FISH POLLUTION WITH HEAVY METALS

*Camelia POPA¹, Petru BULAI²

¹ Ştefan cel Mare University of Suceava, Faculty of Food Engineering, camelia.popa@ fia.usv.ro
² Stefan cel Mare University of Suceava, Faculty of Mechanical Engineering, Mechatronics and Management, Department of Technology and Management, 13 Universitatii Street, 720229 Suceava, Romania bulaipetru@yahoo.com *Corresponding author Received 15 July 2012, accepted 20 August 2012

Abstract: The aim of this work is to identify and to find the concentration of some heavy metals (Cr, Ni, Fe, Hg, Pb) of different assortment of fish that we buy from markets: herring, sprat, hake, pangasius, trout, broad snout, and mackerel. Heavy metal concentrations were measured using EDX and UV-VIS spectrometer techniques. Laboratory studies showed that these fishes don't contain Ni, Hg, Pb. They contain only Cr and Fe but the concentration don't' exceed the maximum admissible limit from current legislation. Also, heavy metals content in bone is higher than in meat. Hake species do not accumulate heavy metals in meat, but they accumulate in the bone, completely.

Keywords: *heavy metals, fish, contaminants*

1. Introduction

In heavy metal group there are a range of chemical elements that have a great toxicity for living organisms. The toxic effect is manifested to overcome a certain threshold below which some (Co, Cu, Fe, Ni, Zn) may even be essential components of proteins involved in different metabolic pathways. Hevy metals are normally found in environment and may come from different pollutants, like nutrients or burning combustible waste gases [1]. Heavy metal content is monitored in environment and in foods. Toxicity of heavy metals is the rezult of their binding to important enzymatic systems from animal cell or their membrane

[2]. Heavy metals discharged into the environment eventually reach the living bodies which in return behave as a filter for them, meaning that they accumulate [3]. Thus, if the food would be totally free of metal it would appear nutritional deficiencies. Heavy metals are found in various concentrations in soil, water, air, vegetable or animal food, depending on various factors that determine their pollution.

The good reputation of fish as healthy food has distant origins, ancient. We know that fish is good food for humans. It has beneficial properties to the development of intellect, because its constituents rich in phosphorus and lecithin which is derived from fish oil. In fish culture we meet growth hormones, antibiotics, pesticides. But the biggest concern that exists is in connection with these contaminants, which accumulate along the food chain. Fishes cannot escape from the effects of these pollutants [4]. Contamination with a wide range of pollutants and heavy metals in particular has become a serious problem that has threatened this important source of food: fish [5]. Heavy metals enter in living organisms by ingestion, breathing and skyn contact and produces intoxications by cumulative effect. They deposite in organisms in various organs, muscles and bones. Depending on environmental contamination, fish can contain small or quantities of heavy large metals. Accumulation depends on the species, fish age, sex, weight and its position in the food chain: an old fish will contain a larger amount of heavy metals than the yanger one grown in the same conditions. A predator fish will be contaminated in "pyramid" [6,7]. The aim of this work is to identify and to find the concentration of some heavy metals (Cr, Ni, Fe, Hg, Pb) of different assortment of fish that we buy from markets: herring, sprat, hake. pangasius, trout. broad snout, and mackerel.

2. Materials and methods

Materials. Different fish species from markets: herring, sprat, hake, pangasius, trout, and broad snout. Were performed in parallel three samples of meat and fish bones from the same type of fish and made the average of determinations.

Sampling. For determinations were weighted on analytical balance about 5 g of each meat sample and 2 g of each bones samples. Samples were dried in porcelain crucible previously dried to constant weight at 105[°]C. Drying and calcination was made gradually on temperature ramp, 3 hours at 600° C. After calcination samples were cooled in desiccator. To solve the metals from ash was used HNO₃ 5% at boiling. Residue was filtered on watman filter, washed with distilled water and completed to 25 ml (solution 1).

Determination of iron. Iron were determined according to SR ISO 805:1995 by spectrophotometric method [8].

