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قياس تراكيز Zn,Fe,Cd,Pb في بعض عينات معجون الطماطم المعلبة باستخدام مطياف الامتصاص الذري (AAS).

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Estimating the Pd, Cd, Fe, and Zn concentrations in a few canned tomato paste samples using an atomic absorption spectrophotometer (AAS).

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الملخص:
يحدث التلوث بالمعادن الثقيلة من الهواء، ويكون مصدره غالبًا من المصانع. ويحدث التلوث أيضاً من التربة والمياه وينتقل إلى المحاصيل الزراعية مسبباً أمراضاً خطيرة لدى الإنسان. يسعى الإنسان دائمًا للحصول على غذاء جيد وخالي من التلوث. يعتبر الطماطم من الأغذية المعلبة التي تستهلك على نطاق واسع ويمكن أن تكون ملوثة، كان الهدف من هذه الدراسة هو قياس مستويات بعض المعادن الثقيلة في عشر عينات بمعدل مكررين لكل عينة من معجون الطماطم المعلبة المستوردة في الأسواق الليبية، حيث تم قياس مستويات الرصاص والكادميوم والزنك والحديد باستخدام مقياس الامتصاص الذري الطيفي .أظهرت النتائج أن تركيز الرصاص في العينات تراوح بين 0.00±0.137 ملجم/كجم إلى 0.00±1.11 ملجم/كجم، وتركيز الكادميوم كان بين 0.00±0.043 ملجم/كجم الى 0.00 ±0.107 ملجم/كجم، بينما تتراوح قيم الحديد من 0.00±0.90 ملجم/كجم الى 3.40±30.3 ملجم/كجم، كما أظهرت النتائج خلو جميع العينات من الزنك باستثناء عينة واحدة. وبشكل عام فإن جميع عينات معجون الطماطم تقع ضمن الحدود المسموح بها لمنظمة الأغذية والزراعة/منظمة الصحة العالمية، باستثناء مستويات الكادميوم التي كانت أعلى من الحدود المسموح بها.

الكلمات المفتاحية: :معجون الطماطم، العناصر الثقيلة ، مطياف الامتصاص الذري، تراكيز ، منظمة الصحة العالمية.

Abstract:
The majority of the heavy metal pollution in the air comes from industry .Apart from originating from the soil and water, pollution also affects agricultural crops and can cause serious health issues in humans .People always want to consume meals that are good for the environment and their health .This study set out to quantify the amounts of different heavy metals in 10 samples (Two replicates for

each sample) of imported canned tomato paste that were sold in Libyan markets. This was necessary since tomatoes are a frequently eaten canned product that might get contaminated. The samples were measured with an Atomic Absorption Spectrophotometer (AAS), and the findings indicated that the lead concentrations in the samples ranged from 0.137±0.00 mg/kg to 1.11±0.00 mg/kg, the cadmium concentrations were between 0.043±0.00 mg/kg and 0.107±0.00 mg/kg, and the iron values are between 3.03±3.40 mg/kg and 0.90±0.00 mg/kg. Additionally, the outcomes showed that every sample—aside from one—was zinc-free. All tomato paste samples usually had levels of cadmium below acceptable norms, while the remaining samples were all below FAO/WHO approved limits.

Keywords: Tomato paste, heavy metals , Atomic Absorption Spectrophotometry, concentration , WHO**.**

