مجلة جامعة بني وليد للعلوم الإنسانية والتطبيقية
Bani Waleed University Journal of Humanities and Applied Sciences
تصدر عن– جامعة بني وليد – ليبيا
Website:https://jhas-bwu.com/index.php/bwjhas/index
المجلد التاسع ـ العدد الخامس ـ 2024 ـ الصفحات (245-254)
ISSN3005-3900

تقييم التلوث بالمعادن الثقيلة في عينات عصير الفاكهة من مدينة طبرق، ليبيا

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Assessment of Heavy Metal Contamination in Fruit Juice Samples from Toubrk City, Libya

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تاريخ الاستلام: 02-10-2024 تاريخ القبول: 27-10-2024 تاريخ النشر: 05-12-2024

الملخص:
في هذه الدراسة تم تقدير تركيز المعادن الثقيلة في عصائر الفاكهة المتوفرة في مدينة طبرق، ليبيا، لتقييم المخاطر الصحية المحتملة المرتبطة باستهلاكها. تم جمع عينات من العصائر المستهلكة بشكل شائع من الأسواق المحلية. باستخدام مطيافية الامتصاص الذري (AAS) تم تحديد مستويات المعادن الثقيلة مثل الرصاص (Pb) والكادميوم (Cd) والزئبق (Hg) والنيكل (Ni) والكوبلت (Co) والكروميوم (Cr) والمنجنيز (Mn)والحديد (Fe) والنحاس (Cu) والخارصين (Zn). ومن المطمئن غياب الكادميوم والكوبالت والكروم والزئبق في جميع العينات، مما يدل على الالتزام بمعايير السلامة في عمليات الإنتاج. ومع ذلك، فإن وجود مستويات متفاوتة من النحاس والمنغنيز والرصاص، يثير مخاوف بشأن المخاطر الصحية المحتملة المرتبطة بالاستهلاك. إن التركيز العالي للحديد بشكل ملحوظ (51.360 ملغم / لتر) أمر مثير للقلق بشكل خاص، حيث تجاوزت العديد من العينات حدود السلامة التي وضعتها المنظمات الصحية الدولية. تثير هذه النتائج مخاوف كبيرة بشأن سلامة الغذاء والصحة العامة في طبرق، مما يسلط الضوء على الحاجة إلى المراقبة المنتظمة والإجراءات التنظيمية للتخفيف من مخاطر التلوث في عصائر الفاكهة.

الكلمات المفتاحية: المعادن الثقيلة، عصائر الفاكهة، التلوث ، سلامة الغذاء، مطيافية الامتصاص الذري.

Abstract:
In this study, the concentration of heavy metals in fruit juices available in Tobruk city, Libya, was estimated to assess the potential health risks associated with their consumption. Samples of commonly consumed juices were collected from local markets. Using atomic absorption spectroscopy (AAS), levels of heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), nickel (Ni), cobalt (Co), chromium (Cr), manganese (Mn), iron (Fe), copper (Cu) and zinc (Zn) were determined. The absence of cadmium, cobalt, chromium and mercury in all samples is reassuring, indicating compliance with safety standards in the production processes. However, the presence of varying levels of copper, manganese and lead raises concerns about potential health risks associated with consumption. The significantly high concentration of iron (51,360 mg/L) is particularly worrying, as many samples exceeded the safety limits set by international health organizations. These results raise significant concerns about food safety and public health in Tobruk, highlighting the need for regular monitoring and regulatory measures to mitigate the risk of contamination in fruit juices.

Keywords: Heavy metals, fruit juices, contamination, food safety, Atomic Absorption Spectroscopy.

