1-Introduction:

There are seven commercial types of tunas, as well as several related species, all of which are members of what is called the *Scombridae* family[1], the best known being albacore, yellowfin, bigeye, bluefin and skipjack. The high fat Albacore weighs in the range of 4 to 30 kgs range and has the lightest flesh and is the only tuna that can be called "white". Yellowfin and bluefin tunas are usually larger than albacores, reaching up to 130 and 450 kgs, respectively. Yellow fin flesh is pale pink with slightly stronger flavored than that of the albacore [1].

Tuna fish are well-known as an important food source of omega-3 fatty acids such as EPA (eicosapentaenoic acid) and DHA (docosahexaenoic acid) (Figure 1-1). Such acids are clearly determined to have anti-inflammatory health benefits and they prevent heart diseases [2]. The consumption of omega-3 fish can increase the presence of omega-3s in the membranes of red blood cells as well as cells along the blood vessel linings. This increased level of omega-3s is associated with better regulation of blood pressure.Canned fish products (tuna, sardine, mackerel, herring *etc.*) are also rich in macro essential elements such as phosphorous and calcium and microelements such as selenium [3]. The essential microelements such as zinc, copper, chromium, fluorine, iodine and selenium play important roles in biological systems and have a variety of biochemical functions in living organisms. Beside the good health benefits of fish consumption, levels of contaminants in fish are of significant concern because of their potential effects on human health.

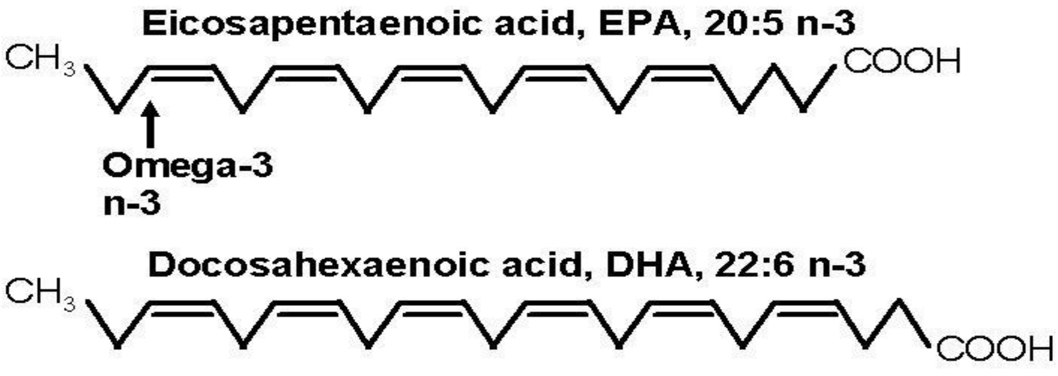

Figure 1-1: chemical structures of EPA and DHA (ω3-fatty acids)

Toxic elements such as mercury, cadmium and lead perform no beneficial biological roles and can be dangerous even at low concentrations when ingested over a long period of time. Essential elements can also pose hazardous effects and health problems at high concentrations [4].The mineral components of canned tuna are classified as macro – and microelements. The macroelemnts present at levels of several to hundreds of milligram per 100 g wet weight (mg/g), examples of macroelemnts are Na, Mg, Ca, K, Fe, S, Cl and P, while the microelements are found at levels of less than 0.1 to few tens of micrograms per 1g wet weight (μg/g) such as Se, Cr, Co, Cu and Mn.

2-Literature Review:

Fish, shellfish and sea foods in general are good sources of many vitamins, minerals and long chain unsaturated fatty acids. However, there are sets of maximum recommended amounts of these foods for human consumption, this is because of the possible adverse health effects caused by exceeding the recommended daily intake of essential elements and the presence of trace amounts of toxic elements such as mercury. In this brief review we will focus on the beneficiary health effects as well as the toxic effects of selected elements possible sources of these elements and bioaccumulation in the seafood web.

2-1: Microelements: (Mn, Cu, Cr, Zn, Co, Li and Hg)

2-1-1: Manganese (Mn)

Manganese is an essential element for both man and plants and it acts as an important co-factor for many enzymes and plays an essential role in the body functions. Mn is associated with bone development, and with amino acid, lipid, and carbohydrate metabolism (5). The adequate intakes (AI) of manganese are set to be 2.3 mg/day and 1.8 mg/day for adult males and females, respectively (6). The excessive or overexposure to Mn could lead to severe neurodegenerative damages and can cause a Parkinson-type syndrome (7)

. 2-1-2: Copper (Cu)

Cu deficiency in humans leads to hypochromic anemia especially in infants and children (8) while the acute Cu intoxication leads to gastrointestinal effects characterized by abdominal pain, nausea, diarrhea, and vomiting. It is important to have diets with good source of Cu such as liver, meats, whole grain and nuts because copper is an essential part of several enzymes and it is necessary for the synthesis of hemoglobin. There is approximately 80 mg of copper in the whole body of human adult and the recommended dietary allowance of copper is 900 μg/day. (9)

2-1-3: Chromium (Cr)

Other than its concentration, and the route of exposure the essentiality and toxicity of chromium is highly affected by its valence state. Chromium (III) has been identified as the active ingredient of the glucose tolerant factor and affects the action of insulin in protein metabolism (10). However chromium (VI) compounds are the most potent animal carcinogens (11,12). It has been estimated that the average human requires nearly 1 μg/day. Deficiency of chromium results in impaired growth and disturbances in glucose, lipid, and protein metabolism.

