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Evaluation of Heavy Metals Contents in Spices Available on Zawia City`s Markets

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A B S T R A C T

While culinary spices offer numerous benefits, they can pose health risks if contaminated with heavy metals. Raising awareness about these dangers is essential, and proactive steps should be taken to detect and reduce contamination, ensuring the safe use of spices. In this study, several samples of different types of mixed spices used in seasoning red meat, chicken, Indomie, pizza and fish were purchased from local markets in Zawia city during September 2023 to study the extent of contamination with heavy elements. Quantification of 11 heavy metals: Pb, Cd, As, Hg, Mn, Ni, Cu, Zn, Fe, Co and Cr was conducted after wet digestion and X-ray fluorescence (XRF) analysis using the XSupreme 8000 equipment. The analysis showed that all tested spices contained varying levels of heavy metals; however, their concentrations were significantly below the international safety thresholds set by Codex Alimentarius and WHO. Among the heavy metals under analysis, the lowest concentration was noted in the case of toxic elements of mercury (0.09 ± 0.03 ppm), Arsenic (0.086 ± 0.03 ppm), and Lead (0.12 ± 0.05 ppm). The highest was detected in the case of an essential nutrient with low toxicity, Manganese (2.43 ± 1.82 ppm). This result underscores the need for continuous monitoring and adherence to safety standards to maintain these low levels and ensure consumer safety, and expanded monitoring of heavy metals in food products within Libya. Additionally, raising consumer awareness regarding the potential health risks associated with the consumption or overconsumption of contaminated spices is essential.

Keywords: *Contamination, Heavy metals, Spices, WHO, X-ray fluorescence*

تقييم محتويات المعادن الثقيلة في التوابل المتوفرة في أسواق مدينة الزاوية

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الملخص

في حين أن توابل الطهي لها العديد من الفوائد، إلا أنها يمكن أن تشكل مخاطر صحية إذا كانت ملوثة بالمعادن الثقيلة. ومن الضروري زيادة الوعي بهذه الأخطار، وينبغي اتخاذ خطوات استباقية للكشف عن التلوث والحد منه، وضمان الاستخدام الآمن للتوابل. في هذه الدراسة تم شراء عدة عينات من أنواع مختلفة من البهارات المختلطة المستخدمة في توابل اللحوم الحمراء والدجاج والإندومي والبيتزا والأسماك، من الأسواق المحلية في مدينة الزاوية خلال شهر سبتمبر 2023 لدراسة مدى التلوث بالعناصر الثقيلة. تم إجراء القياس الكمي ل 11 معدنا ثقيلا الرصاص، الكادميوم، الزرنيخ، الزئبق، المنغنيز، النيكل، النحاس، الزنك، الحديد، الكوبلت والكروم بعد الهضم الرطب وتحليل فلوروسنت الأشعة السينية **(XRF)** باستخدام معدات **X-Supreme 8000.** أظهرت نتائج التحليل أن جميع التوابل المختبرة تحتوي على مستويات متفاوتة من المعادن الثقيلة. ومع ذلك، كانت تركيزاتها أقل بكثير من مستويات الأمان الدولية التي حددتها هيئة الدستور الغذائي ومنظمة الصحة العالمية، ومن بين المعادن الثقيلة قيد التحليل، سجل أدنى تركيز في حالة العناصر السامة الزئبق (09.0 ± 03.0 جزء في المليون)؛ الزرنيخ (086.0 ± 03.0 جزء في المليون) والرصاص(12.0 ± 05.0 جزء في المليون) وسجل أعلى تركيز للعنصر الأساسي ذو السمية المنخفضة المنغنيز (43.2 ± 82.1جزء في المليون) تؤكد هذه النتيجة على الحاجة إلى المراقبة المستمرة والالتزام بمعايير السلامة للحفاظ على هذه المستويات المنخفضة وضمان سلامة المستهلك والمراقبة الموسعة للمعادن الثقيلة في المنتجات الغذائية داخل ليبيا. بالإضافة إلى ذلك، من الضروري زيادة وعي المستهلك فيماي تعلق بالمخاطر الصحية المحتملة المرتبطة باستهلاك أو الإفراط في استهلاك التوابل الملوثة.

