



EFFECTS OF PROCESSING METHODS ON THE CONTENT OF MINERALS IN FISH PRODUCTS

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Abstract

Effects of salting, pickling and smoking processing methods on the mineral composition in fish products were investigated. The concentrations of Ca, P, Mg, K, Na, Cu, Fe, Zn, Mn and Se in fish products were determined during subsequent stages of processing in raw fish, semi-processed products and ready products. Fresh fish contained macroelements in the following order: $K > P > Na > Ca > Mg$. The tendency was similar in semi-processed and ready products, except for the dominance of sodium. The sodium content in marinated products was three-fold higher than in fresh fish and twelve-fold higher in salted herring and cold-smoked fish. The sodium content in a 100 g portion of salted herring exceeded by six-fold the recommended daily allowance and by two-fold the tolerated amount. The content of K, Mg and P in marinated and salted herring tended to decrease throughout processing. No significant differences were observed in concentrations of Ca. The order of the concentrations of microelements was as follows: $Zn > Fe > Cu > Se > Mn$. The content of these elements in fish products was similar to their levels in fresh fish and corresponded to the following shares of the recommended allowances: Se up to 20%; Cu up to 11%; Zn up to 6%; Mn up to 1%; Fe up to 10%. Disadvantageous changes in the mineral composition in fish during processing result from water losses during technological processes, but the primary cause of mineral loss was leaching when the products were soaked in brine solutions with a high sodium content. Significant changes in the content of minerals in salted and pickled herring decreased the nutritional value of these products. Smaller mineral losses that occurred during smoking meant that these products were more valuable nutritionally in relation to minerals.

Keywords: minerals, fish, salting, pickling, smoking.

INTRODUCTION

Fish has long been recognized as an excellent source of animal protein in the human diet. Fish is also eaten in many parts of the world for its high content of unsaturated fatty acids. It contains important *n*-3 polyunsaturated fatty acids, which – in addition to possibly lowering the risk of cardiac diseases in adults – important for the neurodevelopment in infants, children and adolescents, and support good health (ESPE et al. 2002, USYDYS et al. 2011). Fish are also a good source of amino acids, vitamins and minerals (USYDUS et al. 2009, SZLINDER-RICHERT et al. 2011, MALESA-CIECWIERZ, USYDUS 2015). Mineral components such as sodium, potassium, magnesium, calcium, iron, phosphorus, selenium, zinc, copper and manganese are important for human nutrition (GUERIN et al. 2011). The content of primary macroelements occurring in fish (calcium, phosphorus, magnesium) is much higher than in other types of foods. The content of calcium in fish is nearly ten-fold higher than in beef. The highest mineral contents are found in products containing whole, small fish such as sprats and sardines. The content of phosphorous in these products is 15% higher than that in beef or pork Magnesium also occurs at high levels in fish. Fish products are also rich in selenium, manganese, zinc and copper. Mineral concentrations differ depending on a product type and processing method. Technological processes that raw fish are subjected to change the nutritional value of the products. Undesirable changes that occur in products are a consequence of losses of amino acids from proteins, oxidation of lipids, including unsaturated fatty acids, and losses of macro- and microelements. The literature most often presents the mineral content of raw fish (GOKOGLU et al. 2004, TETSURO et al. 2005, 2007, BRUCKA-JASTRZĘBSKA et al. 2009, ERKAN et al. 2009, TÜRKMEN et al. 2009, EROSY, ÇELİK 2010, SZLINDER-RICHERT et al. 2011, USYDUS et al. 2011, STANEK et al. 2014). Much less information is available on minerals in fish products and losses of minerals during processing (TAHVONEN et al. 2000, GOULAS, KONTOMINAS 2005, KALOGEROPOULOS et al. 2012, OĞUZHAN, ANGIN 2013).

The aim of this research was to determine the effect of salting, pickling, and hot- and cold-smoking on the mineral content of fish product. The evaluation was performed after an analysis of fish mineral content at various stages of technological processes used in fish processing plants from raw material to semi-processed and ready products.

