

# Determining the Concentrations of Lithium and Calcium in Canned Tuna Fish Produced by the Factories at Khuzestan province, Iran

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#### Abstract

**Backgrounds and aims:** Nutrition is the main way to receive the elements that human body needs. Lithium (Li) and Calcium (Ca) are two elements, which have important roles in human body. There are a few studies about the amounts of calcium and lithium in canned tuna fish. The aim of this study was to determine the concentrations of calcium and lithium in canned tuna fishes.

**Materials and methods:** To this aim, 150 samples of canned tuna fishes from two well-known brands (Majid and Poolak), marketed in Khuzestan province of Iran, were obtained. Li contents of the samples were measured by Atomic Absorption Spectrometry (AAS) with atomization in graphite furnace. Ca contents of the samples were measured by AAS using nitrous oxide-acetylene flame.

**Result:** The mean concentrations of calcium in canned tuna fish of Majid and Poolak brands were 448.47 and 398.22mg/kg, respectively. Additionally, the mean concentrations of calcium in canned tuna fish of Majid and Poolak brands were 38.42 and 39.67mg/kg, respectively. The mean concentration of calcium in the investigated canned tuna samples fish was lower than Provisional Tolerable Intake (PTI) per day (1000ppm) set by World Health Organization (WHO) and Environmental Protection Agency (EPA). However, the mean concentration of lithium in the studied canned tuna fish samples was higher than PTI/day (0.650-3.1ppm) Set by EPA.

**Conclusion:** The results of current study showed that the marine food industries need a more precise and serious monitoring by public health organizations. Additionally, protecting the marine environment from pollutions is an obligation that needs the attention of related organizations and authorities.

Keywords: Lithium; Calcium; Canned tuna fish; Atomic Absorption spectrometry

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#### Introduction

Consuming healthy natural foods has a great importance for the entire society. In this regard, receiving sufficient amounts of trace elements and avoiding the excess amounts of these elements is an important factor, which should be carefully monitored. Seafood products are important sources of the trace elements [1]. Due to the release of toxic chemicals from point and non-point pollution sources into surface waters, rivers, lakes and finally into seas, marine animals are affected. As a result, nutritionists are concerned about potential health threats related to consumption of the marine animals as seafood. Therefore, it is necessary to monitor the pollution levels of the marine environment and seafood.

Nowadays, using Lithium (Li) is rapidly increasing due to its importance as a vital strategic resource for national economy and protection [2]. Li is an element which appears rather in small amounts both in the environment and in the human tissues or body fluids. Li plays key

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roles in many important vital functions. Li possesses a wide variety of biochemical functions. For example, it settles in the structure of several enzymes, hormones, vitamins, and growth factors [3,4]. Li is found in variable amounts in foods. Main food sources of Li are grains and vegetables; in some geographical areas, the drinking water also provides significant amounts of lithium. Thus, the human dietary lithium intakes depend on the geographical location and the type of foods consumed [5]. Many studies consider Li as an essential element; so that,  $1000\mu g/day$  of it has been suggested as provisional RDA for a 70kg adult person [5]. Receiving excess amounts of lithium via foods may induce lithium toxicity, which include several serious clinical manifestations (e.g., Cardiovascular manifestations and permanent neurological deficits) [6].

The Calcium (Ca) function and its role in the body is well known and expansively defined in literature. It is the most abundant mineral within the body, of which almost 99% happens in the bones and teeth as deposits of calcium phosphates. The remaining 1% in the soft tissue and body fluids has very important regulatory functions [7]. The calcium ion (Ca+2), released from intracellular stores, controls numerous cellular procedures, including cardiac and skeletal muscle contraction, synaptic transmission, and metabolism [8]. Older men and women are recommended to take at least 1000-1200mg/day of calcium for maintaining bone health and prevention of fractures. The average intake in the diet in Western countries is 700-900mg/day, and lower in Asia and Africa. Accordingly, old people need to take calcium supplements to meet these recommendations. The guidelines for calcium intake have been widely implemented in Western countries. So that, more than 30-50% of old women take calcium supplements. However, several clinical trials reported that calcium supplements at doses higher than 2000mg/day lead to adverse effects, including cardiovascular events, kidney stones, and hospital admissions for acute gastrointestinal symptoms. Thus, old people are encouraged to improve their bone health by increasing their calcium intake via food rather than taking supplements. This advice assumes that increasing dietary calcium intake to the recommended level of >1200mg/day prevents fractures without causing the adverse effects of calcium supplements [9].

