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# Estimation of Some Main and Secondary Mineral Elements in Palm Fruits Growing in Different Regions of Libya

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# تقدير بعض العناصر المعدنية الرئيسية والثانوية في ثمار النخيل النامية في مناطق مختلفة من ليبيا

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**Abstract:**
Date palms are exposed to heavy metal contamination, which is dangerous due to its stability and bioaccumulation. The sources of heavy metal contamination in dates are numerous, including environmental pollution from soil, air, and water, as well as agricultural practices such as the use of pesticides and chemical fertilizers. This negatively affects the nutritional properties of dates. Consequently, consuming dates that contain higher levels of heavy metals and their presence in high concentrations harms consumer health. In this study, the concentration of some essential and trace metals in date varieties traded in local markets, randomly selected from the markets of the city of Bani Walid, was determined. The elements (K, Na, Fe, Pb, Cd) were estimated for five Libyan date varieties: (Dakkla, Jafah, Dakkla Waddan, Saidi Date, Apple Date, and Mecca Nucleus Date). Using the atomic absorption and flame method, and comparing the results of this study with the permissible limits set by the World Health Organization and the Food and Nutrition Organization, as well as previous studies, potassium was found to be the predominant mineral. The results were graphically plotted and statistically analyzed. Significant differences were observed in the sodium (Na) and potassium (K) ratios among the studied date varieties. Iron was present in all five date varieties and did not exceed the permissible limit according to the World Health Organization and the Food and Agricultural Organization. Lead was completely absent in the studied date samples. Pearson correlation analysis revealed significant correlations between potassium and sodium in a positive direct relationship, and between cadmium and potassium in a negative inverse relationship.

**Keywords**: Libyan Dates, Mineral Content, Pollution, Primary Elements, Secondary Elements

**الملخص**
ثمار النخيل معرض للتلوث بالمعادن الثقيلة التي تكمن خطورتها في الثبات والتراكم الحيوي، وتتعدد مصادر التلوث بالمعادن الثقيلة في التمور بما في ذلك التلوث البيئي من التربة والهواء والمياه، بالإضافة إلى الممارسات الزراعية مثل استخدام المبيدات والأسمدة الكيميائية، فهذا يؤثر سلبا على الخصائص الغذائية للتمور، بالتالي تناول التمور المحتوية على المزيد من المعادن الثقيلة ووجودها بتركيزات عالية يضر بصحة المستهلك .في هذه الدراسة تم تحديد تركيز بعض المعادن الأساسية والثانوية لأصناف التمور المتداولة في الأسواق المحلية والتي تم اختيارها بشكل عشوائي من أسواق مدينة بني وليد، حيث تم تقدير العناصر ( K, Na, Fe, Pb, Cd ) لخمسة أصناف من التمور الليبية وهي ( دقلة جافة، دقلة ودان، تمر الصعيدي، تمر آبل، تمر نواة مكة ). وذلك باستخدام جهاز الامتصاص الذري واللهب، ومقارنة نتائج هذه الدراسة مع

الحدود المسموح بها في منظمة الصحة العالمية ومنظمة الغذاء والتغذية و الدراسات السابقة، كان المعدن السائد هو البوتاسيوم، وتم جدولة النتائج بيانياً ودراستها إحصائياً، لوحظت فروق معنوية في نسب الصوديوم Na والبوتاسيوم K بين أصناف التمور المدروسة، وأن الحديد موجود في كل أصناف التمور الخمسة ولم يتجاوز الحد المسموح به حسب منظمة الصحة والغذاء، والتغذية الزراعية، وأن عنصر الرصاص غير موجود نهائيا في عينات التمور المدروسة، كشف تحليل ارتباط بيرسون عن ارتباطات مهمة بين البوتاسيوم والصوديوم بعلاقة طردية موجبة، والكادميوم والبوتاسيوم بعلاقة عكسية سالبة.

**الكلمات المفتاحية:** التمور الليبية، المحتوى المعدني، التلوث، العناصر الرئيسية، العناصر الثانوية.

## Introduction

Dates are distinctive fruits that contain small amounts of important minerals, which make up about 2-3% of their weight [1]. It also contains at least 15 different minerals, which is why it is sometimes referred to as a "mine." Among the important minerals found in dates are iron, potassium, calcium, magnesium, copper, zinc, sodium, chlorine, sulfur, manganese, phosphorus, fluorine, and selenium [2]. Due to external factors, dates are exposed to heavy metal contamination, making their consumption unsafe, as soil pollution contaminates dates [3] and water pollution contaminates dates [4]. Heavy metals are defined as those with a density five times that of water (5 mg/cm$^3$), and they are not absorbed through the food chain within living organisms. Even at low concentrations, these metals are toxic and harmful. Essential minerals can also become toxic when their levels exceed the permissible limits [5]. Some heavy metals, such as iron, play a role in cytochrome, ferritin, and hemoglobin at specific concentrations, while zinc is an integral part of proteins and cobalt is one of the components of vitamin $B_{12}$ [6]. On the contrary, other heavy metals, such as lead, cadmium, mercury, and arsenic, are harmful and toxic to living organisms, remaining stable and not degrading even at low concentrations. Plants absorb these heavy metals from contaminated soil, or they may settle on the surface of the plant from the air [7].