Introduction

Fruit juices rank among the popular beverages in Arab nations like Libya, offering a blend of minerals, vitamins, nutrients, and phytochemicals crucial for enhancing overall health. When enjoyed in moderation as part of a well-rounded diet, fruit juices provide numerous health advantages. They contribute positively to well-being, supporting health and diminishing disease risk. Consequently, fruit juices have gained significance as a staple in contemporary dietary practices (1)(2) . Heavy metals are significant contaminants in the food chain, causing serious health issues even at minimal levels of consumption(3). These metals are ubiquitously present in our environment, either occurring naturally in food or entering through human activities such as industrial and agricultural processes(4).Zinc makes up approximately 33 µg/g of an adult's body mass and is crucial as a component of numerous enzymes that play key roles in various physiological processes, including protein synthesis(5) Copper serves as a coenzyme and is an important cofactor for iron utilization, collagen formation, and the neutralization of free radicals. (6) Copper and iron ions are necessary for the synthesis of metalloproteins. However, excessive iron intake can result in Parkinson's disease due to the accumulation of iron oxide(7).Heavy metals pose a significant threat as environmental pollutants, potentially leading to adverse health effects if present in excessive amounts in the food supply. Numerous cases of human diseases, disorders, and organ malfunctions resulting from metal toxicity have been documented(8). Lead and cadmium are industrial pollutants that significantly harm human and animal health. These metals accumulate primarily in the liver and kidneys. To reduce exposure to these toxic elements, it's important to regularly monitor food and feed and establish maximum limits for heavy metal(9) The composition of heavy metals in food is a topic of interest due to their dual nature—some are essential nutrients like iron, zinc, copper, chromium, cobalt, and manganese, while others such as lead, cadmium, nickel, and mercury can be toxic at certain levels(10). Of particular concern for their harmful health effects are mercury, lead, cadmium, tin, and arsenic. The canning process, commonly used for preserving food, can also introduce heavy metal contamination(11). In recent years, the consumption of juices has surged, driven by their widespread availability and the growing emphasis on healthier dietary choices. However, the health benefits of these beverages are undermined when they are contaminated with either organic or inorganic compounds, posing risks to consumers(12) .Industrialized juices, for instance, may harbor various harmful substances such as pesticides and toxic metals (. The primary sources of contamination typically stem from fruit cultivation in polluted soils, the use of contaminated input materials, and inadequate storage practices(13). Consuming foods with high nutritional value like fruits and their products helps prevent and treat many diseases. To ensure the necessary and required level of essential trace elements, heavy metals, antibiotics and pesticide in fruit juices, indicators may create unacceptable implications on humanity(14). Trace elements can accumulate in the human body which may lead to severe health issues, and hence, their content in the juices should be controlled to establish the consumable/safe level.(15) While living organisms need different amounts of essential elements like iron, cobalt, zinc, magnesium, and copper for biochemical processes, exceeding the intake limits can be detrimental to human health(16). Heavy metals found in fruit juices originate naturally, either dissolved from the soil or absorbed from the environment during the fruit's growth process. However, human activities also contribute to heavy metal contamination in soil and water, leading to significant residues in fruits(17). Heavy metals such as lead (Pb), cadmium (Cd), arsenic (As), mercury (Hg), copper (Cu), chromium (Cr), and nickel (Ni) pose potential health risks upon ingestion, especially with prolonged exposure(18). Unlike many other pollutants, heavy metals stored in plants and fruits are particularly hazardous due to their resistance to environmental breakdown, leading to bioaccumulation and heightened toxicity levels. Consequently, they present a significant risk to consumers as they can be transmitted through the food chain..(19) Recent studies indicate that heavy metals are significant contaminants found in packaged food, particularly in beverages. The primary sources of this contamination include high levels of toxic metals in the fruits used, which may stem from polluted agricultural soil and irrigation water, as well as the excessive use of pesticides and fertilizers during fruit cultivation(20). Due to their ability to resist biodegradation, heavy metals often linger in ecosystems and accumulate across various levels of food chains, posing a notable threat to public health(21). Heavy metals have emerged as some of the most persistent food contaminants because they are stable, have long half-lives, are non-biodegradable, can bioaccumulate, are transferable, and are highly toxic even at low concentrations(22).

This study aims to identify the presence of metal elements lead, nickel, cadmium, cobalt, chromium, manganese, iron, copper, zinc, and mercury in industrial fruit juices to enhance food safety for consumers(23). Consequently, to mitigate the global health risk posed by heavy metal pollution, it is imperative to minimize the release and discharge of metals from human activities, thereby lowering metal concentrations in industrial juices, which is likely a primary source of mineral contamination in fruit juices(24).

EXPERIMENTAL WORK

Sample Collection

Eight samples of industrial juices were collected in Tobruk, Libya, with eight different brands purchased from local markets. In the laboratory, the juice samples were filtered through a Büchner filter to prevent the atomization tube in the atomic absorption device from clogging. Standard solutions, prepared from a 100 mg/L solution derived from a 1000 mg/L standard solution, were used for each measurement. The absorbance of lead, nickel, cadmium, cobalt, chromium, manganese, iron, copper, zinc, and mercury was measured using an atomic absorption apparatus.