MATERIAL AND METHODS

The material consisted of raw or frozen fish, semi-processed products such as fillets, or headed and gutted fish as well as marinated, salted, and smoked fish products. Samples were collected during processing at various

fish processing plants in northern Poland. The following material was sampled:

- fresh Baltic herring and imported frozen deep-sea herring primarily from Norway and the Netherlands (6 samples);
- semi-processed marinated and salted products produced with ripening agents (8 samples);
- products salted in assortment: *Fillets from herring ala Matyjas, Persian Sliced Cake, Matyjas, Matyjas old-Polish style* (8 samples);
- a variety of marinated herring products, including marinated herring in vinegar – *Aro rollmops in marinade, Aro rollmops in oil, Luxury rollmops, Bryza, Delicatessen herring fillets with cherries, Rollmops in tarragon marinade, Fried herring fillets in vinegar marinade, Herring rolls with vegetables, Kashubian rollmops, Jewish herring delicacy with mushrooms*, and others (13 samples);
- fresh fish for smoking: sprat, Atlantic mackerel, Baltic and Norwegian salmon (10 samples);
- cold-smoked fish: Atlantic mackerel, Baltic salmon, Norwegian salmon (6 samples);
- hot-smoked fish: Baltic salmon, Norwegian salmon, mackerel, sprats (10 samples).

Brief description of the basic technological parameters used in salting, marinating and smoking processes

Salting fillets and whole headed and gutted fish were put in brine with the saline content ranging from 10 to 12% NaCl or marinated in marinades with the vinegar content ranging from 3.5 to 5% at a temperature from +7 to +10°C. Semi-processed fish was marinated in flavored liquids with the saline content of approximately 2.5% NaCl and vinegar content of 1.4%, depending on a product type. To make fried marinated fish, fresh herring fillets were breaded in a flour and bread crumb mixture and then fried in oil at of 180°C. The fried fillets were cooled and packed in jars with flavoured vinegar solutions.

The traditional method for producing salted herring included both dry and wet salting. Headed herring were mixed with salt in barrels and then covered in concentrated brine solution (approximately 30% NaCl). Brining and ripening took three weeks at a temperature of approximately 12°C. Herring fillets were brined with the wet method using brine solution of salinity of approximately 25% NaCl. Brining lasted from three to four days at temperatures from 12 to 14°C. A ripening agent (Reifer) was used in the salting process at quantities of 330 g 100 kg⁻¹ raw fish, the brine was 16% NaCl, and vinegar (10%) was added at a dose of 2 L 100 kg⁻¹ raw fish.

The pre-processing of smoked fish included defrosting, rinsing, cutting into fillets or heading and gutting whole fish. Then the fish were salted in

brine with varying quantities of NaCl depending on the smoking process. The fish were smoked in smoking chambers; for hot smoking the temperature ensured the thermal denaturation of proteins (usually approximately 100°C), while in cold smoking the temperature in a smoking chamber did not exceed 35°C. The hot-smoked fish had a low sodium content (no more than 2% NaCl), while the cold-smoked fish had a decidedly higher sodium content ranging from 3 to 7% NaCl and contained less water.

The analyses of the mineral contents were performed on raw fish, semi-processed fish and fish products. Only fish tissue was collected for analyses. The samples of raw fish and fish products were rinsed with water before homogenization. Approximately 2 g of wet weight sample, 6 ml of nitric acid (65%), and 2 ml of (30%) hydrogen peroxide were placed into PTF vessels. Each sample in a vessel was placed in a Microwave Digestion System (MARS 5). The solutions were diluted appropriately with 0.1N HNO₃ and transferred to 25 ml volumetric flasks. Concentrations of Ca, P, Mg, Na, K, Zn, Cu, Mn and Fe were determined using inductively coupled plasma in atomic emission spectrometry (ICP-OES, VISTA – MPX Varian). Concentrations of selenium were measured with the atomic absorption hydride generation technique using a Perkin-Elmer spectrometer coupled with a Fias 200 (POLAK-JUSZCZAK 2015, POLAK-JUSZCZAK, ROBAK 2015). Each sample was analyzed in two replicates. Quality of each series of analyses was ensured by making a parallel analysis of Certified Reference Material: SRM 1566b (oyster tissue), SRM 1577b (bovine liver) and CRM 422 (cod muscle). Throughout the validation process, the limits of detection were set as follows: Ca – 0.05 mg kg⁻¹; K – 2.0 mg kg⁻¹, Na – 1.0 mg kg⁻¹, P – 0.1 mg kg⁻¹, Mg – 0.01 mg kg⁻¹, Fe – 0.03 mg kg⁻¹, Cu – 0.1 mg kg⁻¹, Zn – 0.75 mg kg⁻¹, Mn – 0.01 mg kg⁻¹, Se – 0.01 mg kg⁻¹, and recovery for the applied method was: Ca – 108.4%, K – 98.8%, Na – 97.9%, P – 104.1%, Mg – 104.8%, Fe – 92%, Cu – 94.7%, Mn – 95.2%, Se – 95.7%, Zn – 96.5%.

The data were processed statistically using Statistica 8.0 for Windows (Copyright© StatSoft). The non-parametric Kruskal-Wallis H-test was applied to verify statistically significant differences in metal concentrations among semi-processed and processed fish products. The level of significance was designated at $p < 0.05$.

RESULTS AND DISCUSSION

Our study included fish species and products, chosen after a review of products available on the market and consumer preferences. The following were chosen: salted and marinated herring and smoked mackerel, sprats and salmon. The concentrations of minerals in raw fish for processing into fish products varied according to fish species (Tables 1, 2). The content gradient

Table 1

Mineral content in fresh herring, semi-processed products and salted and marinated products
(mg kg⁻¹ wet weight)

Minerale	RDA (mg day ⁻¹)	Salted herring			Pickled herring		
		raw herring	semi- product	product	raw herring	semi- product	product
W(%)		70.8±2	69.2±4.0	68.9±0.6	72.4±3.4	70.2±3.2	66.3±4.8
Ca	1000	353±127 (3.5)	358±139 (3.5)	270±113 (2.7)	447±142 (4.5)	347±105 (3.5)	318±102 (3.2)
P	700	2316±930 (33.1)	1018±615 (14.5)	1010±644 (14.4)	2290±277 (32.7)	1194±238 (17.1)	1067±162 (15.2)
Mg	420	872±438 (20.8)	301±103 (7.2)	266±487 (6.3)	678±349 (16.1)	212±46 (5.0)	182±66 (4.3)
Na**	575	0.27±0.04 (16.9)	4.0±0.5 (697)(170)*	3.23±0.36 (561)(137)*	0.29±0.08 (50.5)	1.56±0.46 (272.4)	0.84±0.29 (145.9)
K	4700	3501±1010 (7.4)	1065±529 (2.3)	727±235 (1.5)	2956±459 (6.3)	920±289 (2.0)	673±297 (1.4)
Cu	0.7	0.8±0.1 (11.7)	0.5±0.01 (7.4)	0.6±0.1 (9.3)	0.8±0.05 (11.1)	0.8±0.08 (11.7)	0.9±0.2 (12.3)
Zn	11	12.9±5.6 (11.7)	6.8±2.6 (6.2)	6.7±2.4 (6.1)	14.1±2.5 (12.8)	8.4±1.4 (7.6)	7.1±1.9 (6.5)
Mn	2-5	0.1±0.04 (0.5)	0.13±0.06 (0.6)	0.11±0.03 (0.5)	0.1±0.01 (1.0)	0.15±0.07 (0.75)	0.25±0.03 (1.25)
Se	0.07	0.25±0.02 (35.7)	0.14±0.05 (20.0)	0.14±0.02 (20.0)	0.21±0.03 (30.0)	0.15±0.07 (21.4)	0.1±0.05 (14.3)
Fe	10	9.2±1.2 (9.2)	7.5±1.5 (7.5)	7.1±2.6 (7.1)	8.9±1.2 (8.9)	8.4±1.1 (8.4)	8.7±1.0 (8.8)

in parentheses: share of the Recommended Daily Allowance, * share of Tolerable Dose, W – content of water (%); RDA – Recommended Daily Allowance; * – % RDA for Na; ** content of Na (%);

RDA Commission Directive 2008/100/EC of 28 October 2008

RDA Norms of Nutrition for Polish Population. (2012). National Food and Nutrition Institute in Poland

of macroelements was $K > P > Na > Ca > Mg$. The concentrations of these minerals in semi-processed and processed products were similar, but sodium dominated. This element was added to semi-processed products in large quantities as brines contained as much as 25% NaCl. The result of brining was an over three-fold increase in the sodium content in marinated products (mean 0.84%) and a twelve-fold increase in salted (mean 3.2%) and cold-smoked (salmon – 2.1%, mackerel – 3.2%) products. The high sodium content (as NaCl) ensured a long-term shelf-life of the products. Although salting effec-