## The mineral elements used in the research

Potassium and sodium are considered essential elements in regulating blood pressure. Dates are very rich in potassium and very low in sodium, making them an ideal food for patients with high blood pressure, who are advised to follow a low-sodium diet. Therefore, increasing date production will play a vital role in improving the nutritional status of people around the world [8]. Iron (Fe), which has an atomic number of 26, is found in group eight and period four of the periodic table. This transition element constitutes 50% of the Earth's crust. It can be detected in the soil by its red color [9], and it is naturally present and can also be found in many foods such as meat, egg yolks, kidneys, liver, and some fruits like apricots, bananas, apples, and peaches. Additionally, it is found in some vegetables, grains, seeds, and honey [10]. High concentrations of lead (Pb) and cadmium (Cd) are considered hazardous air pollutants and are toxic to humans when present in food, Therefore, the presence of these elements in dates at levels higher than the permissible limit poses health risks to consumers. Contamination with them is important [11]. Lead is a toxic element that accumulates in the body, especially in children who are going through a sensitive neurological growth phase. This element easily enters the bloodstream and deposits in the bones, teeth, nails, and hair, quickly reaching the brain, liver, and kidneys, where it accumulates as a carcinogenic substance and reduces hemoglobin blood cell levels.[12]. The primary sources of lead vary from country to country, influenced by the historical and contemporary uses of lead-based products, including activities related to mining, metal smelting, manufacturing, and recycling. Additionally, the use of lead-containing paints and leaded gasoline poses a risk [13], as inhaling lead particles from burned materials containing lead is hazardous. Also, the ingestion of lead-contaminated dust, the consumption of water that passes through lead pipes, the eating of food stored in lead containers, and the use of pesticides and agricultural fertilizers that may contain lead [14]. Car fuel is a major source of lead; organic lead is also released into the air when gasoline is burned, which can be inhaled by humans [15]. Many researchers have suggested that consumers wash dates before consuming them to reduce contamination from dust that settles on the dates [16], [17]. Cadmium, a heavy metal found in the Earth's crust, is a non-essential transition metal and can cause cancer [18]. The use of cadmium has significantly decreased in developed countries, but pollution from it still persists. Concern arises from various human activities such as waste incineration, smelting, and phosphate fertilizers [19], but the main source of cadmium is smoking, and cadmium-contaminated foods are primarily consumed by non-smokers [20]. Cadmium is also found in wastewater and cadmium batteries [21]. The danger of cadmium lies in its ability to quickly transfer to the fetus through the placenta [22], and it can be absorbed from the nasal mucosa and transferred to the central nervous system, causing cadmium poisoning [23]. There are some studies on dates grown in the Libyan region aimed at identifying the important mineral elements in different varieties of dates and estimating the daily intake of these elements from date consumption.

This study aimed to identify some major and minor mineral elements in certain types of Libyan palm dates available in the local market of Bani Walid city using flame atomic absorption spectroscopy. There are some other essential and trace minerals that were not measured, and therefore we can say that dates are rich in many nutrients. A local study examined other varieties of Libyan date palms namely (Bakrari, Tabuni, Deglet, Hammouri, and Aami), and estimated the moisture, ash, and mineral content (iron, zinc, potassium, copper, and cadmium). The atomic absorption spectrophotometer showed that the two types of dates contained higher levels of cadmium and lead [24]. Dates can prevent cancer. It was found that the beta-glucans in dates have antitumor activity, as beta-glucans were isolated from Libyan dates and the structure of the purified glucan was determined [25]. Dates also contain ascorbic acid, folic acid, and vitamins such as thiamine and biotin, which are essential for the human body [26]. Many studies have shown that the air is polluted with heavy metals [27], and one study also found high levels of lead, cadmium, and chromium in dates from the United Arab Emirates, exceeding the permissible limits [28]. Many studies have proven that dates are an important food source due to their content of essential minerals such as calcium, phosphorus, and potassium, which are important for the metabolic processes of human cells [29], [30], [31]. Dates also have many benefits as they possess antiviral properties [32] and act as natural antioxidants [33].

**Material and methods**

In this study, the concentrations of some macro and micro minerals were measured in five samples of Libyan dates (Apple date, Dakkla Jafah date, Dakkla Waddan date, Mecca Nucleus date, and Saidi date). Sample collection: Five types of dates were purchased from the local market in the city of Bani Walid and stored in airtight plastic bags to prevent further contamination. The samples were then air-dried in the laboratory for several days to remove moisture according to the A.O.C.A. (1984) method.1984) [34]. All the reagents and chemicals were of analytical grade, and distilled water was used throughout the analysis period.

**Equipment used**

1- The stove.
2- Electric heater.
3- Flame Atomic Absorption Spectroscopy (FAAS).

All the reagents and chemicals were of analytical grade, and distilled water was used throughout the analysis period. All glassware used in sample preparation was soaked in concentrated nitric acid for a full day and then washed with distilled water.

**Preparation method for measurement**

After separating the seeds and cones from the date pulp, the sample was dried at a temperature of 60 degrees Celsius until weight stability was achieved. It was then cooled for some time, and the dried fruits were crushed. The sample was digested using the wet digestion method: 5 grams of the ground sample were placed in a beaker, and 10 ml of concentrated nitric acid were added. The mixture was then placed on a heater in the fume hood until nearly dry. Subsequently, 5 ml of 0.1 N nitric acid were added, and the mixture was filtered using the standard method. The filtrate was placed in a 50 ml volumetