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ASSESSMENT OF METALS LEVEL IN SEVERAL MEAT PRODUCTS OBTAINED THROUGH CONVENTIONAL AND TRADITIONAL METHODS

I. MANEA[1], L. MANEA[1*], C. RADULESCU[2,3], I.D. DULAMA[3,5], S. TEODORESCU[3], R.M. STIRBESCU[3], E.D. CHELARESCU[4,5], I.A. BUCURICA[3]

[1] *Valahia* University of Targoviste, Faculty of Environmental Engineering and Food Science, 130004 Targoviste, Romania, E-mails: iulia.manea10@yahoo.com; laur_manea@yahoo.com
[2] *Valahia* University of Targoviste, Faculty of Sciences and Arts, 130082 Targoviste, Romania, E-mail: radulescucristiana@yahoo.com
[3] *Valahia* University of Targoviste, Institute of Multidisciplinary Research for Science and Technology, 130004 Targoviste, Romania, E-mails: dulama_id@yahoo.com sofiateodorescu@yahoo.com; stirbescu_nic@yahoo.com; bucurica_alin@yahoo.com
[4] *Horia Hulubei* National Institute for R&D in Physics and Nuclear Engineering, Magurele, Romania
[5] Academy of Romanian Scientists, 050094 Bucharest, Romania
E-mail: dana_chelarescu@yahoo.com

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Abstract. The aim of this study was to assess the content of several heavy metals from meat products (*e.g.* sausages, salami, neck, muscle, and ribs) obtained either by cold or hot smoking or pasteurization, considering that these metallic elements are toxicants for human health. Their toxicity depends on several factors including dose, route of preparation and type of meat. Because of their high degree of toxicity, if they are present in meat products, nine metals, including Cr, Pb, Cd, Co, Ni, Mn, Cu, Fe, and Zn, were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technique of high precision and sensitivity. The first four elements are classified as human carcinogens according with the International Agency for Research of Cancer (IARC). In this research it was obtained a lower content of metals in smoked meat products (*i.e.* muscle, neck, ribs, pulp) and a higher metals content in product without structure (minced meat). The order of the elements in meat products and their concentration ranges in mg/kg d.w. was Fe (11.748–26.131) > Zn (4.282–11.586) > Mn (0.965–5.433) > Cu (1.987–4.154) > Cr (1.119–3.295) > Ni (1.115–2.170) > Pb (0.242–0.477) > Co (0.204–0.301) > Cd (0.091–0.095). Therefore, each metal which has well-established features and physicochemical properties present a specific toxicology within meat products, especially when their procedure of obtaining was not properly conducted.

Key words: meat product, metal, ICP-MS, ash content.

1. INTRODUCTION

The metals are elements able to build covalent bonds with organic compounds, which lead to the formation of lipophilic compounds and ions [1]. It is well-known that a lot of metals have a crucial biological function in animals and plants due to the chemical coordination and oxidation-reduction properties, their conferring a real benefit in the control mechanism, such as homeostasis, transport, compartmentalization and binding to cell constituents [2]. Unfortunately, the heavy metals, including chromium, lead, cadmium, mercury, arsenic, nickel and manganese, from human anthropogenic sources are continuously released into aquatic and terrestrial ecosystems. Contamination with heavy metals is a major threat due to their toxicity, bioaccumulation and biomagnification in the food chain. Industrial pollution is other source to find heavy metals in meat and meat products [3]. Lead and cadmium are known to be entering the meat supply in limited amounts from environmental sources. In these cases, the ultimate source may also be the industrial practices. Control measures to protect his meat supply should be based on how agricultural or industrial chemicals and drugs enter and remain in the edible tissue of the animals [4, 5]. The presence of heavy metals in animal organs can be used, together with other causes, as biomarkers of pollution [6]. Some heavy metals (*e.g.* copper, selenium, zinc) are vital in keeping the human body's metabolism, but they can be toxic at high concentrations. The negative effects of heavy metals for human health may result, for example, through drinking contaminated water, high levels in the concentration of air surrounding the emitting source, or assimilation *via* the food chain [7–11]. Meat consumption with high lead concentrations can affect central nervous system, the kidneys and the immune system. At children, even at low levels, lead is associated with impaired cognitive function, including reduced IQ, behavior difficulties and other problems [12]. Moreover there is the possibility that several heavy metals to combine with good minerals and oligo-minerals from human body becoming blockers for these indispensable elements of life. These blockers can't be degraded or destroyed [13, 14]. Another cause, the possible lack of safety of finished meat products is contamination on the technological flow from the contact with machinery, tools, and installations or after some technological operations *(i.e.* salting, smoking, and drying). Many studies have confirmed the presence of heavy metals in meat products [6, 15–17], and sometimes have exceeded the values provided by the legal regulations [18–21].