الكلمات المفتاحية: *التلوث، المعادن الثقيلة، التوابل، منظمة الصحة العالمية، فلوروسنت الأشعة السينية.*

Introduction

Spices are an essential component of global cuisine, valued not only for their flavour but also for their potential health benefits. However, the presence of heavy metals in spices has become a growing concern due to their potential toxic effects on human health. These toxic elements can accumulate in the body and lead to severe health issues. Some heavy metals like lead (Pb), cadmium (Cd), cobalt (Co), copper (Cu), and zinc (Zn) are the most common elements that cause food contamination and enter food through environmental pollution and agricultural practices.

Zawia, a vibrant city in Libya, is known for its active markets where spices and herbs are an essential part of daily cooking and culture. Although widely consumed, there has been limited research on their safety in relation to heavy metal contamination. This study seeks to analyze the levels of selected heavy metals in popular spices sold in Zawia's markets. This study aims to shed light on whether these products comply with international safety standards and to evaluate any potential health risks for consumers.

1.1. Background on spice consumption in Libya.

Spice consumption in Libya is intensely rooted in the country's history and culture, shaped by influences such as traditional trade routes, perceived health benefits, and diverse culinary customs. Historically, Spices have long held an important habitation in the Mediterranean region, where ancient trade routes carried not just goods, but flavors, traditions, and healing herbs across cultures and generations.

Notably, the ancient city of Cyrene (Shahat) in Libya was famous for the production of silphion, a highly valued spice used for both culinary and medicinal purposes, which highlights the historical significance of spices in Libyan culture [1]. Understanding how spices are used in Libya today requires looking back at their deep historical roots. Over time, traditional Libyan practices have blended with global influences, shaping the way spices are consumed now. Spices are more than just a source of flavor; they're part of daily life, valued for their cultural meaning and health benefits. Modern research continues to highlight their positive effects, from natural antimicrobial action to possible roles in preventing disease, making them both a culinary and wellness staple in Libyan households [2], [3], [4]. For example, spices such as turmeric and chilli pepper have been linked to various health benefits, including anti-inflammatory effects and improved immune function [3], [4]. This growing consciousness of the health benefits of spices has contributed to their increased popularity in Libyan cuisine. Furthermore, the contemporary Libyan food industry is undergoing changes that reflect broader global trends in food consumption. The rise of supermarkets and contemporary shopping practices has had a significant impact on how people purchase and use spices. Nowadays, a lot of people rely on store shelves with spices that are neatly packaged rather than just traditional markets or local vendors because they are drawn to convenience, variety, and branding. In addition to the purchasing process, this change has affected the way spices are used in daily cooking and culture [5]. Despite these changes, traditional spice usage remains prevalent in Libyan households. Spices are integral to many traditional dishes, enhancing flavour and preserving food. The use of spices in Libyan food is often associated with cultural identity and tradition, as families pass down recipes that incorporate specific spices unique to their regional backgrounds [6]. This cultural significance underscores the role of spices not only as flavour enhancers but also as symbols of Libyan culinary traditions.