Principle method: Fe^{3+} ions was reduced to Fe^{2+} with hydroxyl amine chlorohydrin in sodium acetate made with 1,10 phenanthroline, a complex that may be measured at 510 nm.

Reagents and instruments: HCl for analysis, acetic acid-sodium acetate buffer for 4,4 pH, 5 g/L hydroxyl amine chlorohydrin solution, 2,5g/L 1,10 phenanthrolin solution, 10 mg/L Fe^{2+} standard solution, UV-VIS spectrophotometer UVI 1700 Schimadzu model, 1 cm quartz cells.

Calibration curve: was draw calibration curve for 0,1-0,8 mg/L Fe^{2+} field using FeSO₄·7H₂O certified reference material, Figure 1.



Figure 1. Fe²⁺ calibration curve

Handling: a well defined part of solution 1 was transferred into 100ml volumetric flask, add 25ml buffer solution, 5ml of hydroxyl amine chlorohydrin solution and 5 ml 1,10 phenanthrolin solution and distilled water to sign. Blank sample was prepared in the same way using the same volumes of reagents. The red complex was measured at 510 nm.

Results calculation:

$$C(\%) = \frac{C_x}{\frac{M_p}{D}} \cdot 100$$
 (1)

were: $C_x = Fe^{2+}$ concentration from calibration curve; M_p = sample weight (g); D = sample dilution. The report of the components from sample was found using EDX technique, normalization method.

3. Results and discussion

Among of different metals analysed are chemical hazards classified as and maximum residual levels have been prescribed for human (EC 2001, FAO 1983). After EDX analysis of heavy metals from fish for 5 chemical elements (Cr, Ni, Fe, Hg, Pb) were identified and measured the concentrations for two elements, Fe and Cr, the other three elements being in too small concentrations, below the detection limit of the method. Table 1 shows the results obtained for Cr and Fe. EDX technique shows the ratio of the components in the sample. UV-VIS technique shows the real percent of the component in the sample. Knowing the ratio of components in EDX analysis and the real concentration of iron by spectrophotometric technique was calculated the real concentration of Cr.

$$\frac{C_{Fe(EDX)}}{C_{Cr(EDX)}} = \frac{C_{Fe(real\check{a})}}{C_{Cr(real\check{a})}}$$
(2)

The concentrations of heavy metals detected in the samples are given in the Table 2. From this table results the following conclusions: The types of fish studied contain iron and chromium in quantifiable concentrations. The high content in heavy metals studied is contained by broad snout meat and the lowest, zero, it has meat hake. The high chromium content is found in broad snout and trout (meat). The high iron content presents sprat and broad snout (meat). Heavy metals content in bone is higher than in meat. Hake species do not accumulate heavy metals in meat, but they accumulate in the bone, completely. The concentrations of heavy metals studied were lower than maximum admissible levels [9,10]: $Cr = 12 \mu g/g$, $Ni = 70 \mu g/g$, $Pb = 0.3 \mu g/kg$, $Hg = 1 \mu g/kg$.

 Table 1.

 Calculation of Fe and Cr concentrations

Species of fish	Fe (µg/kg)	Cr (µg/kg)
Mackerel	0.75	0.40
Sprat	1.02	0.40
Hake	0	0
Pangasius	0.37	0.19
Trout	0.93	0.63
Broad snout	1.21	0.64
Trout bone	1.06	0.56
Hake bone	2.86	1.71
Mackerel bone	0	0



Figure 2. Fe and Cr meat content for the studied types of fishes

4. Conclusions

Water pollution is a major problem that threatens an important source of food: fish meat. From our studies we see that for the studied species were identified only Cr and Fe, the other elements being in concentrations under the detection limit of the analysis.

This work also shows that heavy metals content for fish meat decreases in the order broad snout, trout, sprat, herring, hake. The high content of these heavy metals is for broad snout meat and the lowest, zero, is for meat hake. The high Cr content is found in broad snout and trout (meat). The high Fe content presents sprat and broad snout (meat). Heavy metals content in bone is higher than in meat and do not exceed the quality rules to date: content in Pb maximum 0.3μ g/kg, Hg maximum 1μ g/kg [10]

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