Table 2

Mineral contents in fresh fish and cold- and hot-smoked fish products (mg kg⁻¹ wet weight)

Mineral	RDA (mg day ⁻¹)	Sprat		Salmon			Mackerel		
		raw sprat	smoked hot	raw salmon	smoked cold	smoked hot	raw mackerel	smoked cold	smoked hot
W(%)		75.5±2.8	64.6±3.4	68.8±2.8	58.6±1.8	61.9±3.4	60.9±1.6	54.4±2.1	59.9±1.7
Ca	1000	2874±359 (28.7)	3412±575 (34.10)	76.5±37.1 (0.8)	84.7±27 (0.9)	90.8±27.9 (0.9)	426±119 (4.3)	552±122 (5.5)	367±115 (3.7)
P	700	3064±302 (43.8)	3970±172 (56.7)	2452±113 (35.0)	2265±149 (32.4)	2564±154 (36.6)	2144±17 (30.6)	1768±171 (25.2)	2224±108 (31.8)
Mg	420	352±16 (8.4)	441±32 (10.5)	355±17 (8.4)	324±28 (7.7)	342±10 (8.1)	370±48 (8.8)	327±21 (7.8)	381±25 (9.1)
Na**	575	0.08±0.01 (13.5)	0.88±0.21 (154)(38)*	0.05±0.02 (8.5)	2.1±1.0 (373)(91)*	0.61±0.04 (106)(26)*	0.13±0.04 (22.5)	3.18±0.22 (554)(136)*	0.44±0.25 (77)
K	4700	2082±291 (4.4)	2494±290 (5.3)	2644±470 (5.6)	2082±340 (4.4)	2579±486 (5.5)	2329±181 (4.9)	1998±205 (4.2)	2162±100 (4.6)
Cu	0.7	0.6±0.04 (8.6)	0.7±0.03 (10.0)	0.2±0.1 (3.4)	0.3±0.2 (4.2)	0.3±0.2 (4.2)	0.5±0.1 (6.6)	0.4±0.1 (5.6)	0.5±0.1 (7.1)
Mn	2-5	0.6±0.2 (2.9)	0.8±0.3 (3.8)	0.03±0.01 (0.2)	0.05±0.03 (0.25)	0.06±0.02 (0.3)	0.06±0.02 (0.3)	0.04±0.01 (0.20)	0.05±0.02 (0.25)
Se	0.07	0.09±0.01 (12.9)	0.1±0.0 (14.3)	0.06±0.02 (8.6)	0.07±0.02 (10.0)	0.07±0.02 (10.0)	0.08±0.03 (11.4)	0.07±0.01 (9.7)	0.08±0.01 (11.4)
Fe	10	12.6±2.2 (12.6)	13.8±2.7 (13.8)	2.9±0.9 (2.9)	2.7±0.3 (2.7)	3.7±1.3 (3.7)	8.2±0.0 (8.2)	8.5±0.4 (8.5)	10.5±1.0 (10.5)

in parentheses: share of the Recommended Daily Allowance, * share of Tolerable Dose, W – content of water (%); RDA – Recommended Daily Allowance; * – % RDA for Na; ** content of Na (%);

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tively prevents both spoilage and the growth of pathogenic bacteria (LEROI et al. 2000), it has been reported that the salt content in fish muscle enhances oxidation of highly unsaturated lipids (AUBOURG, UGLIANO 2002). However, the nutritional value decreased considerably in terms of its health-promoting properties. The sodium content in a 100 g portion of salted herring exceeded by six-fold the recommended daily dose 575 mg day⁻¹ (Commission Directive 2008/100/EC, Norms of Nutrition ... 2012) and by two-fold the daily tolerable dose (2350 mg Na day⁻¹). Such a high sodium content is unhealthy (with large portions eaten and frequent consumption), especially for consumers with diseases of the circulatory system. The contents of K, Mg and P in marinated and salted herring tended to decrease throughout processing, and the decreases in these minerals ranged from 60 to 80% in comparison to their content

in raw fish (Table 1). No such significant differences were observed in concentrations of Ca (about 25%). Disadvantageous changes in the contents of K, Mg, and P occurring in products during processing could have resulted from water loss. Salting reduced water content by just about 2%, while marinating did so by about 6%. These values were significantly lower than the losses of K, P and Mg in products (60-80%). Thus, the main reason for the loss of macroelements was the leaching of these mineral during high-sodium brine and marinade baths.

