Comprehensive Assessment of Heavy Metal Contamination in Locally Consumed Tomato Paste in Libya

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***Abstract*— The problems of food pollution have become a major threat to human society. Evaluation of the pollution status of canned food provides a reference for further work to reduce the risk of heavy metal pollution. In this case, the tomato paste product consumed in Libya and imported from abroad, was selected as a case study. This study assesses the occurrence and levels of heavy metals (zinc, lead, cadmium, iron, and copper) in canned and bottled tomato paste. Atomic Absorption Spectroscopy (AAS) for quantitative analysis. A thorough sample preparation technique was employed, incorporating drying, digestion with nitric and sulfuric acids, and dilution to guarantee uniformity and precision. The results indicated a broad spectrum of heavy metal concentrations: zinc levels varied from 0.00 ± 0.00 to 2.41 ± 0.03 mg/kg, lead from 0.00 ± 0.00 to 1.66 ± 0.01 mg/kg, Cadmium from 0.00 ± 0.00 to 0.62 ± 0.01 mg/kg, iron from 1.36 ± 0.02 to 38.20 ± 1.60 mg/kg, and copper from 0.00 ± 0.00 to 0.62 ± 0.01 mg/kg.**

Although the safety levels set by Libyan and international norms, samples displayed heavy metal concentrations surpassing permitted limits. The elevated quantities of these metals were associated with causes including environmental pollution from dirty irrigation water, soil deterioration, and processing conditions, which may involve leaching from packaging materials.

The levels of heavy metals pollution, in this study, showed that it is necessary to pay attention to the health risks of heavy metals and establish stringent quality control protocols throughout the manufacturing chain.

Keywords—template, Heavy metals, tomato paste, food contamination.

I. INTRODUCTION

Trace elements are essential for various functions in our lives. Some trace elements, like cadmium, lead, mercury, and radioactive metals, are hazardous heavy metals, but others, such as iron, copper, and zinc are necessary and nutritionally significant. Toxic metals typically mimic the function of vital elements in the body, disrupting metabolic processes and leading to diseases. Consequently, the analysis of trace elements in diverse matrices is gaining significance due to the growing interest in assessing the unique compositions of dietary, biological, and environmental samples, as well as nutrients for quality control and public health objectives [1].

Cadmium is a hazardous, non-essential metal that mostly accumulates in blood, kidneys, and liver tissues. Lead is a prevalent metal that is highly harmful to health and the environment, serving no necessary purpose in the body; its presence is associated with numerous ailments [2]. Consequently, the presence of cadmium and lead is undesirable in any sample, regardless of concentration, including ultra-trace levels. Consequently, their quantification at minimal quantities is crucial and serves as a foundation for diagnosing clinical illnesses and intoxication, as well as for monitoring environmental pollution [3].

Copper and zinc are essential constituents of numerous enzymes and crucial elements for people, animals, plants, and microbes. Nevertheless, an excess or lack of any important ingredient might lead to the onset of chronic or acute diseases. Consequently, the accurate and precise assessment of the maximum concentration of metals in food is crucial [4]

Numerous countries have established regulations to limit the use of dangerous substances, safeguard consumers from their detrimental effects, and promote equitable practices in food commerce [5]. While legal limits may differ across countries, regulations typically define a permissible maximum concentration of toxic heavy metals in food. Mechanisms have been instituted to monitor the presence of toxic elements in food to enforce regulatory standards and evaluate long-term exposure [6].

Iron is a crucial component of certain organisms (algae), specific enzymes (cytochromes and catalase), and oxygen-transporting proteins (haemoglobin and myoglobin). Iron serves as the principal transition metal in numerous biological redox processes due to the interconversion between ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions [7].

The source of iron in surface water is anthropogenic and associated with mining activities. Copper is a dense metal utilised in several industries for the manufacture of copper pipes, cables, wires, and cookware. It is additionally utilised in the production of copper intrauterine devices and contraceptive pills. Copper, in the form of copper sulphate, is incorporated into drinking water and swimming pools. As a result of anthropogenic and industrial activity, it can build in the soil and be absorbed by plants. Copper is found in some nuts, avocados, wheat germ, and bran [8]. Table (1) refer to the permissible concentrations of certain heavy metals in tomato paste as documented by the WHO.

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TABLE 1: ALLOWED LEVELS OF SOME HEAVY METALS IN TOMATO PASTE AS REPORTED IN WHO. [9]

Where; Cadmium (Cd), Lead (Pb), Zinc (Zn), Iron (Fe), Copper (Cu).