Introduction

Given the current rise in interest in food product quality monitoring, determining the amounts of heavy metals is crucial[5]. Food scientists and chemists are becoming increasingly concerned about the rising use of tomato paste, particularly in restaurant meals, as both [12&10] have shown that tomato paste contains significant amounts of some substances. Heavy metal contamination of food is regarded as extremely harmful due to the metals' propensity to remain, accumulate, and rise in concentration in tissues and organs, which can result in the formation of illnesses linked to the metals [3]**.** When a person eats food contaminated with heavy metals, he suffers from diseases, and this depends on the percentage and concentration of these metals in the food. Examples of these diseases include pulmonary fibrosis and bleeding in the digestive system. Some elements, such as copper, zinc, and iron, are essential for growth, but eating them excessively leads to kidney disease and other diseases [4]**.** Heavy metals are pollutants in the environment. They accumulate and enter the food chain[16&20]. The main source of heavy metal pollution is human industrial, agricultural and mining activity[7]. Recently, concern has increased due to the increase in cadmium concentration in the air due to increased human activities[7]**.** One of the harmful substances that builds up in the human body and is thought to be responsible for liver, kidney, and blood disorders is cadmium. Additionally very poisonous, lead is a major cause of illness [15]. Because they can result in poisoning, lead and cadmium are therefore hazardous metals, even at low amounts [11]. The human body stores cadmium primarily in the kidneys, where it can build up to a dangerous level and eventually result in renal failure[12]. Heavy elements are important in our lives, but some trace elements, such as cadmium, mercury, and lead, are toxic heavy metals that interfere with metabolic processes and cause serious diseases in humans. However, there are elements such as iron, copper, and zinc that have nutritional and essential importance. It has been proven that lead accumulates in the bones, is released into the blood, and then is excreted in breast milk[1&2]. lation of women with a relatively high lifetime exposure to lead, levels of lead in breast milk were low, influenced by both current lead exposure and redistribution of bone lead accumulated from past environmental exposures [6]**.** Excessive intake of zinc prevents the absorption of copper and iron in the body [19]**,** and free zinc ion is toxic to vertebrates and fish [8]**.**

Review of the Literature

shown that the concentration of chromium is considerably high, the concentrations of copper and iron are somewhat high, and the concentration of manganese is low in a research done to assess the levels of trace element concentration in various brands of canned tomato pastes[[21]. By using OCP-MS, the levels of As, Cd, Pb, Cr, Ni, Sn, and Sb in tomato sauces stored in cellulose, glass, plastic, and metallic containers. The packaging's composition was ascertained using XRF. GF AAS has also been used in this experiment to assess the concentration of Cr and Sn in stimulant solutions intended to come into contact with the four distinct styles of packaging. The results showed that the metal concentrations of items stored in different packaging styles did not significantly vary ($p>0.05$), except for tin and Nickel. While nickel concentrations in canned products varied from 0.05 to 0.1 mg/kg, tin values were higher (0.19 ppm). Cr mg/kg was the only metal with a mean value of 0.3 mg/kg that was higher than the permissible limit of 0.1 mg/kg. Only cans contained tin, while cellulose, plastic, and metallic wrapping all had chromium, according to the XRF. Tin from cans was the sole migrant identified, while chromium migration was not detected in the simulant solution [22]. Orhan and colleagues' investigation to determine the amounts of cadmium, tin, iron, copper, and zinc in liver, rice, tea, and sample livers, as well as standard reference materials Bovine Liver, Rice, and Rice Flour Tea leaves were analyzed by flame and electrothermal atomic absorption spectrometry. The results showed that the limits of detection for Sn, Cd, Fe, Cu, and Zn were 0.66, 0.26, 2.0, 1.9, and 1.2 µg/L, appropriately. The World Health Organization's (WHO) maximum values and those from previous research were compared to the element concentrations detected in the samples[26]. In Nigeria, a study was carried out to determine the concentrations of heavy metals in tomato paste and fresh tomatoes using Atomic

Absorption Spectrophotometry. Not all fresh and agricultural soil samples had cadmium, according to measurements of iron, lead, chromium, copper, nickel, zinc, and calcium. According to these findings, the metal levels in the tomatoes that were analyzed were below the dietary intake that is advised for certain metals in tomatoes [23]. Iron (Fe), zinc (Zn), manganese (Mn), cadmium (Cd), and lead (Pb) levels were measured in 61 tomato paste samples from Ghanaian commercial markets using flame atomic absorption spectrophotometry; mercury (Hg) levels were assessed using a direct mercury analyzer. According to the findings, several brands' measured metal levels were below the FAO/WHO acceptable limits [14]. A study to determine some elements in three types of tomatoes. The results showed that the concentrations were high in all types of tomatoes studied [17]. There is a study aimed at measuring the concentration of heavy metals (cadmium, chromium, copper, iron and brass) in some food products, where the results were a high concentration of iron and cadmium [24]. Concentrations of some elements, such as sodium, magnesium, calcium, and others, were determined in samples of tomato paste in Brazil using X-ray spectra. The results showed variation between different brands and different packages [25]. Tomato paste is commonly utilized in everyday meals and is regarded as a necessary culinary component in Libya as well as many other Arab and international nations. Thus, people of these areas are truly at risk from heavy metal contamination of tomato paste. The purpose of this study was to determine the levels of lead, zinc, cadmium, iron, and copper in a few brands that are commonly purchased in Libya.