Determination of Heavy Elements:

The heavy elements were analyzed using an atomic absorption spectrophotometer (Thermo Scientific iCE 3300 AAS) instrument, manufactured in the USA.

AAS (Model: is 3300, Thermo Scientific, designed in UK, Made in China)

RESULTS AND DISCUSSION

Table 1. shows the concentrations of metallic elements in the samples obtained from industrial fruit juices.

Con.(mg/L)									
Pb	Ni	Cd	Co	Cr	Mn	Fe	Cu	Zn	Hg
N.D	0.032	N.D	N.D	N.D	0.152	0.240	0.918	0.050	N.D
N.D	N.D	N.D	N.D	N.D	0.072	0.097	0.292	0.049	N.D
N.D	N.D	N.D	N.D	N.D	4.390	0.009	0.922	0.042	N.D
0.046	N.D	N.D	N.D	N.D	0.049	N.D	0.678	0.015	N.D

N.D	0.142	N.D	N.D	N.D	0.311	51.360	1.729	0.062	N.D
N.D	0.148	N.D	N.D	N.D	0.257	1.598	1.748	0.093	N.D
N.D	0.345	N.D	N.D	N.D	0.036	N.D	0.803	0.012	N.D
N.D	0.121	N.D	N.D	N.D	0.309	1.076	1.900	0.111	N.D

Where the abbreviation (**N.D**) indicates that it was Not Detected.

The assessment relies on the defined standards for heavy metal constituents in drinking water, established by both the World Health Organization (WHO) (25)and the Libyan National Center for Standardization and Metrology (LNCSM)(26). Its main aim is to confirm that the levels of these elements in industrial juices meet the specified standards, thus ensuring their safety and purity for consumption by the public.

Table2.Guideline in drinking water by Libyan National Center for Standardization and Metrology (LNCSM) and the World Health Organization (WHO)

Heavy element	**LNCSM permissible limit (mg/L)**	**WHO permissible limits (mg/L)**
Lead	**0.005**	**0.01**
Nickel	**0.02**	**0.02**
Cadmium	**0.003**	**0.005**
Cobalt	**0.0**	**0.0**
Chromium	**0.05**	**0.05**
Manganese	**0.05**	**0.5**
Iron	**0.3**	**0.3**
Copper	**1.0**	**1.0**
Zinc	**3**	**5**
Mercury	**0.001**	**0.001**

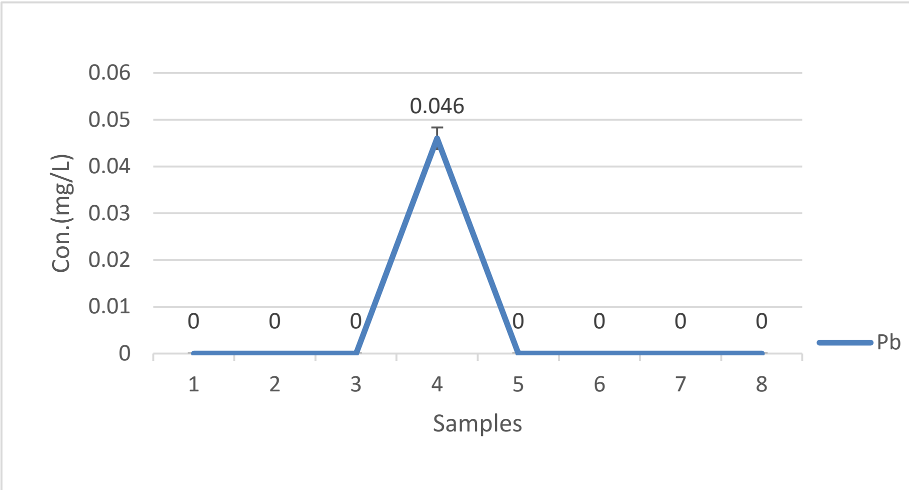

Fig.1: The average Lead (Pb) concentration (mg/L) at different samples.

Only one sample exhibited a lead concentration within the range of 0.046 mg/L, whereas the remaining samples fell below the detection limit. According to both Libyan National Center for

Standardization and Metrology (LNCSM) and World Health Organization(WHO) standards, Therefore, this sample exceeds the permissible limit.