1.2. Heavy Metals in Spices: Sources.

Spices also get contaminated with heavy metals at different life cycle stages, like growth to processing and packaging. Major sources include contaminated soil and water, through which toxic metals are taken up by plants as they grow; industrial activities, such as mining and manufacturing, which lead to pollution into the environment; and the use of agrochemicals, such as fertilizers and pesticides, that may contain heavy metals stress handling, processing or packaging errors may also intensify the amount of contamination if strict quality control measures are not implemented. Researchers specify that the levels of heavy metals in spices are often reflective of environmental pollution and agricultural practices. For example, researchers in [7] described that the heavy metal content in spices available in Tripoli City markets, Libya, is influenced by environmental pollution and the use of contaminated fertilizers and pesticides. The study highlighted that lead and cadmium residues were detectable in various spices, raising concerns about the safety of these products for human consumption. Likewise, in [8], researchers studied heavy metal contamination in five commonly used spices in Libya (hot red pepper, bazaar, cumin, turmeric, and Al-harrarat) purchased from markets in Sabratha and Surman. Using atomic absorption spectroscopy (AAS), the concentrations of zinc, lead, cobalt, and copper were measured. Results show that zinc levels (0.8–14.5 ppm) were within the permissible limit (50 ppm, WHO). However, lead (285.75 ± 93.6 ppm) and cobalt (568 ± 249.6 ppm) exceeded safety limits, posing health risks. Copper concentrations were within safe limits in Sabratha samples but reached hazardous levels in turmeric and bazaar from Surman (285.75 ± 93.6 ppm and 568.4 ± 249.6 ppm, respectively). Likewise, Kowalska's research in Poland establishes that commonly used herbs and spices showed varying levels of mercury contamination, emphasizing the need for monitoring heavy metal levels in food products [9]. The regulatory landscape for heavy metals in spices is also evolving. Ishida pointed out that while certain regulatory measures have been implemented in places like New York, a more comprehensive global approach is necessary to mitigate human exposure to heavy metals from imported spices [10]. This is particularly important as spices are frequently imported from regions where agricultural practices may not adhere to stringent safety standards. Monitoring heavy metal contamination is crucial for assessing the health risks associated with spice consumption. Mohamed [11] highlighted the importance of tracking heavy metal toxicity levels in spices to understand their potential health impacts. The study indicated that spices could serve as a pathway for heavy metals to enter the human body, leading to bioaccumulation in organs and various health complications. This concern is supported by Adugna [12], who observed that the inclusion of contaminated spices in food can substantially contribute to the accumulation of heavy metals in human tissues. The potential for heavy metal contamination in spices is not limited to specific regions. Studies from various countries, including Bangladesh and Ethiopia, have reported alarming levels of heavy metals in spices, underscoring a global issue [13], [14]. For example, research conducted in Bangladesh has shown that spices could accumulate heavy metals during cultivation and processing, thereby posing health risks to consumers [13]. Furthermore, research in [14] highlighted that those spices could act as conduits for transferring toxins from the environment to humans, reinforcing the need for rigorous monitoring and regulation.

1.3. Heavy Metals in Spices: Risks

Heavy metals present significant health hazards, especially with prolonged exposure over time [15]. These elements accumulate in various organs, causing toxicity and disease [16]. The highly toxic lead affects enzymes, causing anaemia, nervous system disorders, cognitive impairments, and even death. Lead poisoning is especially severe in developing countries, with major exposure through contaminated food, water, and air [17], [18], [19]. Cadmium (Cd) accumulates in the kidneys and liver, leading to high blood pressure, kidney failure, and osteoporosis. It has a long biological half-life (20–40 years) [20], [21]. Copper (Cu) is an essential element but toxic in excess, leading to liver damage, neurological disorders, and digestive issues [22], [23]. Also, Zinc (Zn) is an essential element for health. However, excessive intake may lead to neurological and digestive disorders, while prolonged exposure can result in poisoning, manifesting as anemia, muscle weakness, and even paralysis [21], [24]. Arsenic (As) is highly toxic and linked to neurological, cardiovascular, and reproductive issues. Long-term exposure increases the risk of cancer and diabetes, primarily through contaminated water and food [10]. Mercury (Hg) impacts the nervous system and has been linked to memory loss, depression, and developmental disorders, particularly in infants. Mercury exists in many chemical forms (inorganic and organic mercury). The toxicity of mercury depends on its form and concentration within the analyzed substrate, with methylmercury being the most hazardous form [25], [26]. Chromium Cr (VI) is particularly toxic, leading to respiratory diseases, anaemia, and even lung cancer [27]. Cobalt (Co) accumulates in the body, leading to allergic reactions, cardiovascular diseases, and reduced fertility. High exposure has been linked to lung disease [28]. Nickel (Ni) Exposure causes respiratory disorders, DNA damage, and potential carcinogenic effects [29].

Long-term accumulation of heavy metals in the body, even at low exposure levels, can pose serious health risks. These include neurological disorders from lead and mercury, kidney damage from cadmium and lead, increased risk of cardiovascular diseases, and harmful effects on fetal development during pregnancy. Therefore, heavy metal exposure can have severe health consequences, necessitating strict monitoring of food and environmental contamination to minimize risks. The main objective of this study was to determine the concentration of certain heavy metals (iron, manganese, zinc, cadmium, cobalt, nickel, arsenic, mercury, copper, Chromium, and lead) in various types of spices sold in local markets in Zawia city in the west of Libya. The study aimed to assess the levels of 11 heavy metals in different spice samples to evaluate their safety for human consumption.