2-1-4: Zinc (Zn)

Zinc is involved in most metabolic pathways in humans; it involved in the activity of many enzymes as a co-factor for some enzymes such as arginase, RNA polymerase. Cu–Zn superoxide dismutase and others (13). Zn deficiency in human affect the immune system and the excessive zinc amount affect the iron function in the body (14). The human body content of zinc is about 2-3 grams (adult), The recommended dietary allowances of zinc for adult males and females are 11 mg/day and 8 mg/day, respectively(9).

2-1-5: Cobalt (Co)

Cobalt is an integral part of vitamin B12 (cyanocobalamin) in human, little is yet known of the forms in which this element occurs in man, other than vitamin B12. The highest concentration of cobalt in human was found in liver and kidney organs at mean level of about 0.24 mg/g(14) .Excessive ingestion of cobalt is reported to cause congestive heart

2-1-6: Lithium (Li)

Lithium is one such nutrient that has an important connection with the mood of an individual. It is regarded as important for the mental state of human beings (15), The U.S. Environmental Protection Agency (EPA), estimates that the daily lithium consumption for an adult ranges from 650 to 3,100 micrograms. It's difficult to estimate dietary needs in humans and no recommended daily allowance has been set for lithium. Provisionally, the recommended dietary allowance is 1,000 μg per day.

2-1-7: Mercury (Hg)

Mercury is released into the environment from both natural and anthropogenic sources. Once introduced to the surface waters, inorganic mercury can be methylated through biochemical or abiotic processes into methylmercury (MeHg)(16); one of the most toxic forms of mercury species.
Methylmercury has the tendency to accumulate in the aquatic food chain, and most mercury in fish is methylmercury (17). Fish consumption is the major source of organic mercury (methylmercury) in humans. It has been reported that human exposure to mercury and methyl mercury may increase the risk of heart diseases (18).

2-2: Macroelements :(Fe, Na, K, Mg and Ca)

2-2-1: Iron (Fe)

Iron is is an essential part of hemoglobin, myoglobin and the non-heme complexes such as ferritin (19). The recommended dietary allowances (RDA) of iron for adult males and female are 8 mg/day and 18 mg/day, respectively. Iron deficiency causes anemia and excessive iron causes health problems. Iron content in an adult man is about 4 g and iron concentration in blood serum is about 1.3 mg/l.

2-2-2: Alkali and alkaline earth metals (Na, K, Mg, Ca):

The amounts of alkali and alkaline earth metals (sodium, potassium, magnesium and calcium), together with chloride ions, must be in balance in extracellular fluid, which is responsible for muscular irritability. They are important to the human nervous system, and fluid balance (19). Magnesium in particularly is necessary for energy metabolism, and calcium is the major component of boon and help in teeth development.

2-3: Bioaccumulation of heavy metals in food web

The existence of some metals in aquatic ecosystems has been a serious problem for the environment and human health. Marine pollution in particular, can increase aquatic concentrations of toxic metals and negatively affect fish health and consequently the human health as a consumer. Two important sources are contributing to the input of metals to aquatic ecosystems: natural processes (e.g., volcanic activity) and anthropogenic sources such as agricultural drainage, industrial effluent discharges, fossil fuels, sewage discharge, mining and smelting activities and accidental chemical waste spills, although the latter has contributed to a greater environmental impact (20). The metals after entering the aquatic medium is transformed, transported and often gets precipitated, higher concentrations of heavy metals are found in the sediment and enter the food chain via the feeding of benthic species, the dissolved metal ions in water bodies enter the body surface of fish through the gills, whereas the particulate metal fractions in these sediments enter via the alimentary tract (21). Bioaccumulation of metal is the process by which an organism (fish) concentrates metal from abiotic environment (e.g. water, sediment) and through food ingestion, resulting in body concentration that is many folds higher than the metal concentration in the environment (water) (22).

The metal bioaccumulation in fish depends on physic-chemical properties of water, the location, distribution, habitat preferences, trophic level, metal type, feeding habits, age and size, duration of exposure to metals, metal concentration and the rate of scale formation (23). Tuna fish is considered as a top predator, the exposure to, and accumulation of, metals throughout the food web tend to be intensified; the accumulation of mercury in tuna has been documented (24).

3- Materials and Methods

3-1: Sampling

During this project, 12 samples of various brands of canned tuna samples were purchased from popular supermarkets from Riyadh city, capital of Saudi Arabia.

The samples were transported to the laboratory, coded for easy identification. Brand codes, contents and other information are presented in **Table 1**. After opening, the fish sauce and oil contents (liquids) were drained off, a portion of the meat was sub-sampled and weighed for elemental analysis.

3-2: Reagents and materials

All glassware used in the present study were previously soaked in 10 % (v/v) HNO_3 solution for 24 hours and rinsed with distilled water. Nitric acid (HNO3, 69 %) was used for wet digestion. The standards of Na, K, Ca and Li were prepared from pure starting materials and used to calibrate flame photometer.

3-3: Sample preparation and chemical analysis:

Portions of (about 1-3 g) of the tuna meat samples were digested in 200 mL glass beakers with 20 mL of HNO_3 (69 %) solution. Each beaker was covered with a watch glass heated on hot plate at 150- 165 ºC; aliquots of nitric acid were added until the solutions were clear. Solutions were constantly boiled until the volume for each sample reduced to about 5 mL. The solutions were then allowed to cool, filtered and diluted up to 50 mL with acidified (HNO_3) distilled water and then placed in 50 mL polyethylene tube. A blank digest was carried out in the same way. All digested samples were analyzed for Fe, Zn, Cu, Cr, Mn, Co and Mo contents using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Flame photometer (PFP7, Jenway®) was also used for the analysis of Na, K, Li and Ca. **Figure 2** illustrates Schematic of this machine. The calibration curves of these metals are shown in **figures 3 and 4**. Because of the low sensitivity of the machine to Ca, the one point standard addition method was used for the analysis of this element.

