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Investigation by AAS and UV-VIS Spectroscopic methods to estimate some heavy metal concentration, Salinity, and pH in Tuna cans from El-Bayda Markets, Libya

Abdulsalam saleh[1]*, Randa Mahmoud[1], Saleh, M, Bufarwa[2]

[1]Department of Health Food Hygiene, Veterinary Medicine
[2]Chemistry Department, Science Faculty
Omar A-Mukhtar University, EL-Beida, Libya.
abdulsalam.abdullah@omu.edu.ly

Abstract:

A flame atomic absorption spectroscopy (AAS) and spectrophotometric (UV-VIS) determination of the formation of complexes with copper and chromium were used to identify heavy metals in four types of tuna cans (Dwarf, Al-Wafa, Skipjack and Marina) sold in the markets of the city of El-Bayda, Libya. The study concluded that, compared to the Libyan standard specifications for both local and imported tuna cans, the components specified for analysis (Cu, Pd, Cd) are present in tuna meat in fairly excellent quantities in the following ratios: (0.2340, 0.0589, 0.2378 parts per million) respectively. The salinity of the brine is given as a percentage (0.82%, 1.16%, 0.67%, 0.60%), respectively. The tuna pH levels are (6.02, 5.81, 5.62, 5.80), respectively. Therefore, we can draw the conclusion that all of the tuna cans tested in this study complies with Libyan standard specifications. This is because Libyan centers that specialize in product examination are closely monitoring the products to make sure they are free of heavy elements or within permissible limits so that they don't contain any pathogens or trace elements when they reach consumers.

Keywords: Tuna, cadmium**,** copper**,** lead, spectrophotometric determination, EL-Beida, Libya

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التحقيق باستخدام الطرق الطيفية AAS و UV–VIS لتقدير بعض تركيزات المعادن الثقيلة والملوحة ودرجة الحموضة في علب التونة من أسواق البيضاء، ليبيا

عبد السلام صالح[1]*، رنده محمود[1]، صالح بوفروة[2]

[1]قسم الصحة ونظافة الأغذية والطب البيطري، جامعة عمر المختار، البيضاء، ليبيا.

[2]قسم الكيمياء، كلية العلوم، جامعة عمر المختار، البيضاء، ليبيا.

abdulsalam.abdullah@omu.edu.ly

الملخص

تم استخدام التحليل الطيفي للامتصاص الذري اللهب (AAS) والقياس الطيفي الضوئي (UV–VIS) لتكوين المعقدات مع النحاس والكروم لتحديد المعادن الثقيلة في أربعة أنواع من علب التونة (دورف، الوفاء، السكيبجاك والمارينا) المباعة في الأسواق العالمية. أسواق مدينة البيضاء ليبيا. وخلصت الدراسة إلى أنه بالمقارنة مع المواصفات القياسية الليبية لكل من علب التونة المحلية والمستوردة، فإن المكونات المحددة للتحليل (Cu, Pd, Cd) تتواجد في لحم التونة بكميات ممتازة إلى حد ما بالنسب التالية: (0.2340، 0.0589، 0.2378 جزء في المليون) على التوالي. يتم إعطاء ملوحة المحلول الملحي كنسبة مئوية (0.82%، 1.16%، 0.67%، 0.60%)، على التوالي. أما مستويات الرقم الهيدروجيني للتونة فهي (6.02، 5.81، 5.62، 5.80) على التوالي. ولذلك يمكننا أن نستنتج أن جميع علب التونة التي تم اختبارها في هذه الدراسة مطابقة للمواصفات القياسية الليبية. وذلك لأن المراكز الليبية المتخصصة في فحص المنتجات تقوم بمراقبة المنتجات عن كثب للتأكد من خلوها من العناصر الثقيلة أو ضمن الحدود المسموح بها بحيث لا تحتوي على أي مسببات الأمراض أو العناصر النزرة عند وصولها إلى المستهلكين.

الكلمات المفتاحية: التونة، الكادميوم، النحاس، الرصاص، التحديد الطيفي، البيضاء، ليبيا.