The aim of this work is to investigate the concentration levels of several metals (*e.g.* Cr, Pb, Cd, Co, Ni, Mn, Cu, Fe, and Zn), by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique, from different meat products prepared through conventional methods, respectively traditional methods. The traditional meat products are obtained with natural ingredient, which replace chemical synthesis additives, but at the same time must not be contaminated with chemicals. For a well data interpretation the ash content and water content were determined, as well.

2. MATERIALS AND METHODS

2.1. MATERIALS

Different types of meat products were sampled from the commercial network, from three producers. All collected samples were placed in clear polythene bags and brought to the laboratory for preparation and analysis. The quotation used for the samples was presented in Table 1. Ultrapure water (Thermo Fisher Scientific, Germany) was used for standard solutions preparation and blank, as well. All reagents were analytical reagent grade.

2.2. DETERMINATION OF WATER CONTENT

The water content of samples was determined according with SR ISO 1442:2010 by drying in oven method [22]. Thus, the samples were finely chopped, weighed (5 g) mixed with 5 mL ethylic alcohol. After homogenization, the mixture was kept on water bath, at 60–80 °C until complete evaporation of the ethylic alcohol. The obtained sample was dried in oven at 103 ± 2 °C for 14 h. After that, the samples were preserved in desiccator and finally weighed.

Table 1

Samples description and processing method

Sample code	Product type	Processing method
S1	homemade smoked pork sausages	cold smoked
S2	spices sausages	cold smoked
S3	summer salami	pasteurized
S4	smoked	cold smoked
S5	pork pastrami	cold smoked
S6	smoked sausages	cold smoked
S7	dried traditional loin	hot smoked
S8	"Bucuresti" salami	pasteurized
S9	traditional sausages	cold smoked
S10	smoked loin	cold smoked
S11	rustic loin	hot smoked
S12	smoked pork ribs	hot smoked
S13	rustic sausages	cold smoked
S14	dried traditional loin	hot smoked
S15	"Oltenesti" sausages	hot smoked
S16	smoked sausages	cold smoked

Repeat the heating oven (one hour), cooling and weighing until the results obtained from two consecutive weighings do not differ by more than 0.005 g.

The water content was calculated using equation (1):

$$W_c = \frac{m_{wet} - m_{dry}}{m_{wet} - m_0} \cdot 100\,, \tag{1}$$

where: W_c represents the water content [%]; m_{wet} represents the mass of weighing vial with wet sample [g]; m_{dry} represents the mass of weighing vial with sample after dry process [g]; m_0 represents the mass of weighing vial without sample [g].

2.3. DETERMINATION OF ASH CONTENT

The total ash content represents the percentage of minerals and minerals impurities in meat products. For this aim an amount of 1–2 g of sample was weighed in porcelain melting pot, was dehydrate in oven at 125 °C and then was calcined at 550 °C for 4–6 h. After that, the samples were preserved in desiccator and weighed [23]. Repeat the heating oven (one hour), cooling and weighing until the results obtained from two consecutive weighings do not differ by more than 0.005 g. The ash content was calculated using equation (2):

$$A_c = \frac{m_a}{m_s} \cdot 100\,, \tag{2}$$

where: A_c represents the ash content [%]; m_a represents the ash mass after calcination [g]; m_s represents the sample mass before calcination [g].

