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# Determination of Some Heavy Metal Contents in Chips Sample Collected from Some Libyan Markets

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**Abstract**
The global surge in the consumption of ultra-processed foods, particularly potato chips, has raised significant public health concerns regarding nutritional deficiencies and heavy metal contamination. This study aimed to conduct a comprehensive quantitative analysis of selected heavy metals Chromium (Cr), Zinc (Zn), Copper (Cu), and Iron (Fe) in seven different brands of potato chips available in local markets in El-Beida City, Libya. The samples were digested using concentrated nitric acid and analyzed via Atomic Absorption Spectroscopy (AAS). The results indicated that the concentrations of heavy metals fluctuated within the following ranges: Cr (0.121 – 1.401 ppm), Zn (1.9672 – 3.6674 ppm), Cu (0.136 – 0.675 ppm), and Fe (0.520 – 1.995 ppm). Zinc recorded the highest average concentration (2.854 ppm). Notably, Sample 5 exhibited a relatively high concentration of Chromium (1.401 ppm) compared to the other samples. A health risk assessment was conducted using guidelines established by the United States Environmental Protection Agency (US EPA). The Estimated Daily Intake (EDI) values for all metals were found to be very low. The total Hazard Index (HI) was calculated to be 0.00663, which is significantly below the threshold of 1, indicating no significant non-carcinogenic health risk. Furthermore, the Target Cancer Risk (TCR) for Chromium was calculated at falling within the globally acceptable risk range. In conclusion, the consumption of the studied potato chip brands does not pose an immediate health risk regarding the analyzed elements under normal consumption conditions, though continuous monitoring of Chromium sources is recommended.

**Keywords:** Potato Chips, Heavy Metals, Atomic Absorption Spectroscopy, Health Risk Assessment, Target Hazard Quotient, Libya