1.4. Spices investigated in Libya.

Very little research has been conducted to evaluate heavy metal-related risk assessment in spices in Libya. Researchers in [8] investigated the level of zinc, lead, cobalt and copper in Hotred pepper, Bezzar, Cumin, Turmeric and Al-harrarat collected from Sabratha and Surman markets in Libya. The concentration of the heavy metals was measured by atomic absorption spectroscopy (AAS). They found that the concentration of zinc was within the permissible limits of the World Health Organization (50ppm), while the concentration of lead, copper and Cobalt in Turmeric and bazaar were higher than the permissible limits. Several commonly consumed spices in Libya, including cinnamon, ginger, alpinia, cloves, turmeric, black pepper, cumin and, albezzar were collected from two main stores in the Alasaba and Tagasat regions and were wet digested to extract metals (Pb, Cd, Cu, Zn, Fe, Cr, and Mn), and then evaluate the metal levels in the extracted solutions using atomic absorption spectroscopy [31]. The concentration of metals was lower than their permissible levels in spices set by the World Health Organisation (WHO), except for Cd and Cr in most examined spices, which recorded levels more than those recommended by WHO. Some selected spices commonly consumed in Tripoli, Libya, including chilli pepper, black pepper, turmeric and mixed spices (Hrarat) were investigated for lead (Pb) and cadmium (Cd) contamination using atomic absorption spectroscopy after digestion with nitric acid and hydrogen peroxide [7]. The levels found in this study for lead in the samples were below those recommended by FAO. However, levels of cadmium exceeded FAO recommendations. Differences observed between Cd and Pb levels for spices sold in retail and wholesale markets indicate that the quality of spices across the value chain in Libya is highly variable and that several sources supply the market, some of which are contaminated and some of which are not. Another study [31] assessed the levels of heavy metals in several spices (turmeric, black pepper, red pepper, and al hararat) available in the markets of Misrata city. The results of the chemical analysis of this study showed that most of the concentrations of heavy elements in the spices under study were within the permissible limits and at a safe level for consumption. A study [32] was conducted on spice samples collected from markets in the Wadi Al-Shati region in southern Libya to estimate the concentrations of various heavy metals. The analyzed spices included ginger, turmeric, cardamom, black pepper, red pepper, cumin, cinnamon, and coriander. The study revealed a variation in heavy metal concentrations across the different spice samples. Some samples exceeded the maximum permissible according to the standard specifications of the World Health Organization and the Food and Agriculture Organization.

2. Materials and methods

2.1. Sample Collection

Thirteen different samples of various brands of commonly used spices in Zawia City were collected. The samples were purchased from local markets and spice shops during September 2023. The samples collected included fish spices (Libyan Kitchen), red meat spices (Libyan Kitchen), chicken spices (Libyan Kitchen), red meat Spices (Al Tagori, Tunisian Spices), chicken spices (Al Tagori, Tunisian Spices), fish cumin (Al Tagori, Tunisian Spices), Indomie 1 spice, Kabsa rice spices, Biryani rice mixed spices, Pizza mixed spices (Tajouri), Homemade thyme mixture, Bazaar (Uqeda), Indomie 2 spices. They were kept dry and then placed in glass containers after being numbered and labelled.

2.2. Digestion of Spice Samples.

All apparatus and glassware were initially washed with detergent and then soaked in 10 % nitric acid overnight. They were then rinsed with tap water and finally with distilled water. The glassware was dried in a hot oven at 110°C.

For the determination of heavy metal concentrations, wet digestion of the dried samples was done according to the method described by [33], [34] using an oxi-acidic mixture of HNO3 70% and 30 % H2O2 (4:1). All chemicals used in this experiment were from Sigma Aldrich, St. Louis, MO, USA.

A 40 mL of oxi-acidic mixture was added to 4 g of dry-ground sample placed in a 150-ml beaker, the content of the beaker was heated on an electric heater to 130 o C and mixed for 3 hours. This step was replicated unless a colourless solution was generated. Sample digests were then filtered through the Whatman No. 42 filter paper and diluted to volume using double-distilled deionized water [34]. The final filtrate for each species sample was collected to 25 ml. Finally, samples were kept in plastic vessels at 4 °C until analysis. A blank digestion solution was prepared in the same way for comparison.