2.4. DETERMINATION OF METALS CONTENT BY ICP-MS

In order to determine the metals content, the samples were mineralized using the microwave digestion system, TOPwave (Analytik Jena) under extreme conditions of pressure and temperature. Each sample (350 mg) was introduced to the digestion vessel, and then, was added 10 mL of 67% HNO_3 (Merck). After digestion time (40 minutes) the vessels were cooled at room temperature and then, each solution was transferred to volumetric flask and filled to 25 mL with deionized water. The metals content in meat products samples were determined using Thermo Scientific iCAP Qc ICP-MS system. All quantitative measurements in triplicates were performed in the standard mode (STD) using the instruments software Qtegra™ and the relative standard deviation (RSD) values was less than 10%. Several well-known isobaric interferences were automatic corrected [24–30].

3. RESULTS AND DISCUSSION

This study aims to investigate the water and ash content, as well as the metals levels (*e.g.* Cr, Pb, Cd, Ni, Co, Mn, Cu, Fe, and Zn) in sixteen meat products obtained by traditional or conventional methods.

The water and ash content of meat products samples are presented in Fig. 1. The water content ranged between 46.753% in summer salami and 67.909% in pork pastrami. The water content had a deviation from the standard at "Oltenesti" sausages 65.483% *versus* 56%, at summer salami 46.753% *versus* 45% [31].

The ash content has ranged between 2.913% in smoked sausages and 5.083% in pork pastrami. In meat products with structure (loin, neck, and pork pastrami) the ash content was higher than in minced meat (salami, sausages).

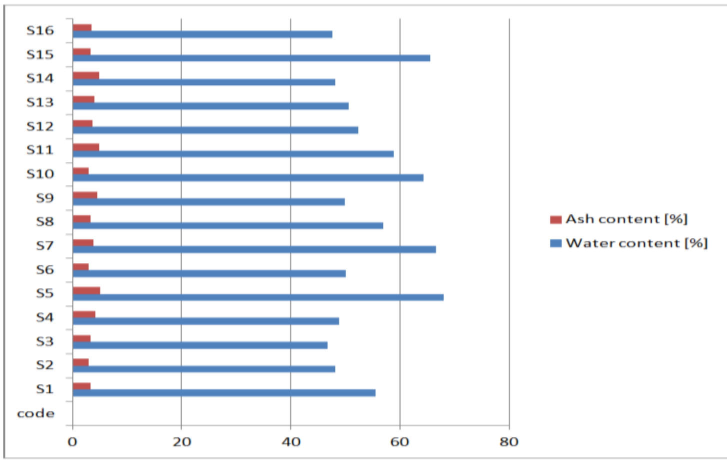

Fig. 1 – Water and ash content of meat products samples.

Values recorded for heavy metals in meat products are summarized in Table 2. According to European Regulation [20, 21], the heavy metals and nitrite, must be below certain limits in meat products.