Significantly lesser macroelement losses than those in salted and marinated herring were noted in smoked fish (Table 2) as long as the decrease of the water content is taken into account. Water loss during cold-smoking was approximately from 6 to 10%, and during hot-smoking it was from approximately 1 to 11%. Differences were about 20% and they were caused more by water loss during smoking than by mineral leaching during brining. The production of smoked fish in Greece resulted in a significant decrease in the moisture content of chub mackerel samples, that is 21.2 and 22.4% in comparison to raw samples (GOULAS, KONTOMINAS 2005). Industrial specifications for "ready smoked products" generally recommend water content in fish flesh of less than 65% (CARDINAL et al. 2001). In the smoked products we analyzed, the mean water content ranged from 54.4 to 61.9%. These values are in complete agreement with those of KOŁODZIEJSKA et al. (2002), who reported that the mean moisture content of smoked mackerel was 56.7%. Despite significant losses of mineral components, fish products remain an important source of P, Mg and Ca, especially hot-smoked fish, in which mineral loss was smaller. A 100 g portion of hot-smoked sprats contained more than 50% of the recommended dose of P, over 30% of that of Ca, and about 10% of that of Mg. Salted and marinated products had the lowest nutritional value, and a 100 g portion contained an approximate 15% share of the recommended dose of P, up to 7% of Mg and about 3% of Ca.

The microelement content in fish products was similar to that in fresh fish. Only the concentration of Zn tended to decrease in subsequent stages of processing, resulting in a nearly two-fold decline in the recommended daily dose: from 12% in raw fish to about 7% in fish products. The contents of Cu, Mn, Se and Fe in a 100 g portion of fish product comprised the following percentages of recommended daily dose: Se up to 20%; Cu up to 11%; Mn up to 1%; Fe up to 10%. These results are similar to those found in other reports (STEINER et al. 1991, GÖKOĞLU et al. 2004, ERSOY, ÖZDEN 2009).

The results of the current study have indicated that significant changes occur in the mineral concentrations of raw fish when it is processed into fish products. These changes were noted primarily among macroelements (Na, P, K, Mg) in salted and marinated herring. Fresh fish had a higher nutritional value with regard to minerals than processed fish, which would suggest that it was better to consume unprocessed, fresh fish. However, there is no tradition of consuming raw fish in Poland, with the exception of infrequent in-

stances of sushi consumption. Before ingestion, fresh fish is generally fried, grilled or boiled, and these processes also cause losses of the fish mineral content. The results of a study conducted by KALOGEROPOULOS et al. (2012) reveal that microelement losses in fried fish are similar to those in smoked fish. Significantly smaller losses of mineral content are noted in smoked fish. In Europe, particularly in Germany, Poland and the UK, there is high market demand for smoked fish, such as mackerel, salmon, sprats, eel, halibut and herring. Smoking is one of the oldest methods of food preservation, and it is still widely used in fish processing. In Europe, about 15% of the total quantity of fish for human consumption on the market is in the form of either cold- or hot-smoked products (STOLYHWO, SIKORSKI 2005).

CONCLUSIONS

The technological processes for fish processing in Poland have an impact on the mineral content of the products. The salting and marinating of herring resulted in significant changes mainly in concentrations of macroelements. Several-fold increases in the sodium content of marinated herring and approximately fifteen-fold increases in salted herring and cold-smoked products were caused by brining in solutions with high concentrations of NaCl. The high sodium content exceeded the recommended daily dose, thus decreasing the nutritional quality of the fish products. The content of Ca did not change significantly, while that of the other macroelements (K, Mg, P) decreased significantly in salted and marinated herring. These decreases resulted from a lowered water content in products, but the main reason for the losses of mineral content was leaching during brining in baths with a high sodium content. Smaller mineral losses were noted in smoked fish. With regard to the health benefits of fish consumption, the best processing method was smoking, and mainly hot-smoking. The technological processes caused changes in the mineral composition of products and decreased their nutritional values. Despite this, salted and marinated herring and smoked fish remain a source of macroelements (P, Mg, Ca) and microelements (Cu, Zn, Se, Mn, Fe), while the organoleptic properties and a wide variety of these products often stimulate high level and frequent consumption of fish.

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