Heavy metal	Concentration, mg/kg
Cd	0.03
Pb	1.5
Zn	19
Fe	30
Cu	10

The impact of heavy metals and their toxicity encompasses two primary facets: (a) their lack of known metabolic function, which disrupts normal cellular processes and induces toxicity in various organs; (b) the propensity of certain heavy metals, notably mercury and lead, to bioaccumulate in biological tissues [10]. Consequently, it is imperative to regulate the concentrations of these harmful metals in food products to safeguard human health, mostly based on research with individuals exposed to lead in occupational settings. Acute exposure to elevated lead concentrations can result in neurological impairment, paralysis (lead palsy), anaemia, and gastrointestinal manifestations. Prolonged exposure may result in harm to the kidneys, reproductive and immunological systems, as well as adverse effects on the mental system [11].

Low-level lead exposure critically impacts intellectual development in young children because, similar to mercury, lead traverses the placental barrier and accumulates in the foetus. Infants and early children are more susceptible than adults to the harmful effects of lead and exhibit a higher absorption rate of lead [12].

Even minimal, low-level exposure to lead in young children is deemed to impact neurobehavioral development. The primary source of lead exposure for the general population is the consumption of food containing lead. The primary harmful effect of cadmium is its nephrotoxicity. However, it has also been linked to pulmonary damage (including the induction of lung tumours) and skeletal alterations in occupationally exposed groups [13].

Despite the various adverse effects of zinc on human health, it remains a significant element in daily living. However, as previously said, when its concentration surpasses normal levels, it induces anaemia, hepatic disorders, renal failure, emesis, diarrhoea, and a reduction in the human body's immunity. Excessive and insufficient copper levels can influence cerebral function. Impairments have been associated with Menkes disease, Wilson's disease, and Alzheimer's disease [14].

Iron toxicosis manifests in four stages. Iron toxicosis occurring six hours’ post-iron overdose is characterised by gastrointestinal manifestations, including gastrointestinal haemorrhage, emesis, and diarrhoea. (ii): Iron toxicosis occurring 6-24 hours’ post-iron administration is regarded as the phase of apparent medical recovery (latent interval). (iii): Iron toxicosis occurring 12-96 hours’ post-iron administration is characterised by shock, lethargy, tachycardia, hypotension, liver necrosis, metabolic acidosis, and occasionally, mortality. Iron toxicosis occurring 2-6 weeks post-iron administration is characterised by the emergence of gastrointestinal ulcerations and the creation of strictures [15].

A. *Literature Review*

In a study, the concentrations of various heavy metals, including cadmium, cobalt, copper, iron, manganese, lead, and zinc, were quantified in tomato paste using atomic absorption spectrometry. The concentration values of cadmium, cobalt, copper, iron, manganese, and lead surpassed the permissible limits set by Iraqi standards and the World Health Organisation (WHO) for all study samples, however the concentrations of copper and zinc remained below acceptable limits. Four hundred samples of canned tomato paste from twelve common brands were analysed for the levels of lead, cadmium, zinc, cobalt, and iron in both fresh and canned tomato paste. The results indicated that the highest concentration in canned food samples was tin. Variance analysis indicate that the concentration of heavy metals and histamine in canned food samples was considerably influenced by the manufacturing business. A positive link existed between storage duration and heavy metal concentrations, particularly tin, zinc, and iron, which exhibited significant variation. After 6 and 12 months of storage, the heavy metal levels in the same brand were markedly higher compared to the younger samples [16].

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Another investigation examining the concentrations of heavy metals in tomato paste available in the markets of Umualhia, Nigeria, utilising spectral atomic absorption, revealed the presence of iron, lead, copper, zinc, and cadmium at levels below the permitted limits indicated for food consumption [18].

Eleyowo & Amusa [19] assessed the heavy metal concentrations in sachet tomato paste products sourced from Lagos State, Nigeria. Different brands of sachet tomato paste were examined for cadmium, lead, zinc, iron, and copper via atomic absorption spectrometry. The investigation demonstrated varied amounts of heavy metals among various brands. Cadmium and lead concentrations were predominantly within acceptable limits, although zinc and iron exhibited higher amounts in certain samples. Copper was detected in minimal quantities, remaining beneath regulatory limits. Antioxidant levels and microbial loads exhibited considerable variation, signifying a lack of consistency in production standards. The authors advocated for more regulatory supervision of sachet tomato paste production to guarantee compliance with safety standards. Public awareness initiatives were proposed to inform consumers about product quality.

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Grochowska-Niedworok et al. [20] evaluated the levels of cadmium and lead in tomatoes and tomato-derived products available in Poland, highlighting the implications for public health. Tomato samples, comprising both fresh and processed products, were analysed for cadmium and lead utilising Inductively Coupled Plasma Optical Emission Spectrometry. The outcomes were evaluated in relation to European Union safety criteria. The study revealed that cadmium and lead levels in fresh tomatoes were negligible; nevertheless, processed tomato products sometimes surpassed safe thresholds, particularly in budget brands. The results indicated contamination occurred during processing rather than originating from the raw ingredients. It was determined that enhanced quality control during the processing phase is essential to reduce contamination. The authors advocated for the consistent surveillance of heavy metals in tomato products, especially those that are imported and economically priced.