## Introduction

The global food industry has witnessed a paradigm shift over the past few decades, characterized by an escalating demand for ultra-processed foods (UPFs). Among these, potato chips (crisps) stand out as one of the most universally consumed snack foods, transcending cultural, age, and socioeconomic boundaries. The burgeoning popularity of potato chips is attributed to their palatability, sensory attributes (such as crunchiness and flavor), extended shelf-life, and aggressive marketing strategies (Monteiro *et al*., 2019) [1]. However, the nutritional profile of potato chips typically high in trans-fats, sodium, and acrylamide, while being devoid of essential micronutrients has long been a subject of public health concern. Beyond these well-documented nutritional deficiencies, a more insidious threat lurks within the food supply chain: the contamination of agro-products with heavy metals. Heavy metals, defined as metallic elements with high atomic weights and densities (typically greater than 5 g/cm³), have emerged as a critical environmental and food safety hazard. Unlike organic pollutants, heavy metals are non-biodegradable and persist indefinitely in the ecosystem (Jaishankar *et al*., 2014) [2]. The presence of toxic heavy metals such as Lead (Pb), Cadmium (Cd), Arsenic (As), Mercury (Hg), and even essential elements like Zinc (Zn), Copper (Cu), and Iron (Fe) at supra-optimal concentrations in food products constitutes a severe threat to human health. The contamination of potato chips with these elements is a multifaceted problem originating at various stages of the production continuum: agricultural practices (soil composition, irrigation with contaminated groundwater, and the application of phosphate fertilizers or pesticides), industrial processing (machinery wear and tear, frying oils), and packaging materials (Zhang *et al*., 2021) [3]. Potatoes, as root crops, possess a unique physiological mechanism that makes them highly susceptible to the bioaccumulation of heavy metals from the soil. They act as efficient "bioaccumulators," transferring toxicants from the rhizosphere directly into the edible tubers (Ebssa & Wondimu, 2021) [4]. When these contaminated tubers undergo industrial processing specifically slicing, blanching, and deep-frying the concentration of certain heavy metals can be altered. While some water-soluble metals may leach into the blanching water, the dehydration process during frying can lead to a relative concentration increase of non-volatile metals per unit weight of the final product (Dghaim *et al*., 2015) [5]. Furthermore, the widespread use of aluminum packaging in the chip industry poses an additional risk of post-processing contamination, particularly with Aluminum (Al) and Nickel (Ni) (Oyeyinka & Oyeyinka, 2018) [6]. Despite regulatory frameworks established by international bodies such as the Joint FAO/WHO Expert Committee on Food Additives (JECFA), the European Food Safety Authority (EFSA), and the U.S. Food and Drug Administration (FDA), frequent violations of maximum permissible limits (MPLs) for heavy metals in snack foods are reported in developing nations. This is largely due to rapid industrialization, inadequate waste management, and the use of untreated wastewater for agricultural irrigation (Turkdogan *et al*., 2003) [7]. The rationale for this study is rooted in the disproportionate consumption of potato chips by children and adolescents—a demographic highly vulnerable to the neurotoxic, nephrotoxic, and carcinogenic effects of heavy metals. Even low-level, chronic exposure to Pb or Cd during developmental stages can result in irreversible cognitive deficits, stunted growth, and metabolic disorders (Renzetti *et al*., 2021) [8]. Therefore, it is imperative to continuously monitor the heavy metal concentrations in heavily consumed snack foods to ensure consumer safety, update local regulatory standards, and trace the sources of contamination within the food supply chain.The primary objective of this research is to conduct a comprehensive quantitative analysis of the concentrations of selected heavy metals (Cr, Cu, Zn, and Fe) in various brands of potato chips available in the local market. The specific objectives are: To estimate the dietary intake of these heavy metals through the consumption of potato chips and assess the potential non-carcinogenic and carcinogenic health risks for consumers using the Target Hazard Quotient (THQ) and Hazard Index (HI). The intrusion of heavy metals into the food web is predominantly an anthropogenic phenomenon, driven by mining, smelting, the indiscriminate use of agrochemicals, and the combustion of fossil fuels (Nagajyoti *et al*., 2010) [9]. Once deposited in agricultural soils, these metals undergo complex biogeochemical transformations. Their bioavailability to plants, particularly tuber crops like potatoes, is governed by soil pH, organic matter content, cation exchange capacity (CEC), and the presence of competing ions (Zhao *et al*., 2015) [10]. The transition from raw agricultural produce to ultra-processed foods like potato chips introduces additional variables. Studies indicate that thermal processing, a staple in chip manufacturing, does not degrade heavy metals; rather, the loss of moisture and volatile organic compounds leads to an "enrichment effect," where the residual mass contains a higher proportional concentration of the metal than the raw material (Rojas *et al*., 2020) [11]. A substantial body of literature has investigated heavy metal contamination in potato chips across various geographical locales, revealing