The content of heavy metals was lower in meat products having the structure: smoked muscle, smoked neck, smoked ribs, smoked pulp. The products without structure (minced meat) the content of heavy metals was highest. Therefore, the lead content in meat products was lower than those provided by European Regulation EC 1881/2006 (*i.e.* 0.5 mg/kg) except the sausages product where the obtained value was 0.477 mg/kg. The levels of cadmium in all analyzed samples were lowest and ranged from 0.091 to 0.095 mg/kg d.w. The obtained values are below the codex committee on food additives and contaminants which provided a value of 0.5 mg Cd/kg. Data presented in Table 2 shows there were no major differences in cobalt and cadmium concentrations between samples of meat product obtained through both conventional and traditional methods. The results presented in Table 2 shows that cold smoked products had a higher content of iron in smoked pork sausages homemade (*i.e.* 26.131 mg/kg for S1) as compared to rustic loin (*i.e.* 11.748 mg/kg, sample S11). For the same sample S1 it was observed high concentration for chromium (2.057 mg/kg), manganese (5.433 mg/kg), nickel (2.101 mg/kg) and for cooper (2.817 mg/kg), as well. This may relate to treatments of the product or addition of spices. The levels of manganese in the all samples ranged from 0.965 to 5.433 mg/kg. The National Research Council of Canada has recommended adequate daily intake content for manganese that range from 0.3 to 1.0 $mg \cdot d^{-1}$ for children up to one year, 1.0–2.0 $mg \cdot d^{-1}$ for children up to age 10, and 2–5 $mg \cdot d^{-1}$ for children 10 and older. It is well known that daily intake of lower amounts of manganese is necessary for growing and good health for children and males/females (*i.e.* 2 and 11 $mg \cdot d^{-1}$) otherwise manganese deficiency in body can lead to serious problems of nervous system. Also, the samples S1 (*i.e.* smoked pork sausages homemade) and S7 (*i.e.* dried traditional loin) exhibited higher levels of Ni than the other meat products. According to the Agency for Toxic Substances & Disease Registry (ATSDR), nickel can cause respiratory problems and is carcinogenic. The upper tolerable intake content of nickel for children and males/females is 7 and 40 $mg \cdot d^{-1}$, respectively. The content of nickel was lowest in all samples, minimum 1.106 mg/kg (*i.e.* S5), maximum 2.170 mg/kg (*i.e.* S7), with an average value of 1.428 mg/kg. The nickel content in animals it ranges from 0.1 mg/kg to 5 mg/kg.

Table 2

Metals content of meat products samples

Sample code	**Metals content [mg/kg d.w.]**								
	Cr	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**
S1	2.057	5.433	26.131	0.211	2.101	2.817	5.728	0.092	0.345
S2	1.403	4.252	17.800	0.216	1.176	2.412	6.813	0.091	0.251
S3	1.405	5.589	21.468	0.216	1.115	2.161	4.282	0.091	0.281
S4	1.423	2.169	17.934	0.205	1.152	2.725	4.770	0.092	0.299
S5	1.539	4.005	16.355	0.211	1.106	2.893	9.131	0.091	0.389
S6	1.353	4.933	20.651	0.213	1.330	3.052	8.121	0.091	0.262
S7	1.565	1.103	13.174	0.197	2.170	1.987	7.437	0.092	0.419
S8	1.386	1.940	22.796	0.204	1.580	2.197	4.981	0.094	0.477
S9	1.861	3.419	18.425	0.204	1.342	2.503	11.586	0.091	0.242
S10	1.734	0.965	15.393	0.207	1.779	2.160	10.222	0.092	0.384
S11	1.119	1.230	11.748	0.209	1.245	2.219	8.649	0.094	0.284
S12	3.295	1.068	16.771	0.226	1.229	2.666	5.906	0.094	0.319
S13	1.223	3.325	20.653	0.207	1.208	2.854	7.498	0.093	0.283
S14	1.613	1.560	16.085	0.227	1.138	3.338	7.102	0.091	0.254
S15	1.762	1.880	21.175	0.235	1.813	4.154	9.180	0.095	0.466
S16	1.456	6.141	22.755	0.301	1.366	3.097	11.184	0.095	0.450
RSD* [%]	0.001–0.412	0.001–0.117	0.001–2.101	0.001–0.074	0.001–0.669	0.001–0.198	0.001–3.254	0.001–0.075	0.001–0.125

* RSD – relative standard deviation.

In Fig. 2 are presented the minimum, maximum and average values of the chromium, nickel and copper content of the analyzed samples. On average, the amount of nickel in plant tissues is four times higher than that found in animal products (meat, eggs, milk and derivatives), and the nickel concentration in plants is higher in spring and autumn while halving during the summer. The amount of nickel in food is therefore variable, which is why there are discrepancies between the various lists of high-nickel foods. Indeed, it is from small lists in the 1980s and 90s (such as the Swedish Food Administration published the threshold of > 0.5 mg/kg) to a much wider list in recent years and in particular in Italian sources (in the study of Schiavino *et al.*, the threshold was set at 0.03 mg/kg) [32]. The Codex Alimentarium Commission has set the maximum permissible limit of zinc in meat as 50 mg/kg for muscle and 80 mg/kg for edible offals [33].

