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Evaluation of heavy metals in spices: A case study from local market in Wadi Otbba south of Libya

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Abstract:

In this work, five of the most popularly used spices were studied to determine of some toxic metals (cadmium, chromium and lead) in turmeric, red pepper, caraway, ginger, and cinnamon plants Microwave digestion was used in the preparation of the samples. This was analyzed using Atomic Absorption Spectrophotometer (AAS). The results were compared with the safety standards (WHO). The average concentration of heavy metals as Pb detected ranged from 3.469ppm-5.369ppm, Cd ranged from 0.052pm-0.554 ppm. While Cr was found to range between 0.04 ppm – 0.01 ppm, most of them were well within the permissible limits, except Pb in Turmeric was found to be 5.369 ppm and Cd in red pepper was found to be 0.554ppm, the calibration curves for the analyzed metals demonstrated strong linearity, with R^2 value more than 0.955 this, indicated that the reliability of the curves.

Key Words: Evaluation, heavy metals, spices, Wadi Otbba, South Libya.

1- Introduction:

Heavy metals are naturally occurring elements with high atomic weights and densities, known for their potential toxicity even at low concentrations. Among these, cadmium (Cd), chromium (Cr), and lead (Pb) are of particular concern due to their widespread industrial use and harmful environmental and health effects [1]. Cadmium is primarily released through mining, battery production, and industrial processes, accumulating in the environment and posing risks to human health, particularly affecting the kidneys and bones [2]. Chromium exists in various oxidation states, with hexavalent chromium (Cr^{6+}) being the most toxic, linked to carcinogenicity and environmental contamination [3]. Lead, historically used in paints, gasoline, and pipes, is a persistent toxic metal that affects neurological development, especially in children [4]. pathways, and effects of these heavy metals is crucial for mitigating their impact on ecosystems and public health, so, it was necessity to follow the proportion of toxic heavy metals in spices, the most popular spices using in southern food in Libya such as turmeric, red pepper, caraway, ginger, and cinnamon. Spices have played a crucial role in culinary traditions, as well as to medicine. Beside enhancing the flavor of food, they also offer numerous health benefits due to their rich nutritional and medicinal properties [5]. Forth more, the widely used spices, each of these spices has a unique flavor aroma, and cultural significance. Turmeric is renowned for its brilliant color and anti-inflammatory properties, while red pepper adds heat and boosts metabolism. Caraway is valued for its digestive benefits, ginger is enhanced for its warming effects and immune-boosting properties, and cinnamon is recognized for its sweet, aromatic flavor and ability to regulate blood sugar. During the processing, packing and packaging of these spices, some chemical dyes are added that enhance the color in the spices, this may be contaminated with heavy metals to food as a habit may result in accumulation of these metals in human organs and lead to different health troubles [2]. These metals can infiltrate and contaminate plants, vegetables, fruits, and canned foods through air, water, and soil during industrial

processing and packaging. Therefore, this study is crucial, as toxic heavy metals pose potential hazards not only to various compounds but also to human health. Their cumulative nature and toxicity make them particularly concerning, even though they are typically found in agricultural soils at low concentrations [2-4]. According to Food Organization in south of Libya, spices serve various purposes however, limited information is available regarding their safety concerning heavy metal contamination Assessing the levels of heavy metal toxicity in spices would help determine their potential health risks and provide valuable data on their safety within the country, the previous studies were achieved in Tripoli, Ashatti, and Musratta [6-8], therefore, the main objective of this study was to determine the content of some heavy toxic metals (Cd, Cr and Pb) in some common spices available in markets of Wadi Otbba in South of Libya.

2- Materials and Methods:

The experimental material consists of Five spices, turmeric, red pepper, caraway, ginger, and cinnamon Samples were purchased from the local market in Wadi Otbba, South of Libya, they were classified as shown in Table (1) according to their English, scientific names and the used part of the plant. The samples were directly subjected to analysis as parched in powder shape.

Table 1: Scientific and common names of the studied spices

Common name	Scientific name	Used part
Turmeric	Curcuma longa	Rhizomes
Red pepper	Capsicum Frutescens	Fruits
Caraway	Carum carvi	Seeds
Ginger	Zingiber afficenalis	Rhizomes
Cinnamon	Cinnamomum verum	Bark

Chemicals included nitric acid, sulphonic acid and hydrogen peroxide were used as received. Standard sample solutions of Cd, Pb, and Cr were obtained from Merck company. For determination of heavy metal concentrations, a wet digestion of the dried samples was achieved according to the method described by M. Mreamy and etals [3-7]. 0.6 grams of the sample was weighed and placed in a condensing flask, then 6 mm of mixture HNO_3 and H_2SO_4 concentration of 65% (Sigma Aldrich manufacturing) was added, then placing the flask in the existing condensing chamber in the gas cabinet above a heat source for an hour and a half. After, the sample was left to cool, then 3.5 mm of H_2O_2 (30 % concentration) from Sigma Aldrich company was added. The sample was repositioned in the condensation chamber in the gas cabinet above a heat source for about 45 minutes. After the sample was completely dissolved, the sample was left to cool to room temperature and then fed into a standard flask with a capacity 25 mm and muzzled with water distilled to the mark, The digestion process was repeated multiple times until a clear solution was obtained the contents of the standard decanter into plastic containers and kept in refrigerated under 8°C until the sample is measured. A standard solution for each heavy metal of (Cd, Cr, Pb) to be analyzed was prepared and used for calibration .

The measurements were performed with Atomic Absorption Spectrophotometer (Perkin Elmer 2380) model double beam, cathode lamps of Pb, Cd and Cr were used at specific wavelength o

3- Results and Discussion:

The concentrations of Pb, Cd, and Cr in the specified spices were evaluated against the Maximum Permissible Limit (MPL) established by the National Food Standards. The levels of heavy toxic metals were assessed in accordance with the relevant safety standards set by the MPL for "other food and condiments. Lead, Cadmium and Chromium concentrations have been performed on five spices samples were collected from Wadi Otbba market as shown in table1.

Table 2: Content of Pb, Cd, Cr in spices samples (in ppm).

no	Sample name	Pb (in ppm)	Cd (in ppm)	Cr (ppm)
1	Turmeric	5.369	0.152	Nd
2	Caraway	3.671	0.133	Nd
3	Red pepper	4.513	0.554	0.02
4	Ginger	3.972	0.064	0.01
5	Cinnamon	3.469	0.052	0.04
6	MPL	5 ppm	0.2 ppm	0.1ppm

MPL: Maximum Permissible Limit, Nd: Not detected.

Lead is recognized as one of the most toxic environmental pollutants, as it interacts with various biomolecules and has severe impacts on the nervous, reproductive, gastrointestinal, renal, cardiovascular, and immune systems, as well as multiple developmental processes [8]. The lead concentrations in different samples presented in Table 2, ranged from 3.67 ppm in caraway, and 4.15 ppm in ginger to 3.97 ppm in red pepper and 3.58 ppm in cinnamon. These levels remain below the Maximum Permissible Limit (MPL) set by FAO/WHO (1984) therefore considered tolerable with the except turmeric 6.36 ppm which is over the maximum allowed, In the previous study [6] carried out to measure the concentration of lead spices sold in the market in the city of Tripoli, an increase in the concentration of lead was observed in turmeric samples and it is similar to this sample, while study was done in Wadi Ashatti region shown that the concentration of Pb was below the MPL [3]. In other similar studies [1,4,8,13] conducted in different parts of the world on various spices, it was found that lead concentrations did not exceed the maximum permissible limit set by the WHO. However, despite remaining within the allowed limit, these studies indicated that consuming large amounts of these spices daily could pose health risks to consumer.

Cadmium, though present in smaller quantities, is classified as a human carcinogen [10]. An increase in its concentration in food can pose a potential health risk. As indicated in Table 3, cadmium levels in all five experimental samples remained within the Maximum Permissible Limit (0.2 ppm) established by FAO/WHO (1984), except for the red pepper sample. The cadmium concentrations recorded were 0.15 ppm in turmeric, 0.13 ppm in caraway, 0.11 ppm in ginger, and 0.05 ppm in cinnamon. However, the red pepper sample exhibited a significantly higher concentration of 0.45 ppm. This elevated level may result from the use of cadmium-containing fertilizers or the cultivation of these crops in soil treated with sewage sludge, a previous study was carried out in Korea found that cadmium concentrations exceed the maximum permissible limit in red pepper similar to this case [4], other investigations in Gana and Egypt [5,1,], and local investigations in Al-shatti, Musrata, and Tripoli were found different concentrations of cadmium in red pepper according to surrounding environments [3,6,7].

Chromium, contamination in the environment primarily arises from industrial activities, including metal plating, textile dyeing, and the leather industry, Chromium can leach into groundwater and is a significant environmental pollutant [8]. Long-term inhalation of chromium compounds can increase the risk of lung cancer, Short-term exposure can lead to irritation of the respiratory tract, coughing, wheezing [11], The concentration of chromium in different experimental samples is shown in Table 3. As revealed by the analytical data no high concentrations were found in red pepper and cinnamon, they were well within the limits of the MPL, while concentrations of chromium not detected in turmeric, caraway and ginger, these results were found to be harmonious to many previous studies [12,13].

4- Method Validation:

Method validation is a crucial analytical technique used to assess the reliability and reproducibility of analytical data. The validation process involves evaluating key parameters such as accuracy, precision, and the limit of detection [9]. In this study, the following parameters were examined: linearity, repeatability, reproducibility. The sample analysis was conducted following the recommended

methodologies. In current study calibration curves for the three toxic elements were constructed using at least three different element concentrations along with a blank as shown in Table 3, the calibration curves for the analyzed metals demonstrated strong linearity, with an R^2 value more than 0.955.

Table 3: Calibration curves for metals

no	Metal	Equation	R^2
1	Lead	Y= 0.064	0.985
2	Cadmium	Y= 0.039	0.966
3	Chromium	Y= 0.008	0.962

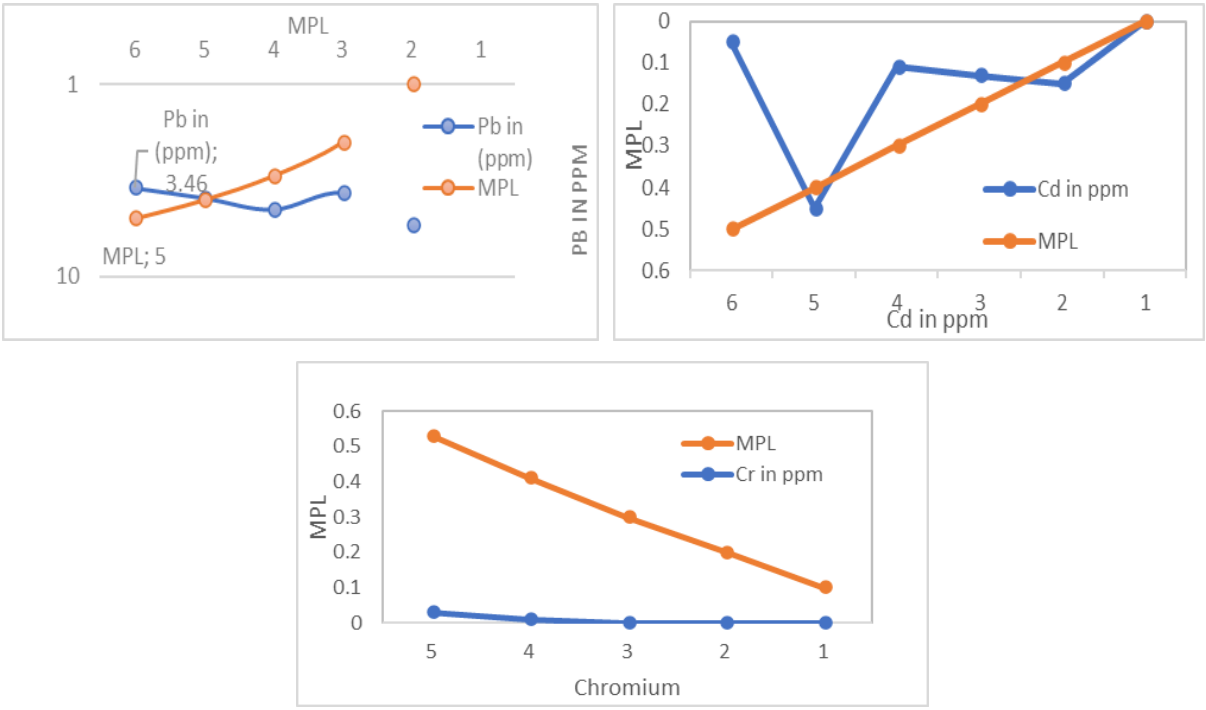

Figure (1): The concentrations of Pb, Cd and Chromium versus concentration of MPL.

5- Conclusion:

The findings of this study indicate that the level concentrations of lead, Cadmium and Chromium in most of the analyzed spice samples fall within the permissible limits established by the WHO and FAO. However, certain samples exceeded the maximum allowable levels, suggesting variability in the sources of these spices within the local market in Wadi Otbba South of Libya. While these levels concentrations are considered safe when spices are consumed in moderate amounts, excessive daily intake could pose risks. This underscores the importance of regulatory authorities in conducting regular monitoring of spices available in the local market and educating the public about potential health hazards associated with their overconsumption. To gain deeper insights into the safety and suitability of these spices for human consumption, a more comprehensive study covering a wider range of spice samples from different regions of Libya—both locally produced and imported is recommended. Additionally, investigating the presence of other heavy metals beyond lead, Cadmium and Chromium would offer a more thorough assessment, particularly given the frequent use of these spices in daily Libyan cuisine.

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