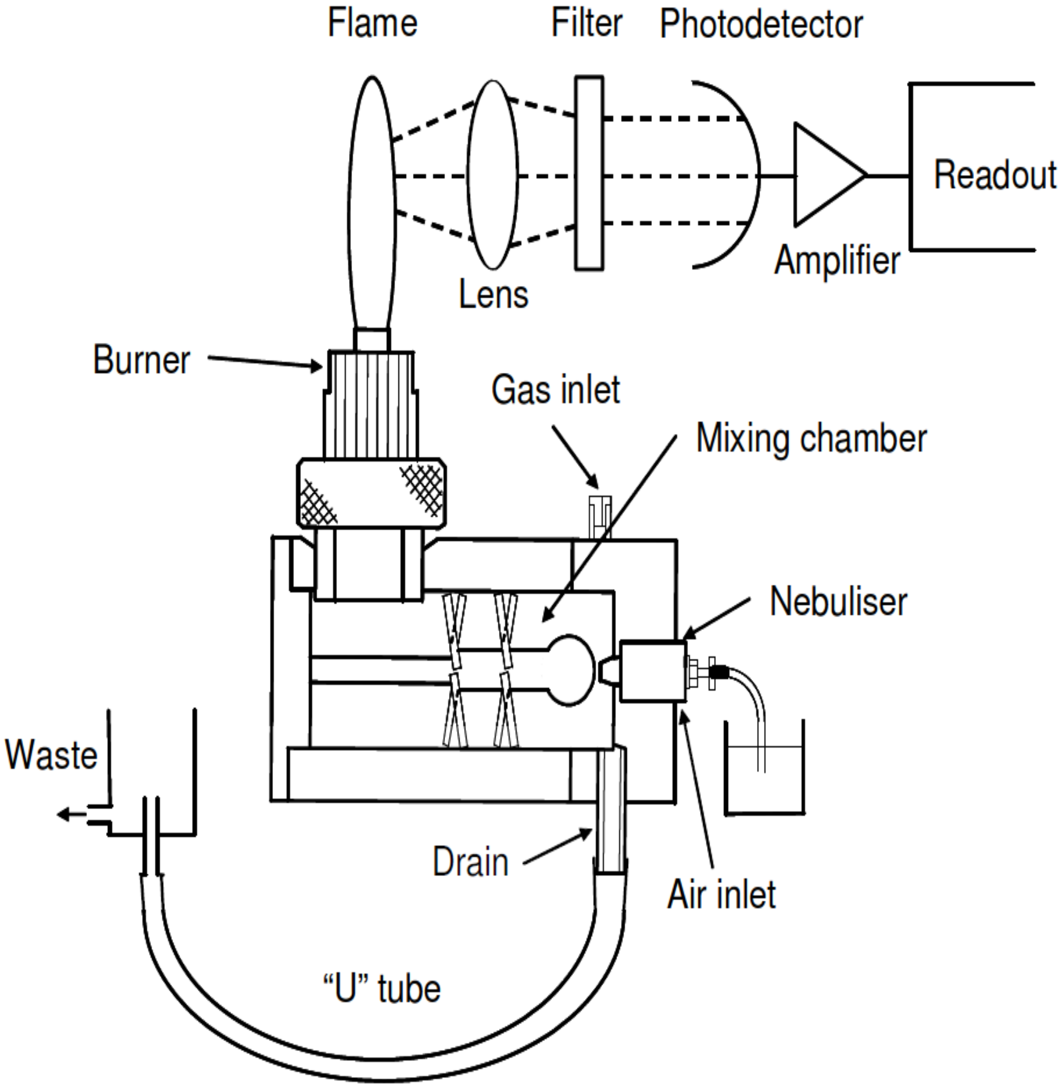

Figure 2: Schematic diagram showing the component parts of a flame photometer (adapted from manual of PFP7, Jenway®)

Table 1 : General information about canned tuna used in this study

Sample Code	Brand name	Oil content	Tuna meat	Weight/ g	Made in	Added Salt	Production date	Expired date
M1	California Garden	Soya bean	light	95	Thailand	yes	7\2014	7\2016
M2	Rio mare	Sun flower	light	160	Thailand	yes	5\2015	5\2018
M3	Blank							
M4	Alalali	Sun flower	light	170	Thailand	yes	1\2015	1\2018
M5	Alkhair	Sun flower	light	95	Thailand	Solid shape	7\2014	7\2016
M6	Geisha	Sun flower	light	100	Thailand	yes	6\2015	6\2017
M7	Sallati	Sun flower	light	95	Thailand	In Water ,salt	6\2014	6\2016
M8	Al-riyah	Vegtable oil	white	100	Yemen	yes	2\2015	2\2017
M9	An-nur	Vegtable oil	white	200	Yemen	yes	6\2013	6\2015
M10	Freshly	Sun flower	white	200	Thailand	In Water ,salt	4\2015	4\2017
M11	Al-taie	Sun flower	white	200	Thailand	yes	9\2014	9\2016
M12	Foodys	In water	white	200	Thailand	In Water ,salt	9\2015	8\2017
M13	Freshly	In water	white	200	Thailand	In Water ,salt	7\2015	7\2017
M14	Blank							

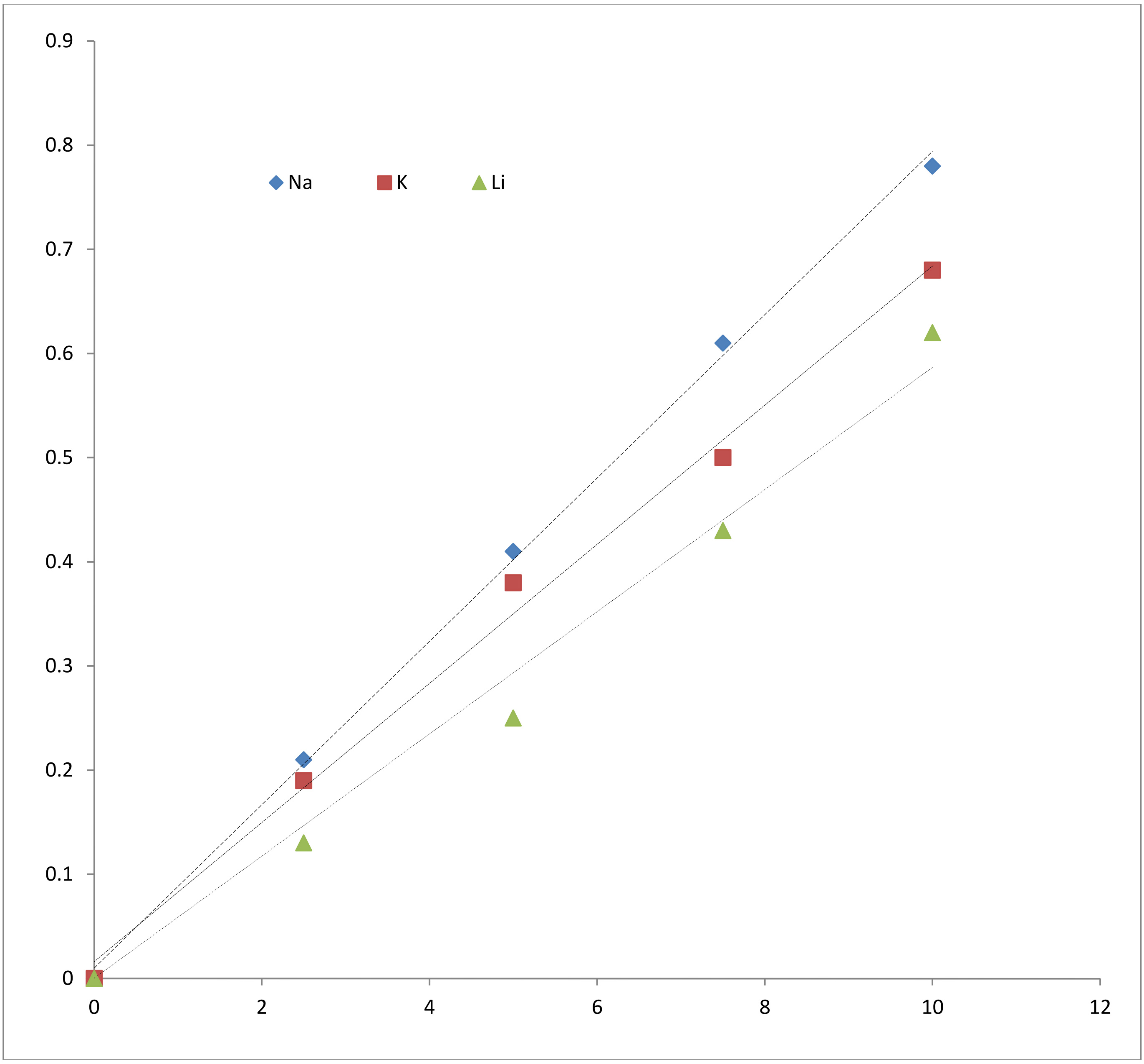

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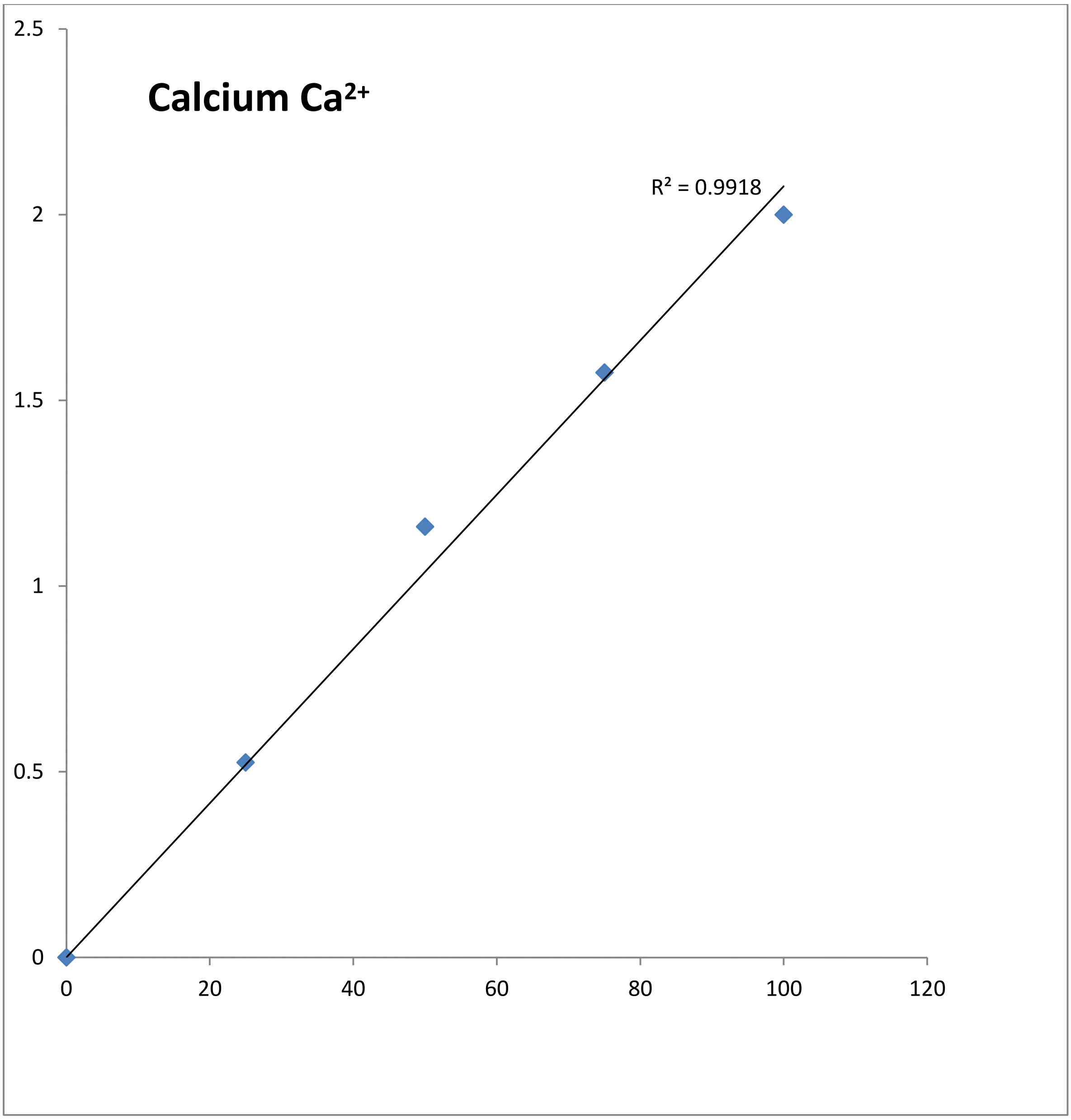
Figure 3: Calibration curves of Na, K and Li



PPM

Figure 4: Calibration curve of calcium

4- Results and Discussion

The water content of the meat samples of tuna was determined because some international publications expressed the metal content of tuna as mg/kg (dry wet). The results of % water content are shown in Table 2.

Table 2: Mass percentage (%) of Water content in tuna sample:

Sample	Water%
M1	65.2%
M2	63.7%
M4	61.0%
M5	62.0%
M6	58.5%
M7	58.9%
M8	55.1%
M9	60.5%
M10	63.5%
M11	59.4%
M12	65.0%
M13	66.3%

The average mass % of water was found to be 61.5% which is in good agreement with the worldwide values.

4-1: Contents of Na, K, Li and Ca

The elements of Na, K and Ca were detected in all the analyzed tuna samples. However, Lithium was below the detection limit of the machine in all the analyzed samples.

The order of decreasing mean concentrations (mg/kg) for these elements was:

K (3012)> **Na** (1188) > **Ca** (288) > **Li** (nd), this trend is clearly represented in Figure 5. Concentrations of these elements in all the analyzed canned tuna samples are presented in Table 3.

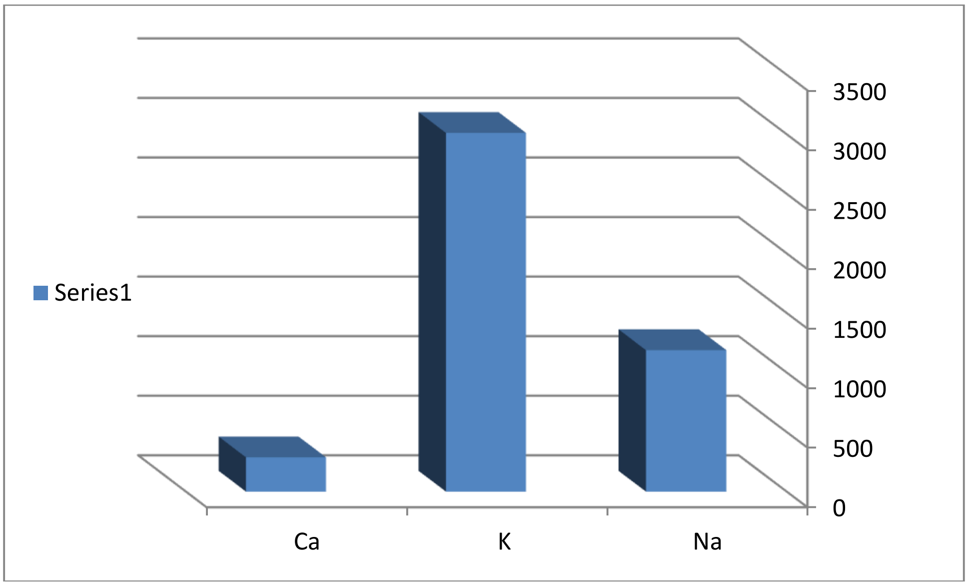


Figure 5: Comparison of the average K, Na and Ca contents (mg/kg) of tuna samples

Potassium content was found the highest among the analyzed elements, it was found in the range of 2718-3286 mg/kg with an average of 3012 mg/kg. Potassium concentration in tuna was reported slightly higher than our values, being 4070 mg/kg (25). Sodium was quantified within a range of 427-2353 mg/kg and an average of 1188 mg/kg which is in good agreement with that reported for canned tuna commercialized in Venezuela with average value of 2345 mg/kg, dry wet (equivalent to 797 mg/kg, wet wt.) and data ranged from 1710 to 3200 mg/kg, dry weight (equivalent to581-1088 mg/kg, wet wt) (26).

The mean content of calcium was found to be 288 mg/kg with a range of 205-337 mg/kg. In comparison to this result, calcium concentration was reported as 473 ± 189 mg/kg (wet weight) (27). In another study, calcium concentration was reported as 215 mg/kg (dry wet) in bluefin tuna (28).

Lithium occurs in food stuff at very low concentration, in a recent study(28) the highest mean levels of lithium in food was found in ‘‘tofu’’ (0.037 mg/ kg), followed by ‘‘fish and fish products’’ (0.035 mg/ kg), these values are far below the detection limit of flame photometer used in this project.

The daily consumption of 250 g or even 500 g of tuna samples will not expose the consumer to harmful level of these essential elements; however the sodium content must be of concern especially for people with high blood pressure.

Table 3: Element content of canned tuna in mg/kg

**********	**Concentration mg/kg**			
Sample code	**Na**	**K**	**Ca**	**Li**
M1	2260	2882	253	Nd
M2	1221	3030	280	Nd
M4	1120	3236	245	Nd
M5	2065	2781	325	Nd
M6	624	2986	318	Nd
M7	834	3011	329	Nd
M8	2353	3122	280	Nd
M9	756	2956	276	Nd
M10	690	2876	337	Nd
M11	654	3286	291	Nd
M12	427	2956	205	Nd
M13	1250	3018	312	Nd

Nd: not detected (below the detection limit) (less than 10 mg/kg)

Statistical analysis of the results show that the variation of sodium concentration was very high with RSD value of 56% followed by calcium 13.7% and the least variation was observed for potassium with RSD value of 4.8%. These results are illustrated and observed in Figure 6.

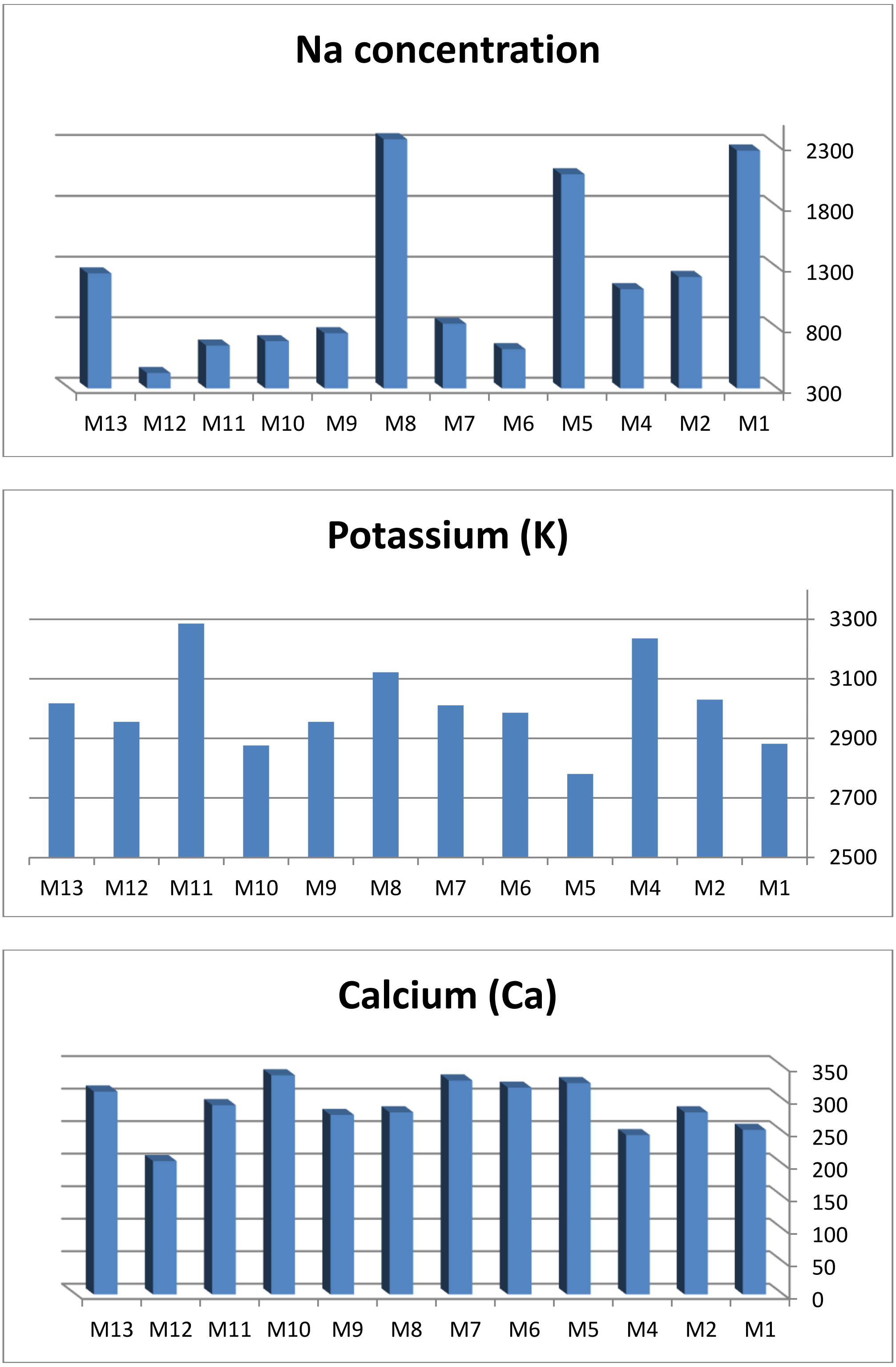


Figure 6: Variations in Na, K and Ca contents of tuna

4-2: Contents of Fe, Zn, Cr, Mn, Co and Cu

The concentrations of these elements in canned tuna are presented in Table 4. Among the elements, iron, zinc and copper were detected in all the analyzed samples. However, manganese, chromium and cobalt were detected in 84%, 46% and 31 % of the analyzed samples, respectively.