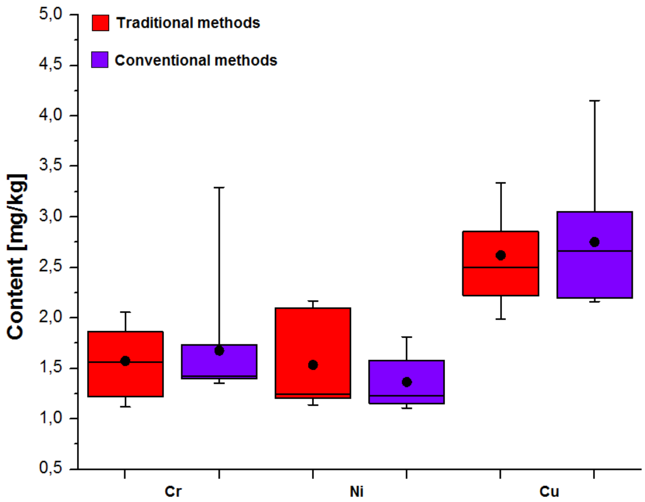

Fig. 2 – Content of Cr, Ni and Cu in meat products samples.

The content of copper was lower than the standard value 5 mg/kg [31]. The average copper content is lower than the maximum allowed. For traditional meat products the average value and maximum value of Cu is significantly lower than for conventional products, possibly because the products obtained by conventional methods use additives and water that can be impregnated with this metal.

Chromium varies within larger limits to traditional products and conventional ones very easily, even if the average is higher in the latter. The maximum value was in smoked pork ribs S12, 3.295 mg/kg. Janefrances *et al.*, reports in the beef consumed in Nigeria a chromium content ranging from 1.24 to 4.28 µg/g [34].

In Fig. 3 are presented the minimum, maximum and average values of the manganese, iron and zinc content of the analyzed samples. The maximum admissible limit of zinc for meat products is 50 mg/kg [31]. In the analyzed samples the highest value was in traditional sausages (11.586 mg/kg) and minimum values was in summer salami (4.282 mg/kg). Djinovic-Stojanovic *et al*. found in pork products 11.4–32.7 mg/kg zinc [34]. According to Bartik and Piscac [35], quoted by Alturiqi and Albedair [36], normal concentrations of zinc in meat samples are 35–45 $mg\cdot d^{-1}$ therefore all investigated samples in this study contained lower levels of zinc.

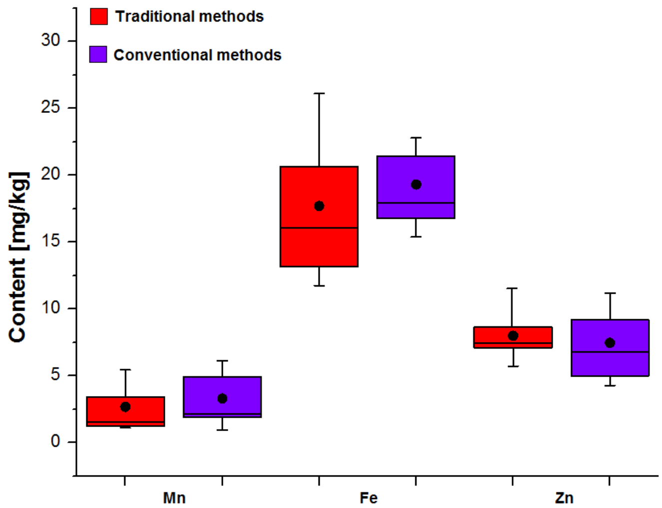

Fig. 3 – Content of Mn, Fe and Zn in meat products samples.

The content of iron was higher in conventional products, than traditional products. Maximum value was in homemade smoked pork sausages, 26.131 mg/kg and minimum value in rustic loin, 11.748 mg/kg. Alturiqi and Albedair found in pork products iron in limits 44.87–250.23 mg/kg [36]. According with [17] the content of Fe in meat products is 11–623 mg/kg. Zahran and Hendy reported a concentration of Fe in sausages which ranged from 82.9 to 270 mg/kg with mean 135.00 ± 10.48 mg/kg [15].