Bonemann et al. [21] examined the overall amounts and bioaccessible percentages of metals, specifically cadmium, lead, zinc, iron, and copper in tomatoes and tomato products utilising microwave-induced plasma optical emission spectrometry. Fresh tomato samples and processed derivatives (sauces, pastes) underwent bioaccessibility assessments and were analysed for heavy metal concentration to ascertain the extent of metal absorption by the human body. Although the overall concentrations of heavy metals remained within permissible limits, bioaccessibility assessments indicated that specific metals, including cadmium and lead, exhibited elevated potential absorption rates. The bioaccessibility of zinc, iron, and copper remained well below hazardous thresholds. The authors concluded that bioaccessibility must be incorporated into risk assessments of heavy metal exposure. It was advised that forthcoming rules take bioaccessibility into account, particularly with cadmium and lead in processed items.

Sirajo et al. [22] evaluated the phytochemical composition, heavy metal presence, and antioxidant vitamin levels in tomatoes grown in proximity to a cement industry in Sokoto, Nigeria, specifically examining contamination by cadmium, lead, zinc, iron, and copper. Samples were analysed with flame atomic absorption spectrometry to quantify heavy metals. Cadmium and lead concentrations surpassed allowable thresholds in samples obtained near the cement industry. The quantities of zinc, iron, and copper were within permissible parameters. The results emphasised the detrimental effect of industrial pollution on agricultural output. The study concluded that industrial pollution substantially contributes to heavy metal contamination in tomatoes. Recommendations including the relocation of farms from industrial zones and the implementation of more stringent environmental rules.

Izah & Aigberua [23] examined heavy metal contamination in edible tomatoes (Lycopersicon esculentum) available in Port Harcourt, Nigeria. The study employed atomic absorption spectroscopy to quantify levels of cadmium, lead, zinc, iron, and copper. The investigation identified cadmium and lead amounts exceeding regulatory thresholds in multiple samples, presenting health hazards. The concentrations of zinc, iron, and copper were within acceptable thresholds. The authors advocated for more stringent enforcement of agriculture and food safety regulations to mitigate heavy metal contamination. It was also recommended to educate farmers and vendors on appropriate handling and storage techniques to reduce microbial dangers.

Veloo & Tan [24] sought to examine the concentrations of heavy metal residues in canned tomato paste and bottled tomato sauce to evaluate food safety and adherence to health regulations. Atomic absorption spectrometry was employed for the accurate measurement of heavy metal contents in specific processed tomato products. Samples were procured from local marketplaces and examined under laboratory settings. The results indicated substantial discrepancies in heavy metal levels between the two products, with several samples beyond allowable thresholds. The research underscored the health hazards associated with the consumption of processed tomato products containing high amounts of heavy metals, stressing the necessity for more stringent regulatory protocols and regular surveillance.

Yohanna [25] assesses the content of heavy metals in candies and tomato paste, emphasizing the identification of potential health risks linked to their intake. Heavy metal analysis was performed with established analytical methods, and the findings were juxtaposed with worldwide safety standards. In several samples, notably imported products, elevated concentrations of lead and cadmium were identified, presenting a possible health hazard. The research emphasized the imperative for improved quality control in food goods to protect public health and advocated for stricter import rules.

Zambiri et al. [26] sought to examine and contrast the proximate composition and heavy metal concentration of fresh and dried tomatoes. Fresh and dried tomatoes underwent laboratory investigation, encompassing proximate analysis and atomic absorption spectrometry, to ascertain heavy metal contents. The dehydrated tomatoes displayed elevated heavy metal contents relative to fresh samples, presumably due to concentration during the drying process. The research indicated that drying methods could intensify heavy metal buildup and advocated for enhanced agricultural practices to mitigate contamination at the source.

Uroko et al. [27] assess the concentrations of heavy metals in canned tomato paste marketed in Ubani-Umuahia, Nigeria, and analyze their possible health hazards. The research utilized atomic absorption spectrometry to assess heavy metal concentrations in different brands of canned tomato paste. The findings revealed that several brands included heavy elements such as lead and cadmium exceeding permissible thresholds, hence presenting a health hazard. The study emphasized the significance of regulatory enforcement and consumer knowledge in reducing health hazards associated with contaminated tomato paste.

Usman et al. [28] investigate the health concerns associated with heavy metals in tomatoes consumed in Gombe Metropolis and their effects on consumer health. Tomato samples were procured from local markets and examined for heavy metal concentration utilizing sophisticated spectroscopic methods. A health risk assessment approach was utilized to evaluate potential health concerns. The research identified increased concentrations of heavy metals, especially in tomatoes cultivated in regions subjected to industrial contaminants. The results emphasized

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the necessity for environmental regulation and consistent surveillance of agricultural products to guarantee food safety.

Safta et al. [29] investigate metal migration and ascertain the sources of corrosion in canned tomatoes and sardines. Analytical methods, such as spectrometry, were utilized to measure metal migration from cans under various storage conditions and durations of exposure. Substantial metal migration, especially of tin and iron, was observed, associated with the corrosion of can linings in acidic environments. The research highlighted the enhancement of canning materials and production techniques to minimize metal leaching into canned goods.

Mehrin et al. [30] investigate the nutritional quality and evaluate the potential health concerns linked to industrially processed tomato ketchups in Bangladesh. Samples underwent testing for heavy metals, nutritional composition, and related health hazards utilizing risk assessment models. Concentrations of lead and cadmium in certain ketchups surpassed allowable thresholds, presenting significant health hazards. The nutritional quality differed among brands. The results necessitated enhanced quality control and regulatory supervision of processed food items.

Mohammed and Mainasara [31] assess the concentrations of heavy metals and biological pollutants in locally processed tomato, pepper, and onion puree in Maiduguri, Nigeria. Samples underwent spectrometric analysis for heavy metals and microbiological testing for biological contamination. Increased concentrations of lead and mercury were identified, accompanied with bacterial contamination, signifying inadequate processing conditions. The research emphasized the necessity for enhanced food safety protocols and consistent oversight to safeguard public health.

Liu et al. [32] examine the capacity of γ-PGA-producing bacteria and biochar to diminish heavy metal levels and enhance tomato quality. Field tests were executed, utilizing bacterial strains and biochar in soil, while assessing heavy metal absorption and tomato quality metrics. The integrated treatment markedly diminished heavy metal levels in tomatoes while improving their nutritional and sensory attributes. The method demonstrated promise as a sustainable agricultural practice to alleviate soil pollution and enhance crop quality.

Maina [33] analyzes fluoride and heavy metals in tomatoes and kale from horticultural farms in Nakuru County, Kenya, and evaluates the associated risks. Fluoride and heavy metal concentrations were assessed using spectroscopic methods, and health risk indices were computed. Increased concentrations of lead and cadmium were detected in crops irrigated with contaminated water. The study advocated for rigorous oversight of water sources and agricultural methods to reduce health hazards.

Birghila et al. [34] investigate the concentration of heavy metals in soil and tomatoes and examine their health repercussions. Soil and tomato samples were examined for heavy metal concentrations by trace element analysis. Tomatoes grown on contaminated soil exhibited elevated heavy metal buildup, surpassing safety thresholds for consumption. The study emphasized the significance of soil quality management and food safety measures to mitigate heavy metal exposure via diet.

Abdullahi et al. [35] examine heavy metal concentrations in tomatoes, bell peppers, and onions cultivated under the Kano River Irrigation Project. Metal concentrations were quantified using spectroscopic analysis, and health risk evaluations were performed. Increased concentrations of cadmium and lead were detected, linked to industrial effluents in irrigation water. The study advocated for improved waste management and consistent monitoring of irrigation water to safeguard agricultural quality and public health.

Ahmed et al. [36] evaluate the hazards of trace metals in tomatoes cultivated using wastewater irrigation. Tomatoes irrigated with wastewater were analyzed for trace metal buildup, and health risk assessments were conducted. A substantial concentration of toxic metals such as cadmium and chromium was identified, presenting serious health hazards to consumers. The research recommended the restriction of wastewater utilization in agriculture and the adoption of safer irrigation methods.

II. MATERIALS AND METHODS

A. Atomic absorption spectrometer

An Atomic Absorption Spectrometer is characterized as a quantitative analytical technique that measures the absorption of light at a certain fixed wavelength by free atoms. The radiation intensity at this wavelength escalates with the augmentation of the cycles of the element in the rays' trajectory. Consequently, as spectrum pertains to concentration, it enables the identification of over 60 components of a single element with remarkable precision, reaching up to 1 million. Consequently, it is feasible to identify the constituents of the sample, even if present in minimal proportions. An atomic absorption spectrometer typically comprises four primary components: the hollow cathode lamp, flame, monochromator, and detecting system (Figure 1).

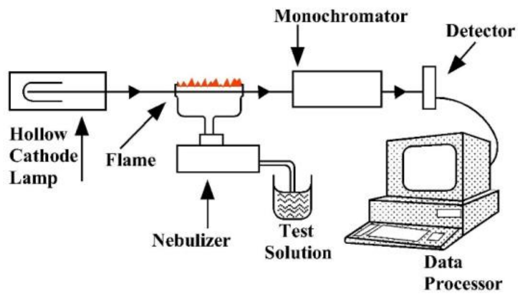

FIGURE 1. ATOMIC ABSORPTION SPECTROMETER COMPONENTS

This method relies on transforming the metallic substance into free atoms, so transferring it to the atomic state, and quantifying the radiant energy received by these atoms. The absorption degree of the atomic number present in the sample of the element to be analysed is directly proportional to the concentration of that element. In their ground state, atoms absorb light at a certain wavelength, transitioning to a "excited state." The quantity of absorbed rays at this wavelength escalates with the augmentation of the atomic number of the wave element in the rays' trajectory.

This method relies on the fragmentation of the substance's units into atoms and the study of the radiant energy absorbed by these atoms. Electronic transitions transpire between energy levels due to energy absorption.

The indicated substance must be in a liquid condition. The conversion of elements from bound molecules to free elements is achieved by exposing the compounds to thermal energy adequate to disrupt chemical bonds, accomplished by spraying the compound solution into a flame of suitable temperature.

B. *Sample preparation and analysis*

The canned and bottled tomato sauce samples were poured into a container and thoroughly mixed using a blender. The samples were then dried in an oven at 70°C for 24 hours. Once dried, they were ground into a fine powder using a blender [37].

For digestion, 5 g of the dried sample was weighed and placed into a 100 mL beaker. Inside a fume hood, 5 mL of concentrated nitric acid (HNO_3, 69%) was added to the sample, and the mixture was heated on a digital hot plate. When a vigorous reaction occurred, resulting in a dark blackish-red residue, 2 mL of concentrated sulfuric acid (H_2SO_4) was added. The mixture was continuously heated until a dark reddish residue formed [37].

Subsequently, 25–30 mL of HNO_3 was added incrementally to maintain oxidizing conditions, ensuring the solution became clear with a reddish-orange color and no solid residue remaining. During heating, a yellow-orange flame was observed. The digestion process lasted approximately 1.5 to 2 hours to ensure complete digestion [38].

After digestion, the solution was cooled in the fume hood. It was then filtered using 0.90 mm filter paper and a glass funnel. The filtrate was further filtered using a 0.45 mm PTFE syringe filter. The beaker was rinsed thoroughly with deionized water to ensure complete sample transfer. The digested sample was diluted with deionized water and made up to 50 mL.

A 50 mL aliquot of the diluted sample was transferred into a centrifuge tube to serve as the stock solution. From this, 15 mL of the stock solution was transferred into a separate centrifuge tube and used as the sample solution. Serial dilutions of the sample solution were prepared to concentrations of 10^{-1}, 10^{-2}, 10^{-3}, and 10^{-4}. These procedures were repeated for all canned tomato paste and bottled tomato sauce samples [37].

The prepared solutions were stored in a chiller at 2°C prior to analysis. A heavy metals (Pb, Cd, Zn, Fe, and Cu) were determined using Atomic Absorption Spectrometry (AAS). The results were presented in mg/L and converted to mg/kg using the appropriate conversion formula [39].

The levels of lead, cadmium, copper, iron, and zinc in tomato paste were quantified using an Atomic Absorption Spectrophotometer (model Varian 220, manufactured in the USA).

A 2.0 g of the examined sample was desiccated and subsequently incinerated at 450°C for 6 to 8 hours. Subsequent to chilling the sample, 10 ml of 6 N HCl (1:1) was introduced, and the solution was evaporated to dryness. The residue was dissolved in 0.1N HNO3 and diluted to the 100 ml mark using distilled water [40].

III. 3. Results and Discussion

A. *Zinc*

The zinc content in tomato paste is detailed in Table (2) and Figure (2), with values ranging from 0.00 ± 0.00 mg/kg to 2.41 ± 0.03 mg/kg. The relative standard deviation (RSD) was between 0% and 1.24%. The highest zinc concentration, 2.41 mg/kg, was found in sample No. 2, while the lowest concentration, 0.00 mg/kg, was observed in samples No. 1, 5, 8, 9, and 10. The reported concentrations of tomato paste were somewhat elevated compared to those indicated by Nathaniel et al. [41], overall, all samples adhered to the allowed limits established by Libyan and international standards of 19 mg/kg. Veloo and Tan [24] observed fluctuations in zinc concentrations attributable to production and packaging, whereas Yohanna [25] and Safta et al. [29] highlighted the influence of contamination during cultivation or can corrosion. Zambiri et al. [26] and Mehrin et al. [30] indicated that drying and storing processes may elevate zinc concentrations, whereas Liu et al. [32] illustrated that biochar and γ-PGA-producing bacteria in culture diminished heavy metal levels, including zinc. Research conducted by Mohammed and Mainasara [31] and Maina [33] emphasized the impact of untreated irrigation water and soil pollution on zinc concentrations in tomatoes. Ahmed et al. [36] recognized wastewater irrigation as a contributing factor to increased zinc levels, albeit below acceptable safety limits. These studies emphasize the necessity of quality management across all phases, from cultivation to processing, to ensure zinc levels remain within permissible parameters and protect consumer health.

Table (2) Mean concentration of Zinc (mg/kg) in tomato samples.