2.3. Heavy metal analysis of spice samples

The heavy metals were determined by the XSupreme 8000 equipment product from Oxford Instruments owned by Azzawiya Oil Refining Company to determine the level of heavy elements present in the spice samples under study. The core function of the X-Supreme 8000 is to conduct Xray fluorescence (XRF) analysis, enabling to identify and quantify the elemental composition of samples. The metal contents of each sample were presented in ppm.

3. Results and discussion

Heavy metals (Pb, Cd, As, Hg, Mn, Ni, Cu, Zn, Fe, Co, Cr) analyses have been performed on 13 species, and the results (concentrations and standard deviations) have been presented in Table 1 and Figure 1. The obtained results were compared with the international food standard framework set by (WHO/FOA Codex Alimentarius), which sets Maximum Limits (MLs) based on toxicological data and risk assessment models. These limits are shown in Table 2.

In the following, these results will be presented and discussed separately

3.1. Iron (Fe)

The concentration of Iron (Fe) in the studied samples was 0.53±0.44 ppm, which is significantly lower than the permissible limit of 300 ppm set by international food safety authorities, as mentioned in Table 2. This suggests that no significant external iron contamination occurred during cultivation, processing, or packaging.

Although the level is low compared to the limit, spices are generally consumed in small amounts, so this concentration contributes only minimally to

Table 1. The Maximum Permissible Limit values for studied heavy metals in Spices (mg/kg, ppm) (EU Regulation 2023/915 & FDA Guidelines)

Metal	*EU Limit (ppm)*	*FDA Action Level (ppm)*	*Codex Alimentarius (ppm)*
Pb	0.5 - 3.0	2.0	5.0
Cd	0.1 - 0.5	0.1	0.3
As	0.5 - 1.0	1.0	1.0
Hg	0.03 - 0.1	0.1	0.1
Mn	Not regulated	No limit	No limit
Ni	1.0 - 5.0	No limit	5.0
Cu	20 - 50	50	50
Zn	50 - 100	100	100
Fe	100 - 300	No limit	300
Co	Not regulated	No limit	No limit
Cr	2.0 - 10.0	No limit	10.0

Table 2 The average concentrations (ppm) and SD for studied heavy metals in Studied Spices

element	Avrag	SD
Fe	0.53	0.44
Ni	0.65	0.04
Pb	0.12	0.05
Cd	0.2	0.09
Hg	0.09	0.03
As	0.09	0.03
Co	0.5	0
Cu	0.26	0.15
Zn	0.41	0.30
Mn	2.43	1.82
Cr	0.56	0.51

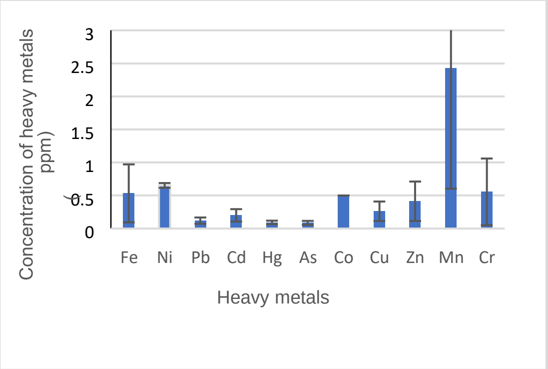

Figure 1. Concentrations (ppm) of heavy metals from spice samples marketed in Zawia city.

Daily iron intake does not constitute any negative impact on the health of the consumer, as iron is one of the important basic elements in the vital processes within the body, which is required for haemoglobin formation and oxygen transport.

The relatively high standard deviation (±0.44 ppm) compared to the mean (0.53 ppm) suggests variation among the individual samples. This may reflect inconsistencies in processing, soil composition, or storage conditions. Moreover, the result implies limited accumulation of iron from soil or irrigation water, possibly due to controlled use of fertilizers or favourable environmental conditions. The iron concentration in the Zawia spice sample is notably lower than that reported in other regions such as Musrata [32], Wadi Ashati and Nafsa Mountain [30]. The low iron level in the Zawia sample indicates a minimal risk of iron-related health issues from its consumption.

3.2. Nickel (Ni)

The results showed that the average concentration of Ni in all spices studied was 0.65 ± 0.04 ppm. This level falls well beneath the (1.0-5.0 ppm) threshold set by [35] for Ni in spices, indicating no immediate health risk from dietary exposure [36]. The Ni levels in the Zawia spice samples are lower than those reported in comparable studies from other regions [34], [37], [38], [39].