The order of decreasing mean concentrations (mg/kg) for these elements was:

Fe > Zn > Cu > Mn > Cr > Co. Illustration of this trend is clearly shown in Figure 6.

Concentration levels obtained in this work were in general comparable to those previously reported. In human, Iron acts as a catalyst and it is an essential part of hemoglobin. The recommended dietary allowances (RDA) of iron for adult males and females are 8 mg/day and 18 mg/day, respectively [29]. Iron deficiency causes anemia and excessive iron causes health problems. In this study, the average iron concentration in canned tuna was 9.6 mg/kg with data ranged from 2.6 to 30.8 mg/kg. Similarly, the mean iron level in tuna was reported as 8.45 mg/kg[30] and 9.13 mg/kg[31].

The recommended dietary allowances of zinc for adult males and females are 11 mg/day and 8 mg/day, respectively [32]. Zinc level in this study was 7.2 mg/kg with a range of 4.1 to 9.8 mg/kg, these results agree well with the published values of 10.15 mg/kg [33] and 10.38 mg/kg[34].

The recommended dietary allowance of copper for adults is lower than that of iron and zinc being 900 µg/day. In this work, copper levels obtained for canned tuna ranged from 0.2 to 0.67 mg/kg, with an average value of 0.39 mg/kg. Higher

Value of copper concentrations in canned tuna being 2.5 mg/kg had been reported [35].

Manganese is needed for bone development and involved in the formation of thyroxin in the thyroid gland. Manganese was detected in 84% of the analyzed canned tuna samples with an average concentration of 0.08 mg/kg (wet weight) and data ranged from < dl to 0.18 mg/ kg. Previous studies reported similar results for manganese concentrations in tuna.

Table 4: Trace elements concentrations, means and ranges (mg/kg) in canned tuna

Sample Code	Concentration mg/kg					
	Fe	Zn	Cu	Mn	Cr	Co
M1	5.03	4.15	0.21	0.13	0.08	0
M2	2.64	7.87	0.321	0.093	0	0
M4	7.43	5.82	0.67	0.088	0.06	0
M5	12.23	8.34	0.55	0.06	0	0
M6	9.75	6.51	0.37	0	0	0
M7	6.32	7.25	0.2	0.078	0.073	0.025
M8	4.88	6.38	0.22	0.1	0.1	0.043
M9	11.32	4.88	0.32	0	0	0
M10	5.67	9.62	0.27	0.092	0	0.035
M11	4.71	8.43	0.51	0.087	0.034	0
M12	30.78	7.25	0.46	0.14	0	0.04
M13	14.29	9.87	0.57	0.11	0.07	0
Average	**9.5875**	**7.1975**	**0.38925**	**0.0815**	**0.03475**	**).011917**
Maximum	**30.78**	**9.87**	**0.67**	**0.14**	**0.1**	**0.043**
Minimum	**2.64**	**4.15**	**0.2**	**0**	**0**	**0**

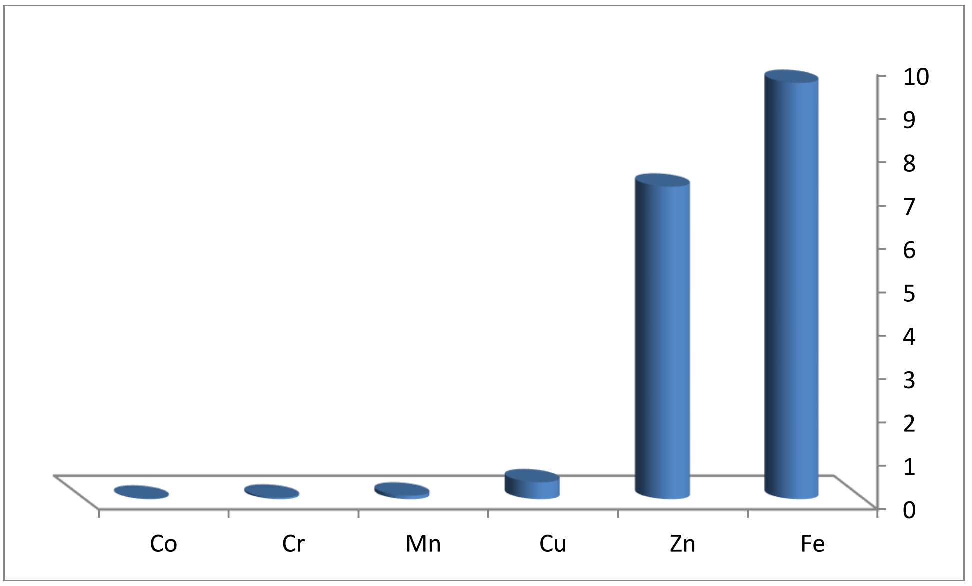


Figure 7: Trends of trace element mean concentrations in canned tuna

Chromium (III) is very important for human health, in this work total forms of chromium was found at levels of 0.035 mg/kg and a range of below detection limit to 0.1 mg/kg. Cobalt which is an integral part of vitamin B12 was quantified at an average of 0.011 mg/kg and a range of 0 to 0.043 mg/kg. The results of chromium and cobalt are comparable to the worldwide published data.