Materials and methods

Sample

Collection

An atomic absorption spectrophotometer (AAS) was used to evaluate lead, cadmium, iron, and zinc levels in ten samples of imported tomato paste that were gathered from the Libyan market. The investigation was conducted in 2023, and each sample underwent two repeats of analysis. The table (1) displays samples of tomato paste along with the country of origin.

Table (1) Samples as country of origin

Sample No.	Country of Origin
STB 01	Tunisia
STB 02	Tunisia
STB 03	European union
STB 04	Tunisia

STB 05	Italia
STB 06	Italia
STB 07	Italia
STB 08	Algeria
STB 09	Egypt
STB 10	Egypt

Analysis by Atomic Absorption Spectrophotometer

The concentration of lead, cadmium, copper and iron in Tomato Paste was measured by using Atomic Absorption Spectrophotometer (model Varian 220 G is for graphite-furnace atomic absorption analysis of solutions. The graphite furnace is equipped with an auto sampling system, 4 lamp positions, and an automatic lamp selection system, produced by USA ,Figure(1) . Two grams of the substance were placed in a 200 milliliter beaker, and ten milliliters of pure HNO3 were added. After covering the beaker with a watch glass, the sample was left to digest in the acid for the whole night. The dissolved material was heated on a hot plate until all of the intense reactions ceased and a clear solution was formed. The digest was allowed to cool before being transferred into a 50 mL volumetric flask and suitably diluted with distilled water [14].

Figure (1) Atomic Absorption Spectrometry (AAS)

Result and Discussion

The Table(2) displays the findings from the heavy metal analysis . There have been reports of Pb in tomato paste in various samples. In Figure 2, the values range from 0.137±0.00 mg/kg to 1.11±0.00 mg/kg. Sample No. 3 had the highest value of Pb at 1.110±0.00 mg/kg, while Sample No. 10 had the lowest value at 0.137±0.00

mg/kg. The stated values differ somewhat from those stated by Kelech.E et al. [22]. Every result was within the 1.5 mg/kg allowable limits.

Table (2): Mean concentrations of heavy metals in tomato samples

Samples No.	Pd(mg/kg) mean ±SD	Cd(mg/kg) mean ±SD	Fe(mg/kg) mean±SD	Zn(mg/kg) mean±SD
STB 01	0.520±0.00	0.253±0.00	8.82±0.00	0.0±0.00
STB 02	0.623±0.00	0.073±0.000	30.3±3.40	0.46±0.00
STB 03	1.110±0.00	0.107±0.000	12.9±0.05	0.00±0.00
STB 04	0.413±0.002	0.043±0.000	19.6±0.06	0.00±0.00
STB 05	0.383±0.001	0.093±0.000	5.0±0.00	0.00±0.00
STB 06	0.54±0.00	0.057±0.000	28.7±0.90	0.00±0.00
STB 07	1.013±0.00	0.053±0.000	1.0±0.00	0.00±0.00
STB 08	0.950±0.004	0.270±0.002	0.9±0.00	0.00±0.00
STB 09	0.323±0.002	0.057±0.000	22.3±0.8	0.00±0.00
STB 10	0.137±0.00	0.043±0.000	25.6±0.09	0.00±0.00
WHO/FAO [11&22]	1.5	0.03	30	19

Values are Means ± Standard Deviation, or mean ±SD. The same column's values with the same superscripts do not differ substantially ($p < 0.05$). Maximum Permissible Limit (FAO/WHO).

