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ORIGINAL RESEARCH PAPER

QUALITY CONTROL OF *Scomber Scombrus* (MACKEREL) MARKET IN ROMANIA♦

Simona Dobrinas*[1], Gabriela Stanciu[1], Alina Soceanu[1], Danut Tiberiu Epure[2], Valentina Bold[1]

[1] *"Ovidius" University of Constanţa, Department of Chemistry, 124 Mamaia Blvd, 900527 Constanţa, Romania*
[2] *"Ovidius" University of Constanţa, Department of Economic Sciences, 1 Universităţii Alley, Constanţa, Romania*

*Corresponding author: sdobrinas@univ-ovidius.ro

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Abstract: Different types of *Scomber Scombrus* (mackerel) available on the Romanian market (frozen, smoked, oil canned) have been analyzed, in order to highlight the differences in chemical composition between foods obtained using different preservation methods. For this, water content, total acidity, NaCl content, ammonium, total nitrogen and eight essential and/or potentially toxic elements (Cu, Cd, Fe, Mn, Zn, Pb, Cr, and Mg) were determined in five types of mackerel commercial products. The analyses were completed with sensorial analysis, and qualitative identification of antiseptic preservatives (hydrogen sulfide, formaldehyde and benzoic acid) has been performed. Hydrogen sulfide was not detected in any of the products studied, but benzoic acid and formaldehyde were detected in frozen and canned mackerel samples. The highest concentrations of essential elements were observed in frozen mackerel muscles, except iron (the highest value was found in canned mackerel). It can be concluded that concentrations of many essential elements decreased in the fish muscle due to smoking and sterilization. This study showed that the analyzed mackerel samples contain potentially toxic elements at levels without health risks.

Keywords: *FAAS, frozen, smoked and canned mackerel, quality control, sensory assessment, trace elements*

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INTRODUCTION

Good quality measurements are essential to control and maintain food products and processes quality, both in manufacturing, trade and research. Fish is a very important part of human diet since is widely consumed in many parts of the world. This aquatic food are a source of high protein content, low saturated fat and also contains omega fatty acids known to support good health. On the other hand fish are constantly exposed to chemicals in polluted and contaminated waters. Fish have been found to be good indicators of heavy metal contamination in aquatic systems [1], although for many trace elements the effects are cumulative and it is necessary to control their levels in consumed fish.

Many reports indicate the presence of trace elements contamination in fish and canned fish samples [2 – 8]. However, data on trace metal levels in frozen, smoked and canned fish samples produced in Romania are very limited.

Scomber Scombrus (mackerel) is a migratory species. After spawning, adults belonging to the southern and western components migrate to the feeding areas, the Norwegian Sea and the North Sea. This species supports valuable fisheries of great importance in several European countries, with annual mean landings of 675×10^6 kg from 1972 to 2002 [9].

Many studies investigated the changes in chemical composition of mackerel due to the freeze-drying effects during the long term storage [10 – 12]. The proximate chemical composition of mackerel varies greatly from one species to another depending on size and seasonal variations [13].

The goal of this study was to analyze the differences in chemical composition of frozen, smoked and canned mackerel. To assess the quality control of these samples were identified the antiseptic preservatives and was determined the water content, total acidity, alkalinity, NaCl content, ammonium ion, total nitrogen content and eight essential and/or potentially toxic elements. Also, a sensory evaluation of mackerel was done.

MATERIALS AND METHODS

Reagents and solutions

The nitric acid (65%) and hydrogen peroxide solutions used were of ultra pure grade, purchased from Merck.

The stock standard solutions of Cu, Cd, Fe, Mn, Zn, Pb, Cr, Mg at concentration of 1000 $\mu g.mL^{-1}$ and all the other chemicals were obtained from Merck (Germany). Deionized water was used for the preparation of all solutions. All working standard solutions were stored in polypropylene bottles.

All glassware was initially washed with detergent and water and then the glassware was rinsed several times with deionized water and dried.

Sampling

Mackerel samples (frozen, smoked and canned in oil) were purchased from private manufacturers and local markets in the city of Constanța, Romania. A minimum of three samples per type of mackerel samples was randomly purchased from these locations. Frozen mackerel samples were kept in deep freezer before analyzing and smoked and canned mackerel samples were stored in a clean dry place until time for sampling of fish muscles and analysis. For canned mackerel sample, the fish sauce was carefully drained and a portion of the muscle in minimal contact with the sauce was sub sampled and weighed. Basic information about the mackerel samples were presented in Table 1.