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1. \Introduction

It is one of the main sources that countries rely on to provide protein, such as fish meat, whether marine or river. This importance comes from the presence of fish in large quantities, at prices that suit everyone, and available throughout the year.[1] It has more than 19 thousand different types in the form and taste of food and its high efficiency in converting nutrients that reach their bodies with the highest level of energy and a distinct vital value in that its meat contains important nutritional components that are indispensable for building a healthy and sound body, as it contains general rates It reaches 75 grams of water, 19 grams of protein and 8 grams of fat to 100 grams of meat, in addition to 50, 250, 1.1, 0.01, 1.4, 0.20, 0.30 mg/100 grams of calcium and phosphorus , iron, and vitamins (B1, B2, and B3), respectively, and because in recent years, as a result of environmental pollution from various sources, most products have become infected. [2] To protect consumers and ensure compliance with food safety laws, it is necessary to monitor the quantities of metals found in fish meat, especially imported ones, and many unhealthy industries need to be monitored periodically. [3] Especially about toxic metals that can bioaccumulate in different parts of their bodies, the most important of which is the muscles, which are the main part of canned tuna. These elements that reach fish include lead, cadmium, copper, and zinc. [3] The majority of these minerals can have adverse effects on health, including kidney failure, osteoporosis, and cardiovascular, blood, reproductive, and immune system problems, even at very low concentrations. [4] One of the most prevalent contaminants in our food supply is heavy metals, which may pose the greatest threat to our ecosystem[5]. Both naturally occurring processes and human activity releases heavy metals into the environment, which then build up in the tissues and organs of living things and interfere with normal bodily functions. [6] The majority of people get their exposure to metals through their diets, so it's critical to evaluate the risks these elements pose to humans when consumed in food. [7] Accumulation of metals in edible fish may be harmful to

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human health, especially for populations that consume a lot of fish. Therefore, there are many studies in order to ensure that heavy metals remain within permissible limits. [8]

2. Materials and Methods

2.1. Method Determination of Cadmium Using Dithizone.

The sample is digested with 1ml H_2SO_4 and 3ml HNO_3 (1:3). All reactive metals are removed from the solution (after adjusting to pH ca 9) with dithione-$CHCl_3$. Cu, mercury and most of any Ni or Co present are removed by stripping $CHCI_3$ from the solution with dil. Hydrochloric acid. Aq. Layer modified to 5% NaOH, expanded with dithizone-CCI_4. In this alkaline state, zinc, lead, and dithione are not transformed, while cadmium dithizonate is relatively stable. Stripping with del. The hydrochloric acid was refined and the cadmium dithizonate was developed in 5% NaOH. The Cd is finally optically identified as a ditheron. Zn constitutes a major intervention.[8, 9]

2.2. Standard Curve of Cadmium

Prep in duplicate for six standard deviations in 0, 5, 10, 15, 20, and 25 µg Cd as follows: To Squibb-type separators (125 mL size is convenient), add the appropriate volume of standard solution; adjust to 40 mL with 0.2N HCI; add 10 mL NaOH solution (soln is then 5% concerning NaOH); and add 25 mL dithizone solution; shake vigorously for precisely one minute; let stand for precisely three minutes; and filter the organic layer through a pledge of absorbent cotton, discarding the first 5 mL. Fill the absorption cell (a length of one centimeter works well) and det. An at 510 nm. Plot the standard curve or compute the reference using the least squares approach.[8, 10]

2.3. Determination of Cupper By UV-ViS

It is ensured that there is no silica or sulfate in the oil. If it is present, it is transferred to separator number 125 with the addition of 10 parts of H_2O, with the addition of 2 g of citrate reagent and 1 ml of thymol blue, and to adjust to hydrogen number 8 by adding an ammonia solution. Slowly and intermittently until the color of the solution changes from yellowish green to bluish green. Dilute the

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solution by adding 125 ml of water and 5 ml of diathazone reagent until the $CHCl_3$ layer becomes green, and add about 40 ml of standard HCl 2N to the diathazone mixture. Finally, the solution is thawed spectrophotometrically.[8]

2.4. Preparation of sample

The sample was digested using H_2SO_4 and HNO_3. Using EDTA as a chelating agent, copper is separated and recovered chromatographically at pH 8.5 as diethyl Di thiocarbamate. Bi and the cover-colored carbamates at pH 8, but they decompose to colorless compounds in sodium hydroxide. Weigh the sample 20 g based on the anticipated Cu concentration. To get this diln, add H_2O if the sample contains less than 75% H_2O. Add the first volume of HNO_3 to equal about twice the weight of the dry sample and 5 mL H_2SO_4 or around 5 mL of H_2SO_4 as g of dry material. The sample was digested and then filtered through acid-washed paper, rinsed the paper with H_2O, and filtered. To 100 ml., to equip. Similarly blank reagent.[8, 10]

2.5. Determination of Cupper by UV-ViS

25 ml dissolved sample was pipetted into a 100 or 250 ml short-stem separator and 10 ml citrate-EDTA reagent added.Two drops of thymol blue indicator, (e), and 6N NH_4OH were added dropwise until the solution turned green or blue-green.It was cooled, and 1 ml of carbamate solution and 15 ml of CCI_4 were added to it.Shake vigorously for 2 minutes. September classes were let. And drain CCI_4 By pledging cotton into a tube or g-s vial. Det A or T in a suitable instrument at approximately 400 nm.[8, 10]

2.6. Standard Curve of Copper

0, 1, 2.5, 5, 10, 15, 20, and 25 ml of CuStd Solen (2 µg/ml) were transferred to the separators and 2.0N H_2SO_4 added. To make the total folder, 25 ml.10 ml of citrate-EDTA reagent was added and 2 drops of thymol blue indicator were added, A was plotted against µg Cu on plain graph paper. Since there is usually some deviation from linearity, read sample values from a smooth curve.[8, 10].

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2.7. Preparing samples for analysis by AAS

This experiment was completed at the Central Laboratory of Omar Al-Mukhtar University in 2020. Table 1 shows the four distinct sample types collected as well as the different tuna selling locations. After removing the preservative from the meat, we mixed the tuna meat well and placed it on a paper towel.

2.8. Preparing samples for analysis by AAS

The pieces of tuna meat were placed in a filter paper, rubbed, and the filter paper was replaced repeatedly until the sample was completely dry. About 5 grams of the sample (dry weight)were weighed and then placed in the digestion tube.[11] About 5 ml of Conc. nitric acid was added, followed by 5 ml of Conc. sulfuric acid to the sample.[12] The sample was left for a few minutes to allow it to react and mix. The sample was placed in a hot mass digester and heated slowly at 60°C for 30 min. The digestion tubes were removed from the device and left to cool, and then 10 ml Conc. nitric acid was added. The tubes were returned to the hot block apparatus and heated slowly to 120 °C, and then the temperature was increased to 150°C. Remove the tubes from the apparatus when the tubes were black and left them to cool. 1 ml of H_2O_2 was added, and we returned the sample to the hot mass device again, and the process of adding H_2O_2 to the sample was repeated until the color of the tubes became clear. The sample was removed from the hot block apparatus, and approximately 50 ml of deionized water was added. [11, 13]

2.9. The preservative content

The preservative medium was extracted in five milliliters using the same procedures. The results for the heavy elements in ppm uni were then computed using atomic absorption spectrometry. Using a pH meter (Mettler Toledo, SevenGo SG2-FK2, Switzerland), the pH of tuna meat was measured. The ground meat from tuna had a pH of precisely

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quantified. Two methods were used to determine the salt concentration of tuna meat: the auto-titrator and the manual titration method. For the auto-titration method (Potentiometric Method) (Mettler Toledo, G20,Switzerland), the salt content was measured in duplicate; for the manual titration method (AOAC official method 937.09), it was determined in triplicate. [8]

3. Results Discussion

Determination of (Pb, Cd, Cu) in the four samples are in Table (1) and figure (1) shows the contents of the studied metals in the selected samples. The results are clarified in Tables (2,3) and can be discussed as follows:

Table 1. Showing the Types of Tuna Included in the Study

Type	Canning	Made in	Preservative
DWARF	Metal cans	Vietnam	Vegetable Oil+ Salt Solution
ALWAFA	Metal cans	Libya	Salt Solution+Soybean Oil
SKIPJACK	Metal cans	Thailand	Salt Solution+Sunflower Oil
MARINA	Metal cans	Thailand	Salt Solution+Sunflower Oil

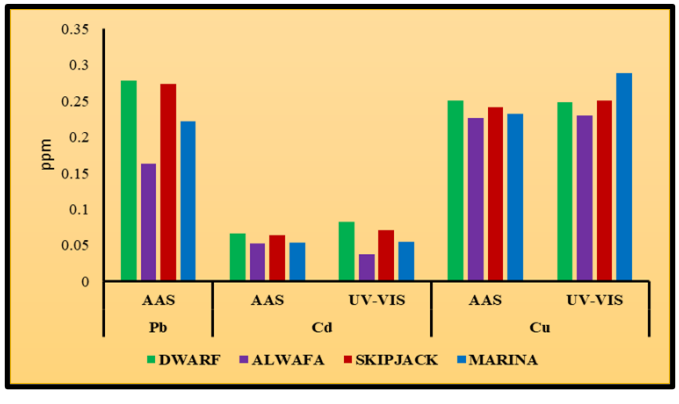

Figure 1.The contents of the studied metals in the selected samples.

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As listed in Table 2, the values, with a standard deviation of 0.0102and a correction factor R^2=0.92, were rather comparable when the findings from the atomic absorption method and the electronic absorption method were compared. Due to the interference of some metals at the wavelengths of copper and cadmium, concentrations in the electronic absorption have increased.[14]

Table 2. The concentrations of Cu, Pb, Cd metals in Tuna samples.

Type	Pb	Cd	Cu
		AAS	AAS
		UV-VIS	UV-VIS
DWARF	0.2779	0.0659	0.2501
		0.08221	0.2487
ALWAFA	0.1629	0.0521	0.2268
		0.0374	0.2296
SKIPJACK	0.2733	0.0646	0.2419
		0.0705	0.2509
MARINA	0.2220	0.0533	0.2325
		0.0546	0.2883

- **Salt Percentage, and pH in the preservative**

Typically, tuna fish has a salt content of 0.1% to 0.2%.When tuna is stored in brine, it will absorb salt at a higher rate over time.[15]Salt may seep into the tuna meat during two or more phases of on-board handling and freezing processes. Higher salt concentrations are found in the brine than in the fish, and osmosis forces the salt through the fish's skin and into its flesh. 3.5% of the weight of seawater is salt. [16, 17] Table (3) it shows the salt of percentage and pH in the tuna samples that were analyzed for its preservative medium.

The pH of the tuna in Table 3 generally rose with the length of storage. This is because bacteria break down proteins when fish is being stored. The fish's pH rises as a result of this process of production of alkaline substances such as ammonia, trimethylamine,

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and other volatile basic chemicals. [18, 19] Moreover, the build-up of these basic volatile chemicals raises the pH level by making the fish meat more alkaline. Thus, we conclude that the pH range in Al-Wafa and MARINA tuna (5.81 and 6.02), respectively, is high for Al-Wafa tuna, but remains within the permissible limits in the standard specification Libyan. [20]

Table 3. The salt of percentage and pH in tuna samples

Type	pH	Salt Percentage
DWARF	5.80	%0.82
ALWAFA	5.81	%1.16
SKIPJACK	5.62	%0. 67
MARINA	6.02	%0.60

4. CONCLUSION

Through this study, the results proved that there is no danger in consuming these products, so this study recommends the need to determination and know the proportions of the rest of the heavy elements such as Mercury, additives, other sources of food and additives, such as olive and medium water sources. The additives used in prolonging the roasting period and analyzing the histamine percentage and also the specifications of the metal can used for boiling and comparing them with the international specifications for boiling and their suitability in addition to the study of research in monitoring the environmental pollution of fish and supporting the development of this research Industry as an important food source, taking into account the control over imported products.

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