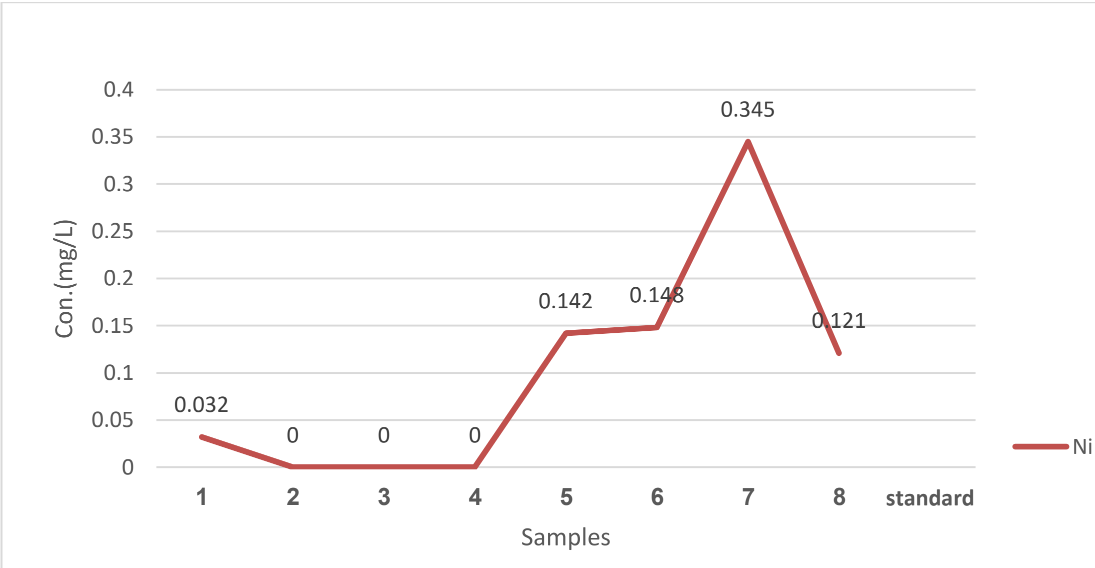

Fig.2: The average Nickel (Ni) concentration (mg/L) at different samples.

The concentration of nickel in only five samples ranged between (0.032 mg/L - 0.345 mg/L), while the rest of the samples were less than the detection limit, and according to both Libyan National Center for Standardization and Metrology (LNCSM) and World Health Organization(WHO) standards, The five samples are not within the permissible limits.

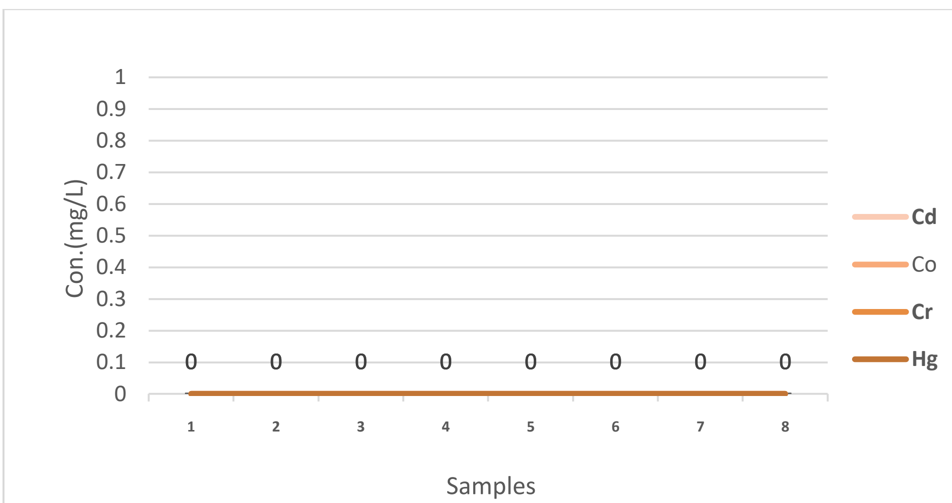

Fig.3: The average cadmium, cobalte, chromium and mercury (Cd,Co,Cr and Hg) concentration (mg/L) at different samples.