4-3: Selected elements and daily intake

By assuming the daily consumption of only one meal of canned tuna which weighs 100 g, the calculated amount of Zn, Fe, Cu, Mn and Cr provided to the consumer will be 0.72, 0.96, 0.038, 0.008 and 0.003 mg of these elements, respectively.
The comparison of the amount taken by consumption of 100 g canned tuna and the recommended daily intake are presented in figure 8.

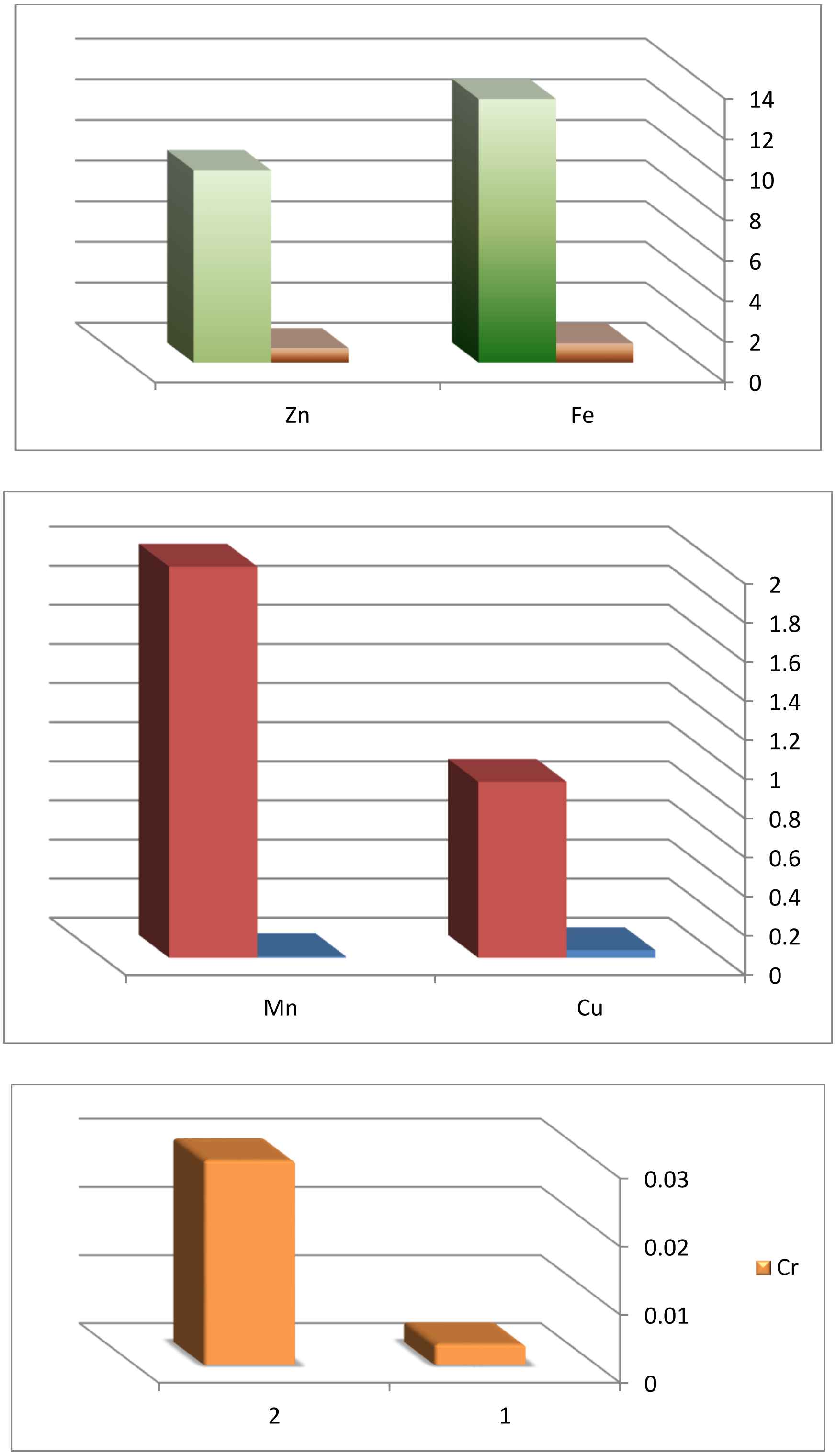


Figure 8: The daily intake of metals (mg) compared to the mean recommended values

The consumption of only 100 g of canned tuna will provide the consumer with,10%, 7.5%. 7.3%, 4.3% and 0.4% of the recommended daily intakes of Cr, Zn, Fe, Cu and Mn, respectively.

5- Conclusion

The levels of trace macroelements (Ca, K, Na, and Li) and microelements (Fe, Zn, Cu, Cr, Co and Mn) in canned tuna samples commercialized in Riyadh-Saudi Arabia were determined and assessed for their quality by comparing elemental concentrations in samples with recommended levels stipulated by WHO.

The levels of the studied elements were found to be close to the results of related previous studies. Based on the recommended dietary allowances and a tolerable upper intake level (UL) of the microelements, the levels of these microelements were unlikely to constitute any health problem to the consumers.

6- Recommendation

While it is recommended to monitor the levels of toxic elements such as Hg, Cd and Pb in various types of sea food, it is also important to evaluate the amounts of essential elements in such food.

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