3.3. Lead (Pb)

The average concentration of lead (Pb) in all studied samples was detected at 0.12 ± 0.05. Codex sets the maximum for Pb at 5.0 ppm, so this is significantly below the permissible limit, indicating minimal risk from lead exposure through spice consumption. Overall, these findings are consistent with the findings of [7], [13]. As well as being compatible with the results of [31], who found that the concentration of lead in four different spices sold in the Libyan markets of Misurata ranged between

0.90-0.04 µg/g. However, the results reported by [8] show much higher Pb levels in spices from Misurata, which underscores the importance of conducting more studies to verify the accuracy of the results and determine whether there is a hazard from the consumption of spices in the region.

3.4. Cadmium (Cd)

The measured average concentration of cadmium (Cd) in the studied samples is 0.20 ± 0.09 ppm, aligning precisely with the EU limit for fresh herbs is 0.1-0.5 ppm (applied to dried herbs/spices with adjustment), so the detected value is right at the threshold. This indicates that, while the levels are within acceptable safety thresholds, they are at the upper boundary, warranting attention to ensure they do not exceed safe limits. Comparatively, Tripoli's spices [7] exhibit lower cadmium concentrations, while other regions [40], [41] show varying levels, with some exceeding safe thresholds. Ensuring the safety and quality of spices requires adherence to international standards and regular testing to mitigate heavy metal contamination.

3.5. Mercury (Hg)

The measured average concentration of mercury (Hg) in the studied spice samples is 0.09 ± 0.03 ppm. This level is lower than the Codex Alimentarius maximum permissible limit for mercury in spices, which is 0.1 ppm, indicating that the mercury content in these samples is within internationally accepted safety thresholds. A study conducted in Tripoli [42] established mercury concentrations in spices ranging from 0.037 to 3.338 ppm, with some samples exceeding the recommended limits.

Compared to other international studies, the results demonstrated notable variation. For example, researchers in [9] reported generally low levels of Hg in spices in Poland, ranging from <0.005 to 0.030 ppm. In the same way, in Saudi Arabia [41], mercury levels in spices were reported to be below the detection limit, reflecting minimal risk from mercury contamination in that region. On the other hand, [43] examined commonly consumed spices and herbs in Malaysia and found mercury concentrations ranging from 0.06 to 0.52 ppm, with some samples exceeding the permissible limits. This highlights the importance of implementing stringent quality control and monitoring systems to ensure consumer safety.

3.6. Arsenic (As)

The detection of arsenic (As) at 0.086 ppm in spices marketed in Zawia, Libya, is well below the international regulatory limit of 1.0 ppm, as set by the World Health Organization (WHO), Codex Alimentarius, European Union (EU), and the U.S. Food and Drug Administration (FDA). This suggests that, at least in this particular study, the arsenic levels are within safe limits for human consumption according to global standards.

Limited published data exist on arsenic levels in spices marketed in Libya. Unfortunately, there are limited publicly available peer-reviewed studies on heavy metal contamination, mainly arsenic, in spices specifically marketed in Libya. However, a few general observations can be made based on similar North African and Middle Eastern studies. For example, a Study [44] from a neighbouring country (Egypt) has reported arsenic levels in some spice samples ranging from 0.05 to 0.3 ppm, which aligns closely with the studied result. Another study [45], conducted in Egypt, reported arsenic concentrations in spice ranging from 0.1 ppm to 4.8 ppm in spice blends, which exceeded the maximum permissible limits of arsenic. An additional study in Tunisia [46] reported higher arsenic concentrations in certain locally grown herbs due to irrigation with contaminated water. Another study [47] detected arsenic in spices from Lancaster, PA, and quantified it as 0.048 ppm. While the level of detected arsenic in spice from Lancaster, PA and this study appears relatively low, it underscores the need for continued monitoring of heavy metals in the food supply, especially in agricultural regions with potential historical contamination.