a heterogenous global landscape of food safety. In the Middle East and North Africa (MENA) region, where rapid urbanization has strained environmental resources, several studies have reported alarming levels of contamination. For instance, a study conducted in Saudi Arabia by Al-Ahmadi (2019) [11] analyzed 15 different brands of potato chips and found that the concentrations of Pb and Cd exceeded the permissible limits set by the Saudi Food and Drug Authority (SFDA) in 20% of the samples. The study hypothesized that the elevated Pb levels were correlated with the use of certain flavoring additives and packaging materials. Similarly, in Egypt, Saleh *et al*. (2020) [12] evaluated the heavy metal profile of locally produced and imported potato chips. The findings indicated that while essential metals (Fe, Zn, Cu) were within safe ranges, Cd concentrations in locally produced, salted chips were significantly higher than in imported variants, pointing toward localized soil or irrigation water contamination in Egyptian agricultural hubs.In the Asian subcontinent, where agricultural lands are notoriously stressed, research has yielded critical insights. A comprehensive study in Pakistan by Bashir *et al*. (2021) [13] utilized AAS to analyze 30 potato chip samples. The researchers reported mean Pb and Cd concentrations of 0.85 mg/kg and 0.42 mg/kg, respectively, both of which surpassed the JECFA limits of 0.1 mg/kg and 0.2 mg/kg. Furthermore, the study highlighted a statistically significant difference ($p < 0.05$) in metal concentrations between plain and flavored chips, suggesting that the spices and artificial flavoring powders used in products like "Masala" or "BBQ" chips act as secondary vectors for heavy metal introduction. In Iran, Mehrnia *et al*. (2022) [14] focused specifically on the role of frying oils, concluding that the repeated heating of oils in industrial fryers leaches Nickel (Ni) and Chromium (Cr) from the stainless-steel machinery into the oil, which is subsequently absorbed by the potato slices. In European contexts, where agricultural and processing regulations are ostensibly stricter, the prevalence of heavy metals is lower but not absent. A large-scale surveillance study across European Union member states by previous study [3] noted that Cd remains the primary contaminant of concern in potato-based products. The report indicated that while average Cd levels in potato chips were below the EU maximum level of 0.1 mg/kg (wet weight), certain batches originating from Eastern European countries, where soil cadmium anomalies exist, frequently required market withdrawals.An emerging theme in the literature is the migration of heavy metals from packaging materials into the food matrix. Potato chips are highly susceptible to lipid oxidation; therefore, they are often packaged in laminated films that include a thin layer of aluminum foil to act as an oxygen and light barrier. However, if the inner polymer lining (usually polypropylene or polyethylene) is compromised, direct contact between the acidic or salty chip surface and the aluminum layer can facilitate the leaching of Aluminum (Al) into the food. A study by Akhtar *et al*. (2023) [15] investigated this phenomenon by comparing the Al concentrations in chips stored in pure plastic packaging versus aluminum-laminated packaging over a 6-month shelf life. The results demonstrated a 300% increase in Al concentrations in the aluminum-packaged chips at the end of their shelf life, whereas the purely plastic-packaged chips showed no significant change. This underscores the necessity of including elements like Al and Sn in heavy metal analyses of potato chips, despite their traditional classification as "light metals." Modern food toxicology has moved beyond merely detecting the presence of heavy metals; it now emphasizes quantitative health risk assessment. Previous studies uniformly adopt the guidelines established by the US Environmental Protection Agency (US EPA, 2021) [16] to estimate risk.The Target Hazard Quotient (THQ) is the most widely utilized metric in the reviewed literature. If the THQ is < 1, the exposed population is considered to be at no significant non-carcinogenic risk. If THQ ≥ 1, there is a potential for adverse health effects. For example, in a study conducted in Nigeria by Omolaoye *et al*. (2019) [17], the THQ for Cd in children consuming potato chips was calculated to be 2.14, indicating a clear and present health hazard. Conversely, a study in Italy by Di Benedetto *et al*. (2021) [18] reported a THQ of less than 0.5 for all analyzed metals, reflecting the efficacy of European food safety nets. Furthermore, the Carcinogenic Risk (CR) is calculated for metals with established carcinogenic properties, primarily Pb, Cd, and As. The acceptable range for CR is between $10^{-6}$ (neglible risk) and $10^{-4}$ (acceptable risk). Research by Huang *et al*. (2022) [19] in China highlighted that the CR for As exposure via potato chip consumption among adolescents was 1.2 x $10^{4-}$, teetering on the edge of unacceptable carcinogenic risk, primarily attributed to the consumption of chips fried in contaminated groundwater. In Libya several studies were carried out to estimate the contents of heavy metals in different samples foods, fruits, plants, soils by used different methods as Atomic Absorption Spectroscopy (AAS), Ionic coupling plasma (ICP), X-Ray Fluorescence (XRF) and others [23-49], This study aims to evaluate the contents of heavy metals in Chips sample collected from some Libyan Markets by used Atomic Absorption Spectroscopy(AAS).

## Experimental Part

### Sampling

Seven different samples of potato chips were collected from local markets at El-Beida City, Libya, the selected samples were illustrated in Table 1.

**Table 1:** The studied samples of potato chips

| Samples No | Samples Types |
|---|---|
| 1 | Chitos |
| 2 | Brings |
| 3 | Doretos |
| 4 | Big Chips |
| 5 | Mojo Chips |
| 6 | Tiger |
| 7 | Marcellia |

### Grinding / Sample Size Reduction

The dried samples pieces were crushed and grounded by using mortar and piston to fine powder to get homogenized samples. Later, the dried for further process.

### Digestion

0.5g of accurately weighed dry ground samples was taken into the Pyrex beaker of about 100ml then strong acids (oxidizing agents) conc. nitric acid about 5 ml were added to it and stirred with magnetic stirrer on hot plate at 80 $^0$C for 1 hour until the clear solution was obtained. Then, it was cooled and filtered into 50 ml flask through whahtman filter paper no 42, and were diluted with de-ionized water up to the mark of 50ml labeled the flask and kept for further analysis.

### Analysis

The samples were analyzed atomic absorption Type thermos at Central Lab of Omar Al-Mukhtar University, Libya.

## Results & Discussion

### Results

The contents of the studied heavy metals Cr, Zn, Cu and Fe were fluctuated in the ranges of (0. 121 - 1.401 ppm), (1.9672 – 3.6674 ppm), (0.136 – 0.675 ppm) and (0.520 - 1.995 ppm), respectively. The high contents of Chromium was recorded in sample 5 (1.401 ppm), while the higer content of Zinc was recorded in samples 7, 6 and 5 with values of 3.6674, 3.4578 and 3.2236 ppm.

**Table 2:** Concentrations of Cr in the studied Chips samples

| Sample | Cr | Zn | Cu | Fe |
|---|---|---|---|---|
| 1 | 0.268 | 2.6649 | 0.429 | 1.619 |
| 2 | 0.503 | 2.1881 | 0.555 | 1.995 |
| 3 | 0.237 | 1.9672 | 0.423 | 1.147 |
| 4 | 0.457 | 2.8054 | 0.675 | 1.626 |
| 5 | 1.401 | 3.2236 | 0.372 | 1.021 |
| 6 | 0.261 | 3.4578 | 0.534 | 1.724 |
| 7 | 0.121 | 3.6674 | 0.136 | 0.520 |

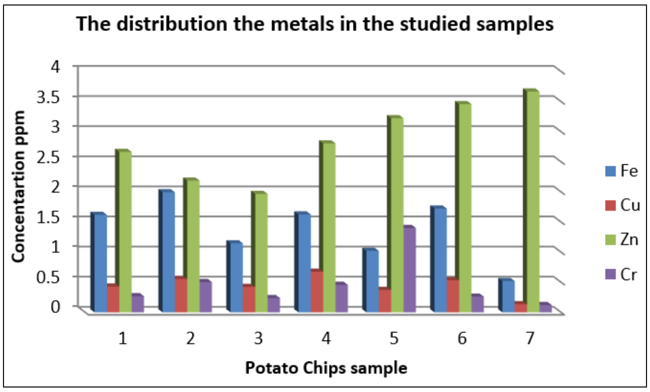


**Fig 1:** The distribution of the studied heavy metals in Chips sample

### Discussion

#### Zinc (Zn)

Zinc recorded the highest average concentration (2.854 ppm). Zinc is an essential trace element for human health. The Food and Agriculture Organization (FAO) and the World Health Organization (WHO) typically set high permissible limits for zinc in food, often ranging between 50–100 ppm. Comparing the results, all recorded concentrations fall well within the safe permissible limits. Iron (Fe): The average concentration of Iron was 1.379 ppm. Iron is also an essential nutrient. The concentrations did not exceed common international limits (which are often set around 15–20 ppm for processed foods). This suggests the chips do not pose a risk regarding iron toxicity.