The concentration of manganese was on average 3.063 mg/kg and maximum 6.141 mg/kg. The content of Mn was bigger in conventional products, than traditional products, the average and maximum limit being higher. The average Mn content of all analyzed products was 3.063 mg/kg. Zahran and Hendy report concentration of Mn in sausages which ranged from 3.32–18.38 ppm and average 8.4 ± 0.97 ppm [15]. Alturiqi and Albedair found in pork products Mn in limits 7.72–13.99 μg/g [36].

The contents of Co, Cd and Pb were higher in conventional products, than traditional products (Fig. 4). Maximum value of Co was in smoked sausages

0.301 mg/kg. The cobalt levels assessed in this study were lower than those found by [17] (0.01–48.00 mg/kg), but higher than 0.008 mg/kg [37].

In the present study, although Cd was detected in all examined meat samples and ranged from 0.091mg/kg to 0.093 mg/kg. According to the FAO limits (0.10 mg/kg) [32] all the samples presented lower cadmium content. The maximum is higher by 47.36% higher than value of European Regulation (0.05 mg/kg wet weight for bovine meat) [20, 21]. Hoha *et al.* found Cd in meat products between 0.11 and 0.21 mg/kg [13].

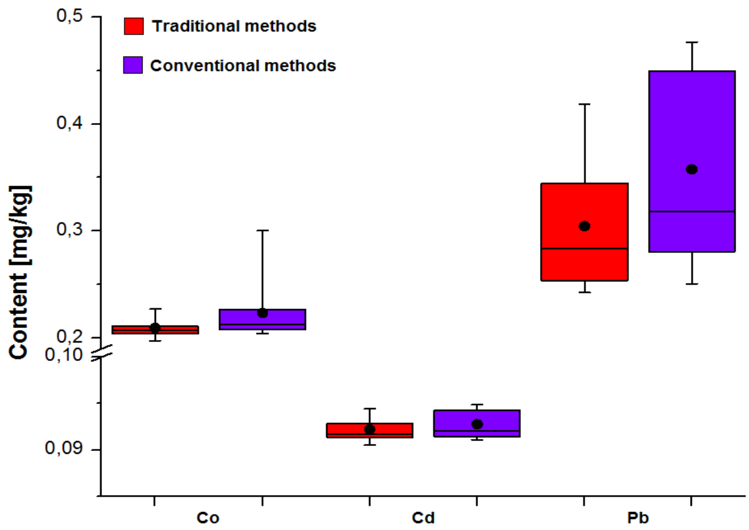

Fig. 4 – Content of Co, Cd and Pb in meat products samples.

The content of Pb (Fig. 4) ranged between minimum 0.242 mg/kg in traditional sausages and maximum value 0.477 mg/kg in "Bucuresti" salami. All samples shown a lower content for Pb, than those reported by [30] (*e.g*. 1.00 mg/kg) and European Regulation (*e.g.* 0.10 mg/kg). In other study [17], in beef roll, chicken wing, and beef pizza it was found the amount of Pb between 0.03–43.00 mg/kg. Hoha *et al.* reported Pb content in meat products in the range of 0.35–1.06 mg/ kg [13]. Lead was present in the range of 10.02–15.43 μg/g in other meat products according with [36].

4. CONCLUSIONS

The ash content was higher in structured meat products (dried traditional loin, smoked neck, dried traditional loin, and pork pastrami) and in traditional sausages which are obtained only from pork with minimal processing. The water content of the analyzed products was within the limits of the quality standards.

The content of metals in the analyzed samples was generally within the limits stipulated by the national and international regulations. The concentrations of several elements, including Co, Cd, Pb, Mn, Fe, Cr, and Cu, in meat products obtained by traditional methods were lower than those obtained by conventional methods, due to the fact that the last procedure involve an intensively process of fabrication and product contains possible chemical additives. A significantly average content in traditional products, probably due to cold smoke, was observed for all metals, excepting Zn and Ni.

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