3.7. Cobalt (Co)

The concentration of cobalt (Co) in the studied spice samples was found to be 0.50 ± 0.00 ppm, indicating a consistent presence across all samples analyzed. Although cobalt is an essential trace element required for vitamin B12 synthesis and other biological functions, excessive intake can be toxic [48]. The World Health Organization (WHO) has not set a specific maximum permissible limit for cobalt in spices; however, dietary exposure should be monitored, especially in regions with potential environmental contamination. The spices sourced from Asian origin consistently show higher cobalt concentrations (0.210-0.680 ppm) compared to those reported in American-origin spices (0.531-0.056 ppm) across all four types of spices studied [49]. This places the current study results within the upper range of the American data and comparable to the lower-to-mid range of Asian spices. This suggests that while cobalt levels in Libyan spices are not alarmingly high, they do warrant continuous monitoring, particularly when benchmarked against international samples known for higher exposure to environmental or industrial cobalt contamination.

3.8. Copper (Cu)

The detection of copper (Cu) at a concentration of 0.262±0.147 ppm in spices marketed in Zawia, Libya, suggests that the levels are relatively low and likely not an immediate health risk, as the WHO/FAO permissible limit for Cu in spices is typically around 20–50 ppm [21]. On the other hand, still present due to environmental contamination, agricultural practices, or processing methods. A higher concentration of Cu than the current study was detected in pieces from Misurata`s markets, using some spices (black pepper, turmeric) had Cu levels ranging from 0.35 to 1.2 ppm [50]. The study by [45] reported copper (Cu) concentrations in Egyptian spices ranging from 3.72 to 21.04 ppm, with the highest levels observed in hot red pepper and the lowest in paprika. These levels are considerably higher than those found in the current study, which may be attributed to several factors, such as spice origin, where spices grown in regions with contaminated soil or industrial pollution tend to accumulate more heavy metals [51]. In addition, regions differ in their use of fertilizers, pesticides, and irrigation methods. Countries that rely heavily on copper-based agrochemicals may have higher copper residues in spices [52]. Additionally, it should be emphasized that processing and handling, including machinery and tools, may introduce contamination [53].

3.9. Zinc (Zn)

The zinc (Zn) concentration of 0.41±0.30 ppm detected in spices from Zawia's markets, Libya, is relatively low compared to international regulatory limits (e.g., Codex Alimentarius recommends <50 ppm for Zn in spices) and falls well below levels of concern. This suggests minimal contamination and negligible health risks from excessive intake. A similar result was detected in [31], which dealt with four types of spice samples (turmeric, heat, black pepper and red pepper) collected from the markets of the city of Misurata, and the results obtained it was noted that the average concentration of zinc in the samples was 0.02-0.61 ppm. In [8], the concentration of zinc was found to be (0.8-14.5 ppm), which is within the permissible limits of the World Health Organization 50 ppm but is noticeably higher than levels detected in studied samples. More comparative data highlights significant geographical variability in Zn contamination: for example, a study was done in Ethiopia to determine the Zn concentration in samples of korarima, red pepper, ginger, and turmeric and found Zn concentrations ranging from 7.30–29.2 ppm, likely due to zinc-rich volcanic soils and traditional farming practices [54], [55]. Another research conducted in Chittagong, Bangladesh, reported zinc levels in turmeric and red chilli ranging from 48.97 to 116.89 mg/kg, significantly higher than the levels detected in Zawia. Numerous factors may contribute to this noticeable difference in zinc levels observed in different spices from different origins. This includes soil composition, where the mineral content of soil significantly influences the uptake of trace elements by plants. Soils deficient in zinc or with high pH levels can limit zinc availability to crops, the use of fertilizers and pesticides, particularly those containing zinc [56].

3.10. Manganese (Mn)

The average manganese concentration detected in this study was found to be 2.43±1.82 ppm, indicating a relatively low level of this essential trace element. There is no maximum permissible limit (MPL) set by Codex Alimentarius or many international food safety authorities for manganese (Mn) in spices because it is an essential nutrient with low toxicity at typical dietary levels, and spices contribute minimally to total intake. Regulatory focus is directed more toward toxic metals with known health risks. The manganese levels identified in the studied spices are notably lower than those reported in various studies. For example, these results are much lower than those obtained by [57], who found that the concentration of manganese in spices and aromatic plants ranges from 12.5 to 192 ppm. Also, less than ten times those results were obtained by [32] for Mn in imported spice samples collected from the markets of Wadi Al-Shati area in Southern Libya. Another study [30] was done in Libya, testing some spices collected from two major stores located in the Alasaba and Tagasat regions to evaluate the levels of some heavy metals, including Mn, and the obtained results for Mn ranged from 0.33 to 1.80 ppm, which is relatively smaller than the level of Mn detected in the current study. The elevated Mn content may be attributed to differences in environmental conditions, agricultural practices, or soil composition in the regions from which the samples were sourced.