Sample No.	(Mean± STDE) mg/kg	RSD%
1	0.00 ± 0.00	0.00
2	2.41 ± 0.03	1.24
3	0.49 ± 0.00	0.00
4	2.36 ± 0.01	0.63
5	0.00 ± 0.00	0.00
6	0.87 ± 0.00	0.00
7	0.00 ± 0.00	0.00
8	0.00 ± 0.00	0.00
9	0.00 ± 0.00	0.00
10	0.00 ± 0.00	0.00

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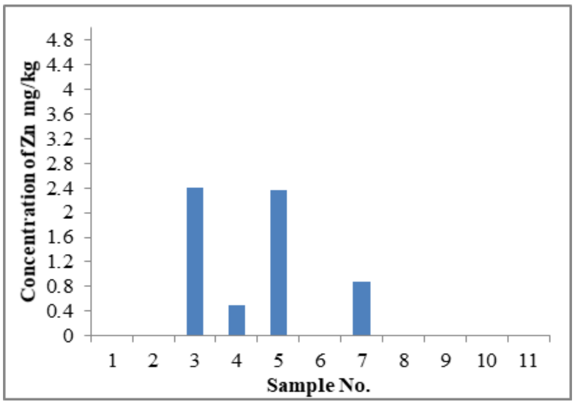
FIGURE (2) ZINC VALUE OF STUDIED SAMPLES



B. Lead

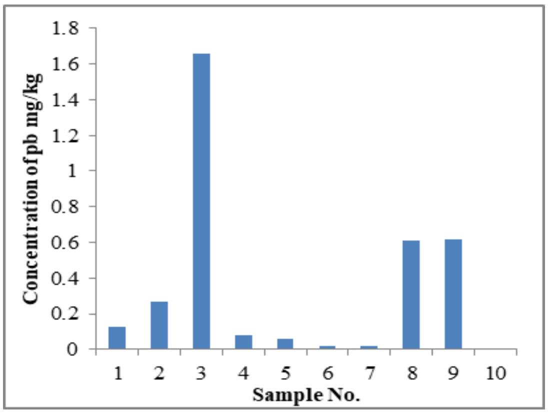
The results presented in Tables (3) and Figure (3) indicate that the Lead content in tomato paste ranges from 0.00 ± 0.00 to 1.66 ± 0.01 mg/kg, with RSD of 0 – 1.66%.

The highest Lead concentration of 1.66 mg/kg was found in sample No. 3, while the lowest concentration of 0.00 mg/kg was observed in sample No. 10. The reported values were marginally elevated compared to those cited by Uysal et al. [42]. All values conformed to the legal limits established by Libyan and international standards, except for sample No. 3, which exceeded the permissible limit of 1.5 mg/kg by 1.667 mg/kg. The lead concentration in tomato paste varies considerably among studies, indicating the influence of agricultural practices, processing methods, and environmental conditions. Usman et al. [28] evaluated tomatoes in Gombe Metropolis, identifying lead contamination predominantly resulting from irrigation with contaminated water. Mehrin et al. [30] indicated that processed tomato ketchups in Bangladesh displayed fluctuating lead concentrations, affected by the sourcing of raw materials and production circumstances. Birghila et al. [34] identified a significant association between soil contamination and lead absorption in tomatoes, emphasizing the necessity for soil rehabilitation. Abdullahi et al. [35] evaluated heavy metal concentrations in tomatoes inside the Kano River Irrigation Project, discovering that certain samples approached or beyond acceptable lead thresholds due to contaminated irrigation water. Ahmed et al. [36] documented increased lead concentrations in tomatoes irrigated with wastewater, with levels nearing safety standards and presenting possible health hazards. These findings collectively emphasize the necessity for rigorous quality control throughout the production chain, the use of sustainable agricultural methods, and enhanced monitoring to reduce lead contamination and safeguard consumer safety.

TABLE (3) MEAN CONCENTRATION OF LEAD (MG/KG) IN TOMATO SAMPLES

Sample No.	Mean± STDE)mg/kg	RSD%
1	0.13 ± 0.01	3.70
2	0.27 ± 0.01	3.70
3	1.66 ± 0.01	0.59
4	0.08 ± 0.00	0.00
5	0.06 ± 0.00	0.00
6	0.02 ± 0.00	0.00
7	0.02 ± 0.00	0.00
8	0.61 ± 0.01	1.63
9	0.62 ± 0.01	1.61
10	0.00 ± 0.00	0.00