Recent studies indicate the heavy metals pollution of seas and seafood in many regions of the world, including Iran [10-12]. The polluted sea food may lead to serious health problems in the people who consume them. Therefore, it is important to prevent and monitor the pollution in seafood products. According to the literature above, the present study aimed to evaluate the concentrations of two elements, calcium and lithium, in canned tuna fish as an important food source of local population at Khuzestan province of Iran.

#### **Materials and Methods**

#### Materials and preparing standard solutions

Chemicals were purchased from Chem Lab and Merck Companies. All the glassware and plastic ware were put in nitric acid (0.1 molar) for 24 hours, and then washed twice with deionized water. Stock standard solutions for Li and Ca were 1000mg/lit. Lanthanum (III) nitrate and ammonium nitrate solutions (1%w/v) were used as modifiers for Ca and Li respectively, to eliminate the effect of disturbing ions. The lithium standard solutions were prepared in five concentrations (40, 60, 80, 100, 120µg/lit) by diluting the stock standard solution in nitric acid (0.1 molar). The Calcium standard solutions were prepared in six concentrations (0.1, 0.2, 0.5, 1, 3, 5µg/lit) by diluting the stock standard solution in Lanthanum (III) nitrate (1%w/v).

## Preparation of samples and standard samples

**Table 1:** Li and Ca content in canned tuna fish, its mean values per 50g of canned tuna fish and their range.

Tuna Fish Sample	Statistical Indices	Li Con.(ppb)	Ca Con. (ppm)	
	Mean	38.42168	448.47464	
	Median	35.521	388.889	
	Variance	387.506	232600.761	
Maiid Buand	Std. Deviation	19.685176	482.287011	
Majid Brand	Minimum	12.169	63.333	
	Maximum	80.956	2630	
	Range	68.787	2566.667	
	Std. Error of Mean	3.937035	96.457402	
	Mean	39.67832	398.22312	
	Median	33.262	282.222	
	Variance	918.486	71997.895	
Perdel Pered	Std. Deviation	30.306527	268.324235	
Poolak Brand	Minimum	13.399	7.778	
	Maximum	134.907	961.111	
	Range	121.508	953.333	
	Std. Error of Mean	6.061305	53.664847	

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150 samples of canned tuna fish (Majid and Poolak brands) were collected from the local markets in Khuzestan Province, Iran. All of the collected canned tuna fish samples were mixed (each brand separately) and a representative mass (50g) was taken and placed in a porcelain crucible for further steps of examination. Samples were transferred into the electrical furnace with controlled temperature (450 °C) for 24h to turn them into their ash. Then the ash samples in the crucible were carefully preserved with 100mL of concentrated HNO $_3$ . By this procedure, the ash samples became readily soluble in water. Sample solutions were stored in washed and dried plastic bottles. The sample solutions were pulverized into spray in the nebulizer and atomized into the nitrous-acetylene flame of the spectrometer. The air oxygen was used as oxidant Table 1 & 2.

**Table 2:** Limits of Detection (LOD), Limit of Quantification (LOQ) for Li and Ca (mg/kg).

Element	LOD	LOQ
Ca	0.03	0.1
Li	0.04	0.012

#### **Instrumental analysis**

The content of Li in the samples was determined by Atomic Absorption Spectrometry (AAS) using Varian AA240FS spectrometer (Palo Alto, California, United States). Measurable analysis was performed in the graphite furnace, GTA 120 Graphite Tube Atomizer (Palo Alto, California, United States). Measurements were performed in the pyrolytically coated tubes under an atmosphere of the inert gas Argon (Ar) in the following conditions: The wavelength was 670.8nm. The temperature of pyrolysis and atomization were 800 °C and 2450 °C, respectively. The concentrations used for drawing the calibration curve were 40.0, 60.0, 80.0, 100.0, 120.0µg/L. the current within the Hollow-Cathode Lamp (HCL) was 5mA. The slit width was 0.5 nm. Single-element hollow analytic cathode lamps were used as the radiation source. The determination parameters of Lithium by AAS method is presented in Table 3.

**Table 3:** The parameters for the determination of Lithium by the AAS Method.

Step No.	Temp. (°C)	Time (sec) Gas Flow (L/min) Ga		Gas Type	Read
1	85	5	3	Normal	No
2	95	40	3	Normal	No
3	120	10	3	Normal	No
4	700	5	3	Normal	No
5	800	1	3	Normal	No
6	800	2	3	Normal	No
7	2300	8	3	Normal	Yes
8	2300	2	3	Normal	Yes
9	2450	2	3	Normal	No

