, essential amino acids, fats and mineral salts, enzymes, vitamins, etc. Their contamination is conditioned by the presence of pollutants in the environment. It is characteristic for some toxic elements (arsenic, lead, cadmium) to accumulate in the tissues of animals, and therefore the diet with contaminated meat, meat products and fish can lead to an increase in the quantities of those elements that have toxic effects on the human organism. The essential elements (copper and zinc) in higher quantities than allowed can have side effects as well. With regular biomonitoring of these food products and determination of the content of toxic elements, but also of essential elements, the quality of the products intended for human consumption is monitored.

From the results obtained by comparative analysis, it was established 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 is in accordance with the results in the literature and under the limits of the maximum allowable quantities. These products are considered safe to use.

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