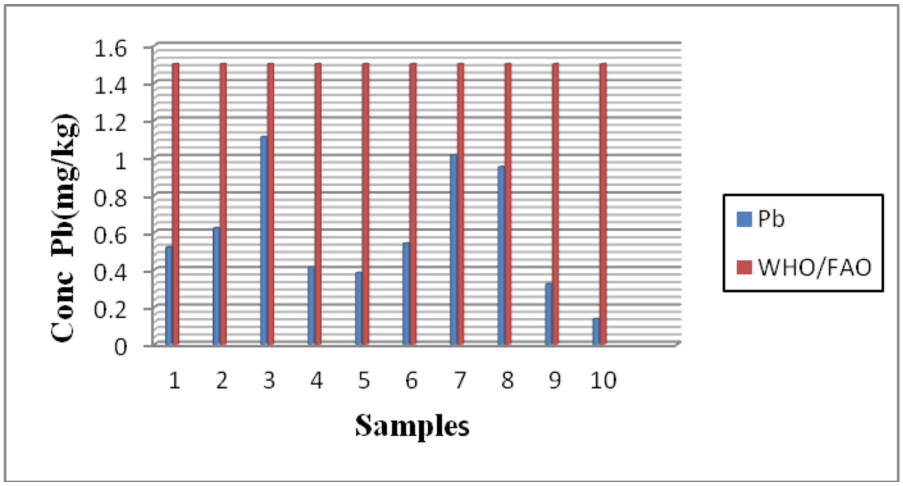

Fig (2): Lead concentration in studied samples

The findings for the tomato paste containing cadmium value are summarized in Figure 3. The values range from 0.043±0.00 mg/kg to 0.107±0.00 mg/kg. Sample No. 3 has the highest value for cadmium (0.107±0.00 mg/kg), while samples Nos. 4

and 10 have the lowest value (0.043±0.00 mg/kg). The stated values are consistent with the findings of Emrah.U et al [18]. Every figure is greater than the 0.03 mg/kg allowable limit.

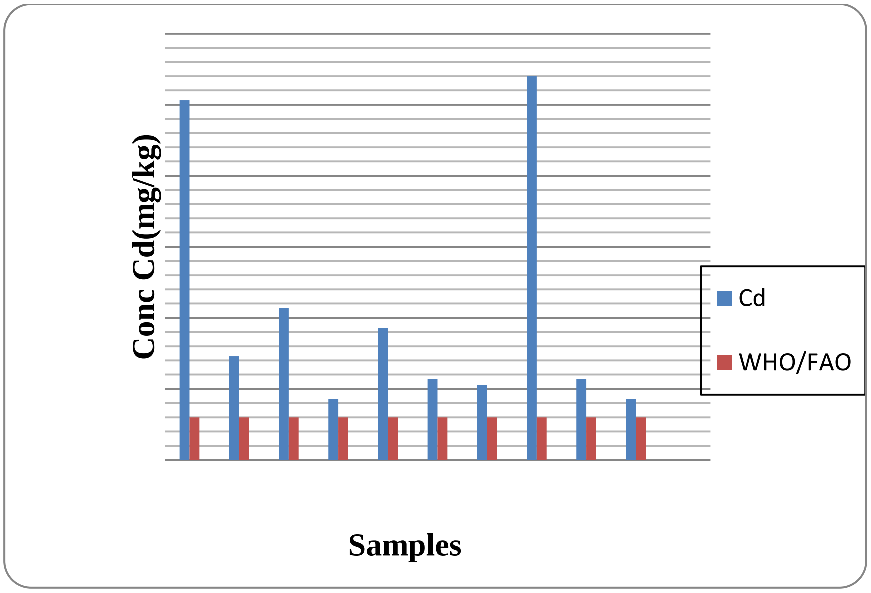

Fig (3): Cadmium concentration in studied samples

The findings regarding the Fe content of tomato paste are displayed in Figure (4). The values range from 0.90±0.00 mg/kg to 30.3±3.40 mg/kg; sample no. 2 has the greatest value for Fe (30.3±3.40 mg/kg), while samples no. 7 and 8 have the lowest value (0.90±0.00 mg/kg). Fe values are within allowable limits of 30 mg/kg but somewhat lower than those obtained before to David [9].