FIGURE (3). LEAD VALUE OF STUDIED SAMPLES



C. Cadmium

The data presented in Table (4) and Figure (4) demonstrate the detection of cadmium in tomato paste samples, with concentrations ranging from 0.00 ± 0.00 to 0.62 ± 0.01 mg/kg, and RSD of 0 to 4.67%. The maximum cadmium concentration of 0.62 mg/kg was observed in sample No. 9, while the minimum concentration of 0.00 mg/kg was found in sample No. 10. The reported values were comparable to those of Emrah et al. (4). Generally, all values exceeded the legal limits, except for the samples (10, 4, 6, 7, and 5), which recorded values of 0.00, 0.01, 0.02, 0.02, and 0.01 mg/kg, respectively, all of which were below the allowable threshold of approximately 0.03 mg/kg according to Libyan and international norms. Research conducted by Veloo and Tan [24] and Yohanna [25] supports these conclusions, revealing the presence of cadmium in processed tomato products, with variability associated with agricultural and processing methods. Safta et al. [29] emphasized that migration from packaging materials may elevate cadmium levels, whilst Maina [33] and Abdullahi et al. [35] underscored the impact of environmental contamination in irrigation water and soil. Liu et al. [32] established that biochar and microbial interventions can diminish cadmium absorption, presenting a viable approach for pollution reduction. The results emphasize the necessity for stringent quality control and mitigation techniques to tackle cadmium contamination in tomato paste and assure adherence to safety standards.

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TABLE (4) MEAN CONCENTRATION OF CADMIUM (MG/KG) IN TOMATO SAMPLES

Sample No.	Mean± STDE)mg/kg	RSD%
1	0.05 ± 0.00	0.00
2	0.06 ± 0.00	0.00
3	0.08 ± 0.00	0.00
4	0.01 ± 0.00	0.00
5	0.01 ± 0.00	0.00
6	0.02 ± 0.00	0.00
7	0.02 ± 0.00	0.00
8	0.61 ± 0.01	1.63
9	0.62 ± 0.01	1.61
10	0.00 ± 0.00	0.00

FIGURE (4) CADMIUM VALUE OF STUDIED SAMPLES

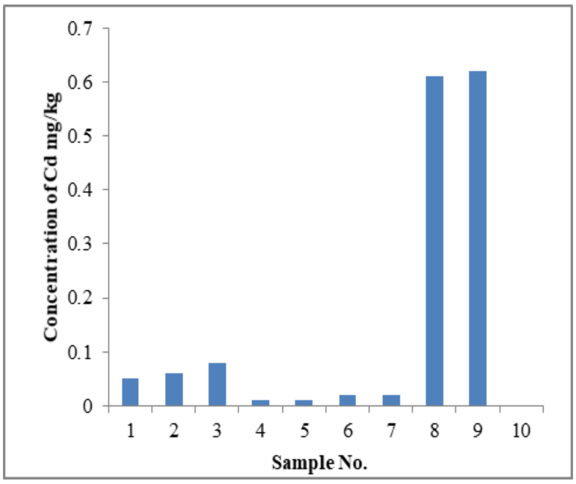
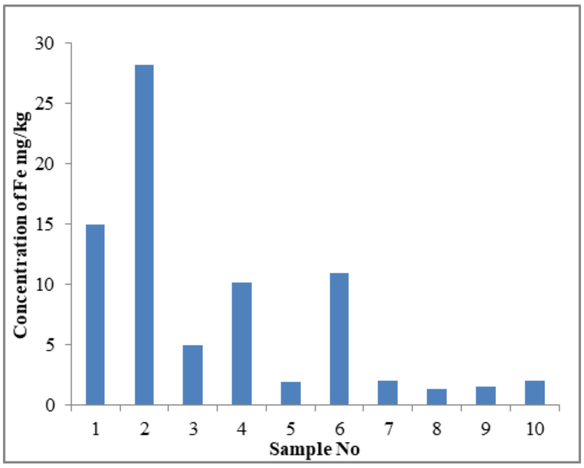


TABLE I. TABLE (5) MEAN CONCENTRATION OF IRON (MG/KG) IN TOMATO SAMPLES

Sample No.	Mean± STDE)mg/kg	RSD%
1	14.90 ± 0.50	3.36
2	28.20 ± 1.60	4.19
3	4.92 ± 0.01	0.34
4	10.16 ± 0.28	2.75
5	1.88 ± 0.01	0.53
6	10.94 ± 0.00	0.00
7	1.97 ± 0.02	1.31
8	1.36 ± 0.02	1.83
9	1.50 ± 0.00	0.0
10	1.98 ± 0.02	1.01

FIGURE (5) IRON VALUE OF STUDIED SAMPLES



D. Iron (Fe)

The iron content results in tomato paste are presented in Table 5 and Figure 5; the values ranged from 1.36±0.02 to 28.20±1.60 mg/kg, with RSD of 0 to 4.19%. The maximum iron concentration of 38.20 mg/kg was observed in sample No. 2, while the minimum concentration of 0.90 mg/kg was found in sample No. 8. The iron results were marginally worse to those acquired prior to David [43]. The values were predominantly below the permitted limits established by Libyan and international standards, with the exception of Sample No. 2, which recorded a value of 38.20 mg/kg, exceeding the permissible limit of around 30 mg/kg. Abdullahi et al. [35]evaluated tomatoes from the Kano River Irrigation Project, observing that irrigation with contaminated water markedly elevated iron contents, especially in areas next to industrial operations. Birghila et al. [34] analyzed soil and tomato samples, revealing a significant association between soil contamination and increased iron concentrations in tomatoes, hence endorsing soil remediation measures to mitigate uptake. Ahmed et al. [36] investigated tomatoes irrigated with effluent and found that iron concentrations frequently beyond safety limits, highlighting the necessity for alternative irrigation methods. Uroko et al. [27] emphasized the heterogeneity in iron concentration in canned tomato pastes, noting that increased levels frequently arise from metallic corrosion during storage.

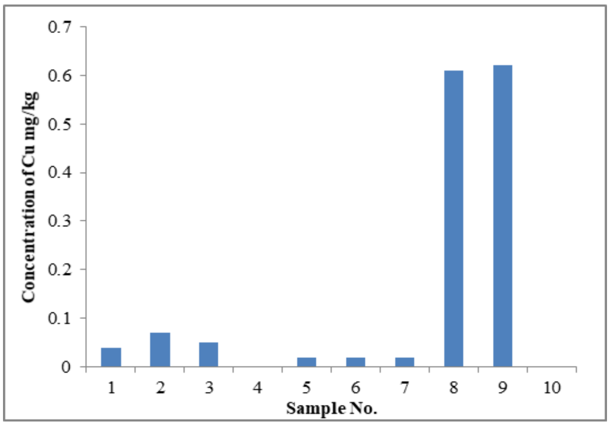
E. Copper (Cu)

The data in Table (6) and Figure (6) indicate that the copper content in tomato paste samples ranges from 0.00 ± 0.00 to 0.62 ± 0.01 mg/kg, with RSD of 0 to 16.27%. The maximum value, 0.62 mg/kg, was recorded for sample No. 9, while the minimum value, 0.00 mg/kg, was seen for sample No. 10 in tomato paste. The copper value results were comparable to those previously reported by RI et al. [44]. All readings were below the allowable thresholds established by Libyan and international norms, around 10 mg/kg. Veloo and Tan [24] indicated comparable copper concentrations in canned tomato pastes, highlighting that these levels were affected by the origin of the raw tomatoes and the processing circumstances. Yohanna [25] discovered that copper concentrations in tomato paste were markedly below international safety guidelines. However, variability was seen due to environmental conditions during cultivation. Zambiri et al. [26] indicated that drying methods in tomatoes may result in minor increases in copper content due to water loss, however the levels remained within acceptable limits. Birghila et al. [34] established that soil pollution significantly influenced copper absorption in tomato plants, resulting in elevated yet permissible concentrations in the fruits. Ahmed et al. [36] and Maina [33] both noted that wastewater irrigation may marginally elevate copper concentrations in tomatoes, however the amounts often adhered to international standards. These data collectively affirm that copper concentrations in tomato paste products are generally well-regulated and remain within permitted limits, contingent upon the maintenance of quality control throughout the production chain.

TABLE (6) MEAN CONCENTRATION OF COPPER (MG/KG) IN TOMATO SAMPLES

Sample No.	Mean± STDE)mg/kg	RSD%
1	0.04 ± 0.00	0.00
2	0.07 ± 0.00	0.00
3	0.05 ± 0.00	0.00
4	0.00 ± 0.00	0.00
5	0.02 ± 0.00	0.00
6	0.02 ± 0.00	0.00
7	0.02 ± 0.00	0.00
8	0.61 ± 0.00	0.00
9	0.62 ± 0.01	1.61
10	0.00 ± 0.00	0.00

FIGURE (6) COPPER VALUE OF STUDIED SAMPLES



IV. CONCLUSION

The examination of heavy metals, such as zinc, lead, cadmium, iron, and copper, in tomato paste samples reveals differing degrees of contamination affected by farming practices, environmental factors, and processing techniques. Although the majority of samples complied with Libyan and international safety requirements, notable exceptions were observed, namely for lead, cadmium, and iron, which at times surpassed allowable limits, thereby presenting significant health hazards. These findings underscore the necessity of rigorous quality control protocols throughout the manufacturing continuum, from cultivation to processing and packaging. To guarantee safety and compliance, it is advisable to apply sustainable farming practices, including the utilization of clean irrigation water, the implementation of soil remediation techniques, and the application of biochar or microbial treatments to mitigate heavy metal absorption. Manufacturers should emphasize superior packaging materials to avert contamination from corrosion and implement stringent monitoring and testing processes during production. Enhancing regulatory frameworks and promoting research into creative mitigation measures would bolster efforts to reduce heavy metal pollution in tomato-based products and safeguard consumer health.

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