3.11. Chrome (Cr)

The concentration of chromium (Cr) in the spice samples collected from Zawia markets was found to be 0.56±0.50 ppm, indicating a relatively low but variable presence of this element across the analyzed samples. The detected level of Mn is below the maximum limits set by many food safety authorities for total chromium in spices (2-10 ppm) [58], [59]. The detected levels in this study fall within a range commonly reported in similar studies from the region. In [30] some spices collected from stores located in Alasaba and Tagasat in Libya were studied, and the concentration of chromium ranged from 0.13 to 1.57 ppm. In [57] the concentration of Cr in the studied spice samples is in the range of 0.06 to 2.94 ppm. Researchers in [60] investigated samples of spices commonly used in Eritrea, and the concentration of Cr in the spice samples was in the range of 0.71 to 2.00 and was 26.63 ± 0.18 ppm in Cumin, which is above the permissible limit of Cr set by the EU (2-10 ppm) [59], [61]. Chromium exists in multiple oxidation states, but the two most relevant forms in food safety and human health are chromium (III) and chromium (VI). It is toxic only at high levels. However, without speciation analysis to distinguish between Cr (III) and Cr (VI), such limits should be interpreted cautiously to avoid misjudging potential health risks.

3.12 Statistical Analysis

The t-test analysis compared concentrations of various heavy metals across different spice samples in this study. The results indicate that there is a statistically significant difference between Hg and Cd ($p = 0.0007$) and between Fe and Mn ($p = 0.0053$), as their p-values are less than 0.05. This suggests meaningful variation in their concentrations. On the other hand, comparisons between Pb and As, Cr and Ni, and Zn and Cu showed no significant differences (p-values > 0.05), (0.08, 0.72, 0.19, respectively), indicating similar levels of these metal pairs across the samples. These findings highlight specific metal pairs with potential differences that may warrant further investigation regarding their sources or effects.

4. Conclusions and recommendations

This study evaluated the concentrations of 11 heavy metals: Lead (Pb), Cadmium (Cd), Arsenic (As), Mercury (Hg), Manganese (Mn), Nickel (Ni), Copper (Cu), Zinc (Zn), Iron (Fe), Cobalt (Co), and Chromium (Cr) in spices marketed in Zawia, Libya. The results revealed that all spices under consideration contained different quantities of heavy elements that were targeted by examination. However, their concentrations were significantly below international safety limits (Codex Alimentarius, WHO). The detected concentrations in Zawia's spices were: iron (Fe: 0.53±0.44 ppm), nickel (Ni: 0.65±0.04 ppm), lead (Pb: 0.12±0.05 ppm), cadmium (Cd: 0.20±0.09 ppm), mercury (Hg: 0.09±0.03 ppm), arsenic (As: 0.086 ± 0.03 ppm), cobalt (Co: 0.50±0.00 ppm), copper (Cu: 0.262±0.147 ppm), zinc (Zn: 0.41±0.30 ppm), manganese (Mn: 2.43±1.82 ppm), and chromium (Cr: 0.56±0.50 ppm). While these results support the overall safety of spices in Zawia's markets, the detection of trace heavy metals highlights the importance of continued monitoring and quality control, particularly for imported spices and potential soil contamination. However, the variation in concentrations calls for further investigation to ensure consistent quality across different batches or sources. Nonetheless, understanding the factors influencing trace element content in imported and non-imported spices is crucial for ensuring food safety and nutritional adequacy. Continuous monitoring and adherence to safety standards are essential to maintain these low levels and ensure consumer safety. The recommendation of this study is to encourage more research institutions in Libya to conduct regular testing of heavy metals in commonly consumed spices and other food items. Inform consumers and traders about the importance of food safety and the potential health risks posed by long-term exposure to low levels of toxic metals such as arsenic and mercury. Developing a comprehensive food safety framework will not only protect public health but also strengthen consumer trust in both locally produced and imported spices.

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