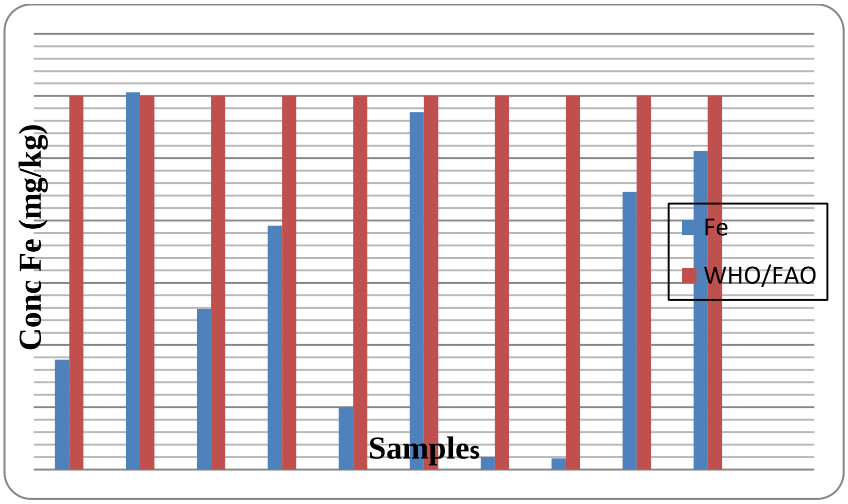

Fig (4): Iron concentration in studied samples

All samples lacked zinc, according to the analytical results, with the exception of sample no. 2, which had a zinc value of 0.46±0.00 mg/kg (Figure 5).Tomato paste reported values are lower than those stated in Kelech.E et al. [23].In general, every sample is under the 19 mg/kg international standard and Libyan allowed limits.

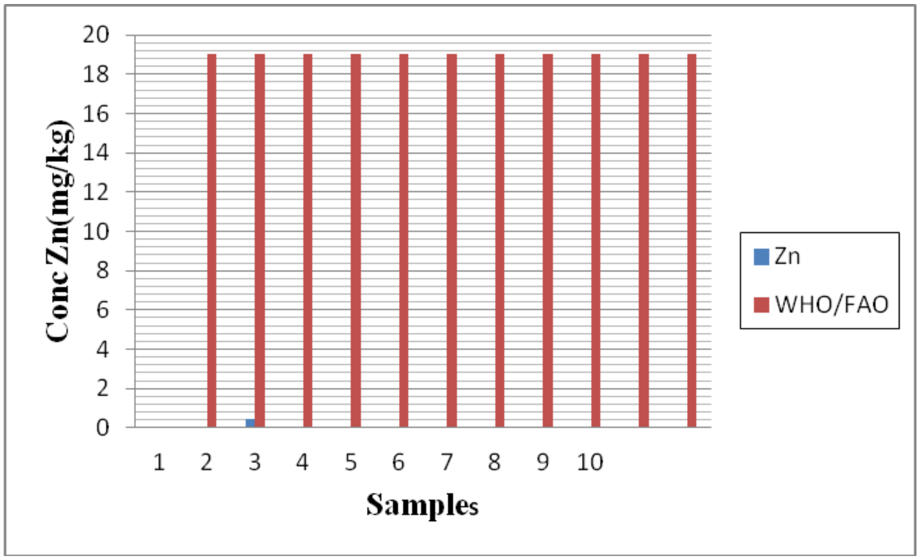

Fig (5):Zinc concentration in studied samples Conclusion

The results indicate that the Pb, Fe, and Zn values are all within the WHO/FAO permissible range. However, the cadmium values are higher than the permissible limits for all samples. This is likely because the company uses metal containers, which are filled from the inside with a Cd-containing substance to prevent rusting. Ov2er time, the metal packaging becomes susceptible to contamination from tomato paste.

Conclusion

The findings show that the levels for Pb, Fe, and Zn are all within the WHO/FAO acceptable range. All samples had cadmium levels that above allowable limits, nevertheless. This is probably because the firm employs metal containers that are filled with a Cd-containing material from the inside to keep them from rusting. The metal container might get contaminated with tomato paste over time.

Recommendations

1. Additional comprehensive study ought to be conducted in other parts of Libya.
2. To obtain precise data, we advise employing more advanced analytical methods.
3. For canning, use glass jars or heavy metal cans that have been lined with an inert insulating substance.
4- Select the right kind of raw material (tomatoes) and other supplies for manufacture.
5. Researching soil to find out how much of these minerals are contaminated.
6. Establish awareness campaigns to encourage people worldwide to use less fertilizer, as this is a major contributor to pollution.

7-Aiming to shorten the storage duration as much as feasible since the amount of heavy metals present and storage time are directly correlated.

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