#### Copper (Cu)

Copper recorded a low average (0.446 ppm). The maximum allowable limit for copper in foodstuffs is generally around 5–10 ppm (according to standards such as those set by the

European Food Safety Authority). The recorded levels are significantly lower than these health limits.

### Chromium (Cr)

The average concentration was 0.464 ppm. It is noteworthy that Sample No. 5 recorded a relatively high concentration of 1.401 ppm. While Chromium (III) is an essential nutrient, total chromium exposure must be monitored. Although the levels in Sample 5 are higher than other samples, they generally remain below strict regulatory limits for snacks in many jurisdictions (often around 2–3 ppm), though this variation warrants attention.

### Health Risk Assessment

To evaluate the potential health risks, the following indices were calculated based on equations recommended by the United States Environmental Protection Agency (US EPA).

### Assumptions used in the calculations

Average Body Weight (BW) = 70 kg.
Daily Intake Rate (IR) = 20 g/day (0.02 kg/day.
Oral Reference Dose (RfD) in mg/kg/day:
Fe = 0.7, Cu = 0.04, Zn = 0.3 and Cr = 1.5 (For Chromium III, the predominant form in food.
Cancer Slope Factor (CSF) for Chromium (for conservative calculation) = 0.5 $(mg/kg/day)^{-1}$.

### Estimated Daily Intake (EDI):

Calculated using the formula:

**EDI = (C \ IR) / BW**

Where C is the mean concentration:

**EDI (Fe) = (1.379 \ 0.02) / 70)** = 0.00039

**EDI (Cu) = (0.446 \ 0.02) / 70) = 0.00013**

**EDI (Zn) = (2.854 \times 0.02) / 70)** = 0.00082

**EDI (Cr) = (0.464 \ 0.02) / 70)** = 0.00013

All EDI values are very low compared to the recommended daily allowances.

### Target Hazard Quotient (THQ) and Hazard Index (HI):

Calculated using the formula:

**THQ = EDI / RfD**

The Hazard Index is the sum of
THQs:

HI = \ THQ

**Total HI = 0.00663**

**Table 3:** The RED, EDI and THQ Values in the studied samples

| Index / Elements | RFD | EDI | THQ |
|---|---|---|---|
| **Fe** | 0.7 | 0.00039 | 0.00056 |
| **Cu** | 0.04 | 0.00013 | 0.000325 |
| **Zn** | 0.30 | 0.00082 | 0.00273 |
| **Cr** | 1.5 | 0.00013 | 0.00009 |

### Discussion

If the value of THQ or HI is less than 1, it indicates no significant non-carcinogenic health risk to consumers. Since the total Hazard Index (HI) is 0.00663, which is significantly less than 1, the consumption of these products does not pose a non-carcinogenic health risk associated with these elements.

### Target Cancer Risk (TCR):

Calculated for Chromium (the element often assessed for carcinogenicity) using the formula:

**TCR = EDI \ CSF**

Note: The CSF used here is for Chromium VI as a worst-case scenario, while chromium in food is typically non-carcinogenic Chromium III:

**TCR (Cr) = 0.00013 \ 0.5,** = 0.000065 **(6.5 \ $10^{5-}$)**

The globally acceptable range for cancer risk is typically between $10^{-6}$ and $10^{-4}$. The calculated value falls within this acceptable range. However, considering Sample 5 contained a higher concentration (1.401 ppm), calculating TCR specifically for that sample yields a slightly higher value, but it remains within acceptable limits for incidental consumption.

### Conclusion

The analysis revealed that the studied potato chip samples contain concentrations of heavy metals (Fe, Cu, Zn, Cr) that fall within the permissible limits set by international standards such as the World Health Organization (WHO) and FAO [50]. The calculations of risk indices (HI < 1) and cancer risk (TCR < $10^{-4}$) indicate that the consumption of these products is safe for health regarding these elements under normal consumption conditions. It is recommended to continue monitoring sources of Chromium, particularly in samples showing higher variability, to ensure continued compliance with health standards.

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