Table 1. *Basic information about the mackerel samples*

Label	Mackerel samples	Production
FM1	frozen	commercial
FM2	frozen	private manufacturer
SM1	smoked	commercial
SM2	smoked	private manufacturer
CM	canned in oil	commercial

Sample analysis

The antiseptic preservatives (hydrogen sulfide, formaldehyde and benzoic acid) were revealed by their identification reactions.

The hydrogen sulfide compound identification is based on lead sulfide formation from the reaction of hydrogen sulfide with Pb^{2+}. For this, in a vial with rubber stopper were inserted small pieces of fish muscle samples, then a strip of filter paper soaked with solution of $Pb^{2+}$was inserted and secured with the stopper; a black color developed in 15 minutes reveals the presence of hydrogen sulfide.

To identify formaldehyde, the samples were treated with sulfuric acid to precipitate proteins. Then the mixture was subjected to distillation and in the distillate was identified the formaldehyde by reaction with phenol, which led to the formation of a red ring on the surface.

Using the reaction with copper sulfate it can be identified the benzoic acid. In the case of a positive reaction, the formed solution of copper benzoate has a greenish blue color and it appears a precipitate.

Sensory analysis was conducted according to Romanian guidelines concerning frozen, smoked and canned fish [14 – 16]. Sensory assessment of the fish included the following parameters: skin, external odor, consistency and flesh odor.

The measurements of water content, total acidity, NaCl content, ammonium ion, total nitrogen content and eight essential and/or potentially toxic elements (Cu, Cd, Fe, Mn, Zn, Pb, Cr, Mg) were realized by the following techniques:

- water content was determined as the difference between the weight of fresh homogenized muscle (1 – 2 g) and the weight recorded after 24 h heating at 105 ^{o}C; the results were expressed as percentage (%);
- titrimetric method with NaOH as titrant for determining the total acidity;

- precipitation titration, with silver nitrate, in the presence of chromate ions for the determination of NaCl content;
- potentiometric method with ion selective electrode for determining the ammonium ion; measurements were performed with a DC 218 ISE ammonium combined electrod/Multiparameter analyser Consort C535, Belgium by homogenizing a 5 g portion of the muscle in 45 mL of deionized water;
- distillation method based on a strongly alkaline medium, followed by capturing the distillate in a concentrated solution of boric acid and followed by acid-base titration of the result with a mixed indicator was used for determination of total nitrogen content;
- flame atomic absorption spectrometry for determining essential and/or potentially toxic metals, after a mineralization step.

A mineralization step is necessary to obtain a finally solution suitable for introduction in the spectrometer. In order to determine essential and/or potentially toxic metals concentrations, the samples were washed with deionized water, dried and homogenized. 0.5 – 0.9 grams of each dry sample was submitted to digestion with 8 mL HNO_3 and 10 mL H_2O_2 at 170 ^oC in a Digesdhal device provided by Hach Company. After the complete digestion the samples solution were filtered, made up to 50 mL with deionized water and Cu, Cd, Fe, Mn, Zn, Pb, Cr, Mg were determined by FAAS in air/acetylene flame using an aqueous standard calibration curve. Analyses were made in triplicate and the mean values are reported.

A Shimadzu atomic absorption spectrometer (Model AA 6200) equipped with air-acetylene flame was used for the determination of metals in mackerel samples. Acetylene of 99.99% purity at a flow rate of 1.8 – 2.0 $L.min^{-1}$ was utilized as a fuel gas and also as a carrier gas for introducing aerosols. Copper was measured using multi element hollow cathode lamp. For Cd, Fe, Mn, Zn, Pb, Cr, Mg monoelement hollow cathode lamps were employed. The characteristics of metal calibration are presented in Table 2.

Table 2. *Characteristics of metal calibration curves*

Metal	λ [nm]	Concentration range [ppm]	Correlation coefficient
Cu	324.7	0.010 – 1.200	0.9990
Cd	228.8	0.008 – 1.600	0.9999
Fe	248.3	0.020 – 4.000	0.9976
Mn	279.5	0.008 – 1.600	0.9984
Zn	213.9	0.016 – 0.510	0.9932
Pb	282.3	0.002 – 6.000	0.9950
Cr	357.9	0.020 – 3.000	0.9874
Mg	289.2	0 – 15.000	0.9748

The precision (expressed as standard deviation SD and coefficient of variance CV) of the results was determined from three replicates of homogenized samples, giving a good standard and precision for the analytical results of essential elements and/or potentially toxic obtained by FAAS.

RESULTS AND DISCUSSION

One objective of this study was to investigate the presence of antiseptic preservatives of the mackerel samples. Following the identification reactions it was observed that hydrogen sulfide was not detected in any samples; formaldehyde and benzoic acid were detected in frozen and canned mackerel. Water content of different mackerel samples was in the range of 46.5 – 66.9%.

After the sensorial evaluation it can be affirmed that mackerel samples maintained good quality. After thawed state, the fish is clean, without cracks or damage. Body is covered by very small scale and the blue-brown back is color in crisscross stripes. Taste and smell after thawing is specific for fresh fish frozen and thawed. The smoked fish presents no traces of blood or viscera. The outside is a uniform golden color and taste and smell was specific for smoked fish. The flash of canned fish is compact and succulent, the oil is yellow and clear after sedimentation and the smell and taste is good.

In the frozen mackerel was not detected the presence of NaCl and the NaCl content decrease from 6.66 $g.kg^{-1}$ in smoked mackerel to 1.40 $g.kg^{-1}$ in canned mackerel. This is a normal evolution and the NaCl content in these samples are similar with the NaCl content observed by Losada *et al.* in horse mackerel [11].

The total acidity is expressed in Thorner degree which represents the volume of NaOH necessary to neutralize 100 mL of milk. The highest values of total acidity were registered for frozen mackerel samples (18.3 Thorner degrees).

TN (total nitrogen), NH_4^+-N (ammonium nitrogen) and nitrate nitrogen are main nutrients enriched in water body. The ammonium nitrogen and the nitrate nitrogen were determined in mackerel samples. From Table 3 it was observed that frozen mackerel samples have the highest concentration of TN, respective NH_4^+-N. All values are lower than the limits imposed by Romanian Standards (35 mg NH_4^+-N/100 g sample) [17]. These values of concentration were comparable with those reported in literature [18].

Table 3. *Variation of NH_4^+-N and TN concentrations in mackerel samples*

Sample	Concentration	
	mg NH_4^+-N/100 g sample	g NT/100 g sample
FM1	32.1	98.1
FM2	29.5	87.4
SM1	19.6	45.7
SM2	17.3	41.0
CM	28.1	91.0

The concentrations ($\mu g.g^{-1}$) of essential and/or potential toxic elements in mackerel samples are reported in Table 4; the values below quantification limits are shown with a less than sign (<) before the quantification limit.

As humans commonly consume muscles (edible parts), Cd and Pb toxicity via fish ingestion is unlikely. At present, the CE Regulation no. 466/2001 establishes a limit for Cd in muscle fish of 0.05 $mg.kg^{-1}$ and for Pb establishes a limit of 0.02 [19]. The Pb concentrations found in mackerel samples were below the quantification limit and so were below MRLs.

Cadmium concentrations in analyzed mackerel samples were higher than the limit imposed by European communities' standard. But CE Regulation no. 466/2001 present

summaries of occurrence data for cadmium in fish in several countries (Cd in frozen fish in the range 0.005 – 6.23 $mg.kg^{-1}$ and in fish canned in oil from 0.02 to 8.56 $mg.kg^{-1}$) and according to this the levels of Cd in frozen and canned mackerel samples were lower than those reported by CE regulation. Cadmium contents, in the literature, have been reported in the range of 0.06 – 0.19 $\mu g.g^{-1}$ in canned fish samples [1], 0.03 – 0.5 $\mu\mu g.g^{-1}$ dry weight in Atlantic horse mackerel [7], 0.003 – 0.02 $\mu g.g^{-1}$ dry weight in fish species from North French coastal waters [20], 0.02 – 3.76 $mg.kg^{-1}$ dry weight in fish species from Mediterranean Sea, Egypt [21] and 0.15 $\mu g.g^{-1}$ dry weight in mackerel [22].

Table 4. *Concentrations of eight essential and/or potentially toxic metals from mackerel samples ($\mu g.g^{-1}$)*

	FM1	FM2	SM1	SM2	CM
Cu	1.25 ± 0.0003*	1.10 ± 0.0009	1.11 ± 0.0009	0.90 ± 0.0018	0.59 ± 0.0022
Cd	0.13 ± 0.0010	0.12 ± 0.0008	0.11 ± 0.0037	0.09 ± 0.0012	0.06 ± 0.0011
Fe	30.43 ± 0.0056	29.14 ± 0.0012	28.82 ± 0.0025	25.14 ± 0.0004	35.44 ± 0.0026
Mn	< 0.028	< 0.028	< 0.028	< 0.028	< 0.028
Zn	22.12 ± 0.0002	23.14 ± 0.0021	14.57 ± 0.0004	11.98 ± 0.0011	8.32 ± 0.0022
Pb	< 0.0049	< 0.0049	< 0.0049	< 0.0049	< 0.0049
Cr	0.43 ± 0.0002	0.41 ± 0.0009	0.91 ± 0.0001	0.87 ± 0.0015	0.88 ± 0.0006
Mg	294 ± 0.0228	290 ± 0.0002	272 ± 0.0096	273 ± 0.0014	254 ± 0.0018

*SD – standard deviation

Copper is a very common substance that occurs naturally in the environment and spreads through the environment through natural phenomena. Copper is essential for animals and plants, as it takes part in enzyme formation and participates in respiratory processes, with accumulation levels varying widely among aquatic organisms [21]. For humans a very high intake can cause adverse health problems. Concentrations values of Cu detected in canned mackerel samples were lower than those detected in other canned fish samples (1.10 – 2.50 $\mu g.g^{-1}$) [1].

The obtained data showed that concentrations of Cd, Cu and Pb are lower than those presented in the report by MAFF food (Cu – 20 $mg.kg^{-1}$, Cd – 0.2 $mg.kg^{-1}$, Pb – 2.0 $mg.kg^{-1}$) [23].

Iron is a mineral essential for life and must be a part of human diet. Although considered trace mineral, diets lacking in iron can contribute to the deficiency condition. Concentrations of iron found in mackerel samples are comparable with those encountered in other fish species [1, 22].

Zinc is widespread among living organisms, due to its biological significance. In air, water and soil zinc occurs naturally, but its concentrations are rising unnaturally, due to addition of zinc through human activities [24]. In the literature, zinc levels in canned fish samples have been reported in the range of 8.61 – 34.4 $\mu g.g^{-1}$ [1], higher values than those found in canned mackerel (see Table 4). Zinc levels, in the literature, have been reported in the range of 3.01 – 88.2 $\mu g.g^{-1}$ dry weight in mackerel [5, 22], 2.1 – 8.7 $mg.kg^{-1}$ for other fish species from Northeast Atlantic [6].

Manganese levels may be affected by food processing [1]. In our study Mn concentrations found in mackerel samples were below the quantification limits (see Table 4).

Chromium is used in many industries. Cr(III) is an essential nutrient, but Cr(VI) is carcinogenic. The concentration values of total chromium detected for mackerel samples were lower than those reported in the literature: for canned fish 0.97 – 1.70 [1], for fish species from Mediterranean Sea, Egypt (< 0.005 – 20 $mg.kg^{-1}$) [21].

CONCLUSIONS

The study was conducted to assess the quality control of frozen, smoked and canned mackerel samples. The results obtained in this study indicate few chemical differences between the studied samples. This may be due to the differences appeared in the processing of the mackerel: freezing, smoking and sterilizing preservation methods.
Hydrogen sulfide was not detected in any of the products studied; instead benzoic acid and formaldehyde were detected in frozen and canned mackerel.
The highest concentrations of essential elements were observed in muscle of frozen mackerel, except iron (the highest value was found in canned mackerel). It can be concluded that concentrations of many essential elements decreased in the muscle of fish by smoking and sterilization.
The levels of cadmium in analyzed mackerel samples were found to be above the legal allowed limits. The level may be reduced by more careful handling practices and processing of raw materials.
This study showed that the studied mackerel samples contain Cu, Cd, Fe, Mn, Zn, Pb, Cr, and Mg at levels without health risks.

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