The concentrations of cadmium, cobalte, chromium and mercury in all samples were less than the detection limit, and according to the Iibyan National Center for Standardization and Metrology (LNCSM) and World Health Organization(WHO) standards , Therefore The eight samples are free from Cd,Co,Cr and Hg

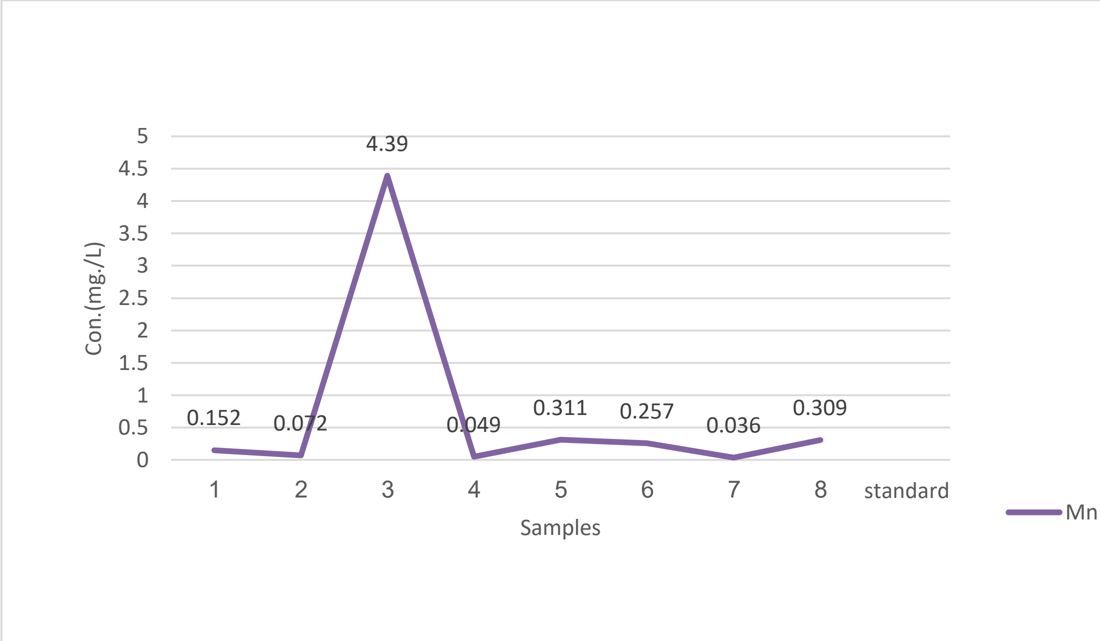

Fig.4: The average Manganese (Mn) concentration (mg/L) at different samples.

according to the Iibyan National Center for Standardization and Metrology (LNCSM) the samples(4,7) were within detection limit while the rest of the samples are not within the permissible limits. While all samples were within the permissible limits according to World Health Organization(WHO) standards, except the sample (3) whose concentration was (4.390 mg/L),

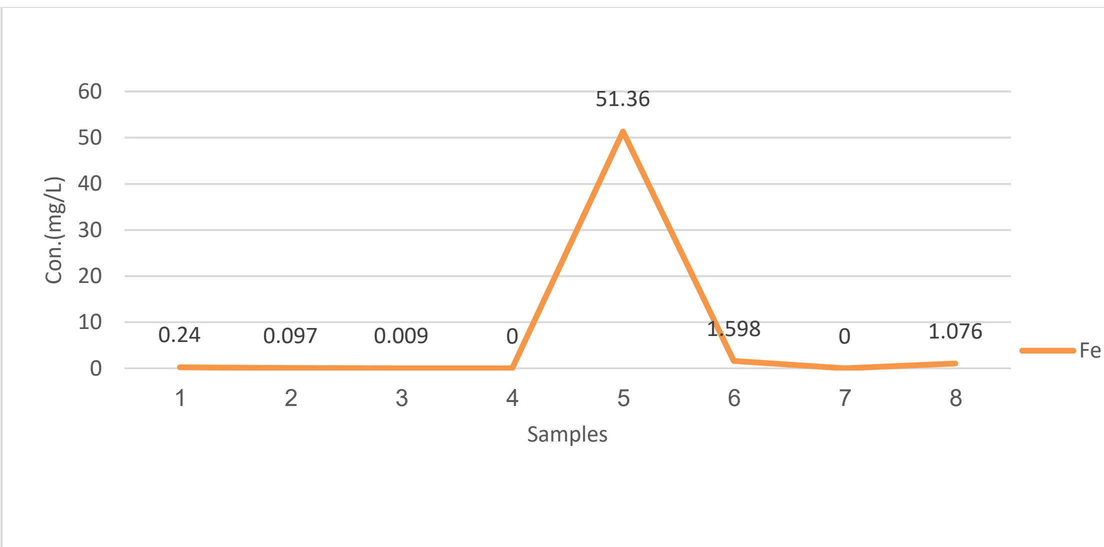

Fig.5: The average Iron (Fe) concentration (mg/L) at different samples.

The concentration of iron in samples ranged between (0.009 mg/L – 51.360 mg/L), while samples 4 and 7 were less than the detection limit, according to the Iibyan National Center for Standardization and Metrology (LNCSM) and World Health Organization(WHO) the samples (1,2,3) were within the permissible limits standards, while (5,6,8) are not within the permissible limits, especially sample No.5,which exceeded the reasonable limit.

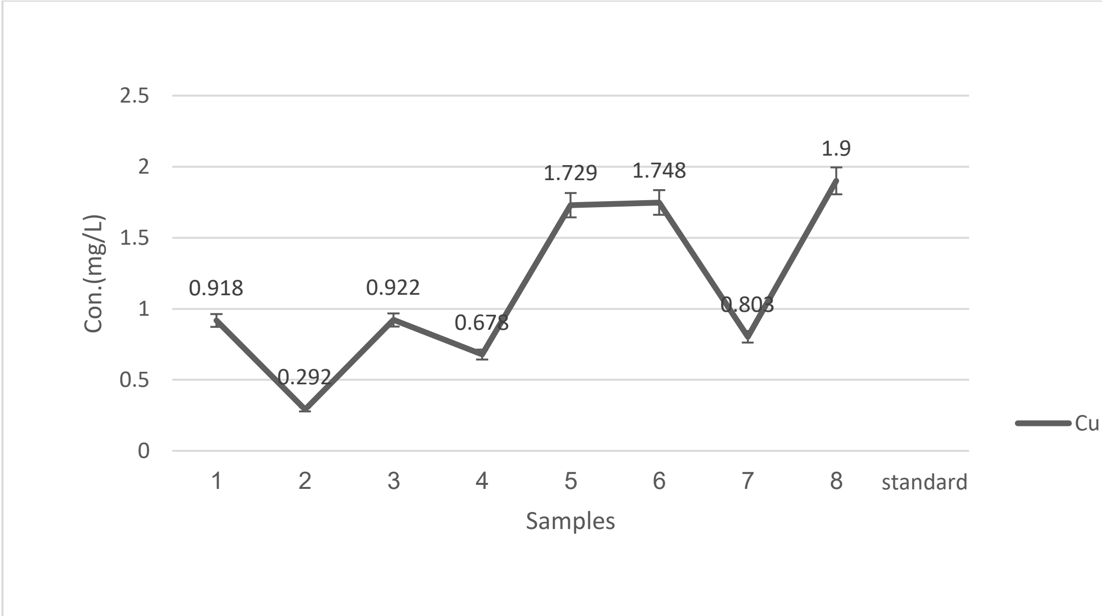

Fig.6: The average Copper(Cu) concentration (mg/L) at different samples.

The results of measuring the concentration of copper for the studied samples ranged between (0.292mg/L - 1.900mg/L), and when looking at the permissible percentages within the Iibyan National Center for Standardization and Metrology (LNCSM) and World Health Organization(WHO) standard, we find that all samples are less than the permissible limits. except the sample (5) whose concentration was (1.729mg/L), the sample (6) whose concentration was (1.748mg/L), and the sample (8) whose concentration was (1,900 mg/L) exceeded the limits allowed in the standard specifications, but it does not pose a threat.

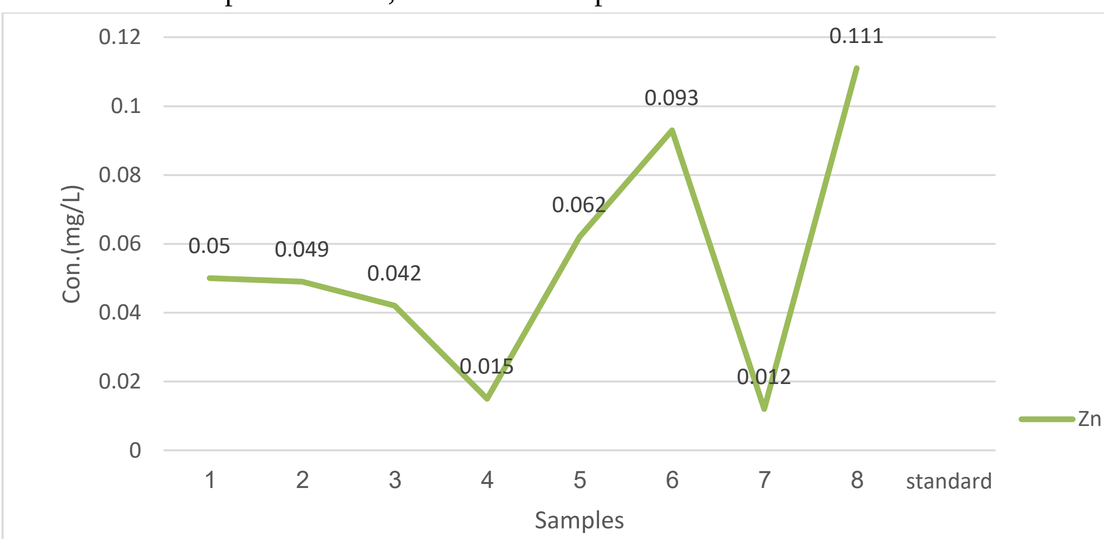

Fig.7: The average Zinc (Zn) concentration (mg/L) at different samples.

The results of measuring the concentration of zinc for the studied samples ranged between (0.012 mg/L - 0.111 mg/L), and when looking at the permissible percentages within the Iibyan National Center for Standardization and Metrology (LNCSM) and World Health Organization(WHO) standard, , we find that the maximum allowable limit for zinc is (3mg/L) and (5 mg/L) respectively, therfore all samples are less than the permissible limits.

Lead:

Only one sample exhibited a lead concentration within the permissible limit.

All other samples were below the detection limit, thus meeting standards.

Nickel:

Five samples had nickel concentrations within the range (0.032 mg/L - 0.345 mg/L).

These concentrations exceed the permissible limits set by both Libyan and WHO standards.

Cadmium, Cobalt, Chromium, and Mercury:

All samples had concentrations below the detection limit, meeting standards.

Manganese:

Except for one sample, all others were within permissible limits.

The single sample with a concentration of 4.390 mg/L exceeded both Libyan and WHO standards.

Iron:

Samples had concentrations ranging between (0.009 mg/L – 1.598 mg/L).

Three samples did not meet the standards, and one sample exceeded Libyan standards but wasn't considered threatening.

Copper:

Most samples were within permissible limits except for samples 5, 6, and 9.

These samples exceeded Libyan standards but were not considered threatening.

Zinc:

All samples were within permissible limits set by both Libyan and WHO standards.

Overall, while most heavy metals are within acceptable limits, there are instances of exceedance, especially regarding nickel, manganese, iron, and copper in some samples. It's crucial to address these exceedances to ensure industrial fruit juice safety.

To sum up, the zinc concentrations in industrial fruit juice were within acceptable limits. However, there were cases of exceeding permissible levels for nickel, iron, and copper. This underscores the critical need for monitoring and managing heavy metal concentrations in industrial fruit juice to ensure consumer safety.

CONCLUSIONS

After examining all samples (comprising 8 samples per element, totaling 80 samples for ten elements), the analysis indicated that the levels of Cobalt (Co), Cadmium (Cd), Chromium (Cr), Mercury (Hg), and Zinc (Zn) did not surpass the specified maximum allowable limits. However, there were varying concentrations of Copper (Cu), Nickel (Ni), Manganese (Mn), and Iron (Fe), with one sample showing an exceptionally high level of Iron. This indicates that although most samples met regulatory standards, some exhibited elevated metal concentrations that require further investigation. The results highlight the importance of vigilance and stringent measures to ensure the safety and well-being of regular fruit juice consumers.

RECOMMENDATIONS

Expand Research on Industrial Juices: Undertake studies on various types of industrial juices to enhance our understanding of the concentrations of mineral elements, especially heavy metals. This research will help maximize their benefits while reducing potential health risks.

Avoid Cultivating Near Polluted Areas: Refrain from growing fruits and vegetables in polluted areas or near factories to prevent contamination, which can negatively impact human health.

Public Education Initiatives: Organize seminars and specialized workshops to inform the public about the health risks of consuming elements at concentrations above international standards. Increased awareness can help mitigate cumulative effects or nutritional deficiencies caused by elevated levels of these elements.

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