The content of Ca in the sample was determined by Flame Atomic Absorption Spectrometry (FAAS). Operating parameters were set as recommended by the manufacturer manual. The spectrometer and the flame conditions were adjusted to yield optimum precision and sensitivity, to maximize absorbance signals and to minimize backgrounds set at 422.7nm wavelengths for Ca. the current within the Hollow-Cathode Lamp (HCL) was 10mA and the slit width was 0.5nm. To establish the precision of the explained and applied analytical procedure, an appropriate validation was performed. The Limits of Detection (LOD) were used to identify any cross corruption or memory effects from sample preparation (calculated from: 3.3 × SD/a, where: SD standard deviation for blanks; the slope of calibration curve). Thus, each test run included one reagent blank control. The LODs of Ca and Li, given that the Limit of Quantification (LOQ), correspond to Table 2. Unfortunately, there are no suitable certified reference materials for Li content in biological media. Its quantity is reported only in a few materials. The instrumental drift was verified in each 100 samples (plus one at the end) by the control of the sensitivity of one calibration standard.

#### Statistical analyses

Statistical analyses were performed using SPSS software version 20. Results were expressed in the form of mathematics mean (x)  $\pm$ SD. Analysis of variance )T test-One Sample) was used to compare results in groups of canned tuna fish (Mann-Whitney test, p < 0.05) and (Independent Sample T Test) for correlation analysis between variables.

#### Result

As shown in Table 1, the results of the study showed that mean ±SD concentrations of Li for Majid and Poolak brands were 38.4±19.6ppm and 39.7±30.3ppm, respectively. Additionally, the mean±SD concentrations of Ca for Majid and Poolak brands were 448.5±448.3ppm and 398.2±268.3ppm, respectively. Other statistical indices are shown in Table 1.

### Discussion

Current study showed that the amount of Li in canned tuna fish was less than 40ppb (<40 $\mu$ g/kg). this result showed that consuming the canned tuna fish as a meal does not increase the Li intake to a level higher than the recommended daily intake of lithium (14.3 $\mu$ g/kg body weight) for an adult person [13]. The Li content of the canned tuna fish was also comparable with the Li contents of other food groups [14]. This finding matches the common sense since marine foods are not usually among the food sources with the highest Li content. Indeed, cereals, vegetables, and dairy products contain the highest levels of Li. Fortunately, current study showed that the canned tuna fish is a safe food, regarding the Li content and it is not affected by probable metal pollutions of the Persian Gulf (Table 4).

The results of current study indicated that the amount of Ca in canned tuna fish was less than 450ppm (<450mg/kg). This amount was consistent with the previous studies, which reported comparable amounts of calcium in tuna fish [15,16]. The findings indicated that tuna fish is a rich dietary source of Ca, which can supply human daily needs, together with other food groups [17]. In this study, the levels of Li and Ca, in samples of canned tuna fish

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in local brands of Khuzestan province was reported. These results showed that there is no risk in canned tuna fish with respect to the concentrations of Li and Ca and their recommended daily intake [18]. These results may provide useful information for measuring of Li and Ca intake from this source. In recent years, fish and its products have become more attractive to human societies, because of their health benefits, compared to the other types of meat. Due **Table 4:** Recovery study of Li and Ca in canned tuna fish.

to the growing trend of consumption of marine products, especially fish and canned tuna fish, the quality control of these materials is essential for maintaining and improving the health of human communities. Therefore, monitoring these products is important with respect to positive and negative effects of Li and Ca on human health.

Li Concentration (ppb)	Mean of A*	SD	CV	Ca Concentration (ppm)	Mean of A*	SD	CV
40	0.8796	0.0067	1.1	0.1	0.0047	0.0001	2.4
60	1.1175	0.005	0.6	0.2	0.0076	0.0002	3.1
80	1.297	0.0064	0.7	0.5	0.0171	0.0001	0.8
100	1.4086	0.0123	1.2	1	0.0315	0.0002	0.6
120	1.5133	0.0052	0.5	3	0.0926	0.0004	0.5
0	0	0	0	5	0.1486	0.0004	0.2

# Conclusion

The canned tuna fish produced by Khuzestan factories were appropriate food sources for Li and Ca dietary intake, while avoiding the toxic effects of receiving excess amounts of the elements. It is also strongly recommended that inclusive and periodic monitoring of the trace and essential metals in the canned tuna fish must be done to ensure the safety and health of the consumers. Comparison of the results obtained in this study with the values reported in literature showed that the consumption of the canned tuna fish provides higher amount of Li and significant amount of calcium. It was, however, recommended that inclusive and periodic monitoring of the trace and essential metals in the canned tuna fish must continue to ensure the safety of the health of the consumers.

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#### **Compliance with Ethics Requirements**

This article does not contain any studies with human or animal subjects.

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