Determination of trace metal, fat content and iodine value in canned fishes; sardine (*Sardinella brasilienses*) and mackerel (*scomber scombus*)

Ibe Awodi* and Nsidibe C Nwokem

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Abstract: Fish is an important source of nutrients to man and is also useful for the production of animal-based foods. However, there have reported cases of contamination of fish products from natural or anthropogenic sources such as; agricultural activities, industrial wastes and others. The corrosion and leaching of heavy metals from cans use for the packaging of the products may contribute to the contamination of foods. The consumption of these contaminated foods has deleterious effects on human health such as; cancer, respiratory diseases, and kidney failure among others. It is therefore pertinent to address this surging global crisis. This study conceived to examine the concentration of metal ions, , fat t and iodine value of fishes consumed in Nigeria. The samples were obtained from a store in Zaria, Kaduna State. A flame-type atomic absorption spectrophotometer, AAS (VARIAN AA240FS Fast sequential model) was used for the analysis of trace metals (Ni, Cr, Cd) content of the sample. The results for the trace metal analysis in mackerel gave the following mean concentrations; 0.39 ± 0.14 mg/kg (Ni²⁺), $0.16 \pm 0.02 \text{ mg/kg}$ (Cr) and < 0.01 mg/kg (Cd). The mean concentration of trace metals in sardine was found to be: 0.09±0.01 mg/kg (Ni), 0.01 ± 0 mg/kg (Cr) and <0.01 mg/kg (Cd). The fat contents in the analyzed fish sample were 25.24±4.16 % and 0.09±0.01 % for mackerel and sardine respectively, while the iodine values of oil in mackerel obtained was 114.84 ± 3.59 I₂/100 g and that of Sardine was 76.14 \pm 3.03 I₂/100 g. The concentration of cadmium in the two fish samples, and the concentration of Cr ions in samples of sardine

were both below the recommended limit by WHO. However, the concentration of Cr in Mackerel and the concentration of Ni²⁺ in the two fish samples were above the permissible limit by WHO.

Keywords: *Trace metals, fat content, iodine value, mean concentration, sardine, mackerel.*

Ibe Awodi*

Department of Chemistry, Ahmadu Bello University, Zaria, Kaduna State, Nigeria Email: <u>awodiohili@gmail.com</u> Orcid id: 0000-0002-6709-035x

Nsidibe C Nwokem

Department of Chemistry, Ahmadu Bello University, Zaria, Kaduna State, Nigeria Email: <u>nsidibe19@gmail.com</u>

1.0 Introduction

Fish is rich in protein, low in saturated fat and contains omega-3 fatty acids which are known for the prevention of coronary artery diseases. Consequently, fish is a valuable source of nutrition worldwide (Abubakar *et al.*, 2014). The high iodine content in seawater can be absorbed by aquatic organisms indicating, that they hae a significant concentration of iodine However, iodine is an essential element required by the human system for proper biochemical functions.

Canned foods are generally processed to increase their shelf life, hence, they do not require special treatment such as lowtemperature storage or smoking (Kowalska *et al.*, 2020). Foods in this category are usually stored in plastic containers, metal cans, or glass jars and are preserved by various processes such as pasteurization, and the addition of chemical preserving additives (Amit *et al.*, 2017). Canned foods sometimes contain chemical contaminants that are deleterious to consumers. These contaminants can be as a result of poor processing and packaging or developed from chemical reactions within the storage environment (Buculei *et al.*, 2014).

Also, the global agricultural and industrial revolution has invariably increased water pollution by heavy metals which have now become a major environmental problem. Natural activities such as erosion, oceanic surge and volcanic eruption also contribute to the pollution of water bodies (Oluyemi et al., 2011). Fish can bioaccumulate heavy metals, which are often higher than the concentration contained in the water bodies. Heavy metal ions can pose a major threat to consumers because they are non-biodegradable and are toxic above certain concentrations (Ociepa-Kubicka, 2012). Therefore, the consumption of contaminated fish can also pose serious health implications such as cancer, kidney disease, and cardiovascular diseases among others.

Cadmium is very toxic and it is dispersed into the environment usually through activities in metal industries. Cadmium can also find its way to the human system through smoking cigarettes or the consumption of foods contaminated with cadmium. Effect of cadmium exposure above the regulatory limit includes hypertension, kidney diseases, brain damage and tumors (Uchechukwu et al. 2015). Exposure to chromium occurs majorly through industrial activities such as electroplating, during the production of pigments, paper, paints and the use of fertilizers and sewage for agricultural activities among others (Jaishankar et al., 2014). Compounds of chromium are generally carcinogenic and can destroy the cells of DNA.

Nickel ions are used in the production of coins, stainless steel and electronics just to mention a few. Humans can be exposed to Ni through the consumption of contaminated food or water,



In addition to the sources of heavy metals discussed, canned foods are sometimes stored using chemical preservatives such as sodium nitrate and potassium nitrate (Amit *et al.*, 2017). Canned foods such as sardines and geisha therefore sometimes contain chemical contaminants as a result of incorrect processing and packaging (Buculei *et al.*, 2014)

Unfortunately, the contamination of the marine environment, as a result of pollution from natural and anthropogenic activities has significantly increased the concentration of toxic metals in the environment (Diediibegovic *et al.*, 2020). As a result, marine organisms can accumulate these metals to toxic levels, which has deleterious effects on human health. This study aims to determine the trace metal content (Nickel, chromium and cadmium) and its health effect, as well as the fat content and iodine value of canned fishes (sardine and mackerel) sold in Kaduna-Nigeria and their health benefits.

2.0 Materials and Methods

2.1 Materials and reagents

All reagents and chemicals used for the study were of analytical grade. Hydrogen sulphate (H₂SO₄), hydrogen nitrate (HNO₃), petroleum ether, glacial acetic acid iodine monochloride, iodine trichloride, tetrachloroethane, potassium iodide, sodium thiosulphate and starch indicator were obtained from Chemistry Department Undergraduate store, A.B.U – Nigeria. The canned sardine and mackerel were obtained from the local market at Sabon gari local government of Zaria.

2.2 Digestion of sample

The fish samples were washed thoroughly with distilled water and oven dried at 50 °C. Subsequently, the sample was further homogenized using a porcelain mortar and pestle. The ground sample (1.0 g) was



transferred into a beaker for the wet digestion process. Nitric acid (100 cm³) was previously added to the fish sample and 50 cm³ was later added and allowed to cool for a few hours. The mixture was washed and filtered using a Whatman no 1 filter paper and transferred to a volumetric flask, which was made up to mark using distilled water.

2.3 Determination of trace metal

The digested sample was further analyzed using a flame atomic absorption spectrophotometer (VARIAN AA240FS Fast model), to determine the concentration of nickel, chromium and cadmium.

2.4 Determination of the fat content

The fat content of the sample was determined using the Soxhlet extraction method. The homogenized fish sample (5 g) was weighed into a thimble, and 300 cm³ of petroleum ether was measured into a weighed and labeled boiling flask. The Soxhlet apparatus was set up and allowed to reflux for 6 h. the thimble was disassembled from the setup, and the content in the flask was concentrated using a rotary evaporator to properly remove petroleum ether contained in it. The sample was allowed to cool and then weighed using an analytical weighing balance and applied to the formula below:

Fat content (%) =
$$\frac{W_2 - W_1}{W} \times 100$$
 (1)

where W_2 is the weight of the flask and fat, W_1 is the weight of the flask and W is the weight of the sample.

2.5 Determination of the iodine content

The iodine value of the fish oil was measured using the Wijis method. The iodine value gives the level of unsaturated fatty acids contained in the oil of fish. To prepare the Wijs' reagent, 8.0 g of iodine trichloride (ICl₃) was transferred into a beaker containing 200 cm³ glacial acetic acid, likewise, 9.0 g of iodine was transferred to a solution of CCl₄ (300 cm³). The two separate solutions obtained were mixed in a 1L conical flask and made up to mark using glacial acetic acid.



The fish oil (0.3 g) was weighed and transferred into a solution of carbon tetrachloride (25 cm^3), and 25 cm^3 of freshly prepared Wijs' reagent was added to the mixture. The solution obtained was properly mixed and allowed to stand in the dark for 30 min. Afterward, 100 cm³ of distilled water and 20 cm³ of 10 % potassium iodide were added.

The iodine obtained was titrated with sodium thiosulphate solution, with starch as the indicator just before the endpoint was attained. An experiment with a blank sample was also carried out. The iodine value was calculated with the equation below:

Iodine value =
$$\frac{V_1 - V_2}{W} \times 126.9$$
 (2)

In equation 2, V_1 and V_2 defined as the volume of thiosulphate used to titrate the blank and the sample respectively (cm³), and W is the weight of the fish oil in grams. The iodine value obtained is measured in mg I₂/100 g oil.

3.0 Results and Discussion 3.1 Trace metal concentration of Mackerel and Sardine

Fig. 1 and Table 1 present information on the concentration of trace metal in Mackerel and sardine fishes.

 Table 1: Mean concentration, fat content

 and iodine content of Mackerel and Sardine

Concentration	Mackerel	Sardine
Ni (mg/L)	0.39 <u>+</u> 0.14	0.09 <u>+</u> 0.01
Cr (mg/L)	0.16 <u>±</u> 0.02	0.01 <u>±</u> 0.00
Cd (mg/L)	< 0.01	< 0.001
Fat (%)	25.24 <u>+</u> 4.16	18.36 <u>+</u> 0.23
Iodine value	114.84 <u>+</u> 3.59	76.14 <u>+</u> 3.03
(/ 100g)		

From the presented results, measured concentrations of Ni^{2+} , Cr^{3+} and Cd^{2+} are relatively comparable. The concentrations of Cd ions in the two samples were below the detection limit of AAS, this aligns with the study carried out by Ogundiran and Ojo, (2012).

The mean concentrations of Ni ions $(0.39\pm0.14 \text{ mg/L})$ and Cr ions $(0.16\pm0.02 \text{ mg/L})$ in mackerel were observed to be higher than the mean concentrations in sardine, which were $0.09\pm0.01 \text{ mg/L}$ and $0.01\pm0 \text{ mg/L}$ for Ni and Cr respectively. The presence of Ni and Cr in the fish samples may be attributed to contaminants in the aquatic environment, their feeding habit, size and age.

 Cr^{+3} is an essential element but Cr^{+6} affects human health even at low concentrations (Minczewski *et al.*, 2001). Food storage in metal cans can increase the concentration of chromium. Chromium concentration in Sardine was within the permissible limit of 0.1 mg/L, recommended by WHO (2011), however, Cr ions concentrations in Mackerel were above the acceptable limit (WHO, 2011)

Nickel is not an essential element; however, its deficiency can result in a reduction in the level of hemoglobin in the blood among others but it reduces the levels of other essential elements in excess concentration (Kowalska *et al.*, 2020). Sardine and Mackerel both contained Ni ions at concentrations above the acceptable limit by WHO of 0.09 mg/kg (WHO, 2011).



Fig. 1: Concentration of trace metals in Mackerel and Sardine

The fat content of mackerel and sardine obtained was 25.24 ± 4.16 and 18.36 ± 0.23 as presented in Fig. 2, this is a little lower than the range (4.36 % - 58.9 %) obtained by Ogunadiran and Ojo (2012). These variances



can be attributed to factors such as geographical location, gender, species and diet which affect the fat content in fish.

Fig. 2 and Table 1 represent the fat content of the fish samples. Sea water fishes among other marine foods are known for being a major source of iodine. The iodine content was highest in Mackerel (114.84 ± 3.59) compared to that of sardine which was 76.14 ± 3.03 . This element is essential for the thyroid hormones to function properly, which affects the development and growth of humans and its deficiency can result in endemic goiter (Kasozi *et al.*, 2014).



Fig. 2: Fat content of Mackerel and Sardine

3.3 Iodine content of Mackerel and Sardine

Fig. 3 and Table 1 also represent the iodine content of Sardine and Mackerel



Fig. 3: Iodine value of Mackerel and Sardine

4.0 Conclusion

The mean concentration of Ni (0.39 ± 0.14) and Cr(0.16+0.02) in Mackerel was recorded to be much higher than the concentration in Sardine of which a mean concentration of 0.09+0.01 and 0.01+0 was obtained for Ni and Cr respectively. The concentration of Cd in the two fish samples was below the detection limit by AAS, hence the concentration of this metal is below the acceptable limit. The Chromium concentration in Mackerel was within the acceptable limit; however, its concentration in Mackerel exceeded the limit by WHO. Mackerel and Sardine contained Ni in a concentration above the permissible limit. The fat content of Mackerel and Sardine obtained and 18.36 ± 0.23 was 25.24 ± 4.16 % respectively. The iodine content of Mackerel was 114.84 ± 3.59 I₂/100 g and 76.14 ± 3.03 $I_2/100$ g was obtained for Sardine. The fat content and iodine content in the fish samples shows that the consumption of the canned fishes in this study is a source of dietary nutrition. However, elemental-wise, especially concerning Ni and Cr, the consumption of mackerel and sardine is not safe for consumption and thorough screening of imported and locally processed canned fish, before distribution is recommended.

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I. Awodi carried out the research and wrote the draft manuscript while N. C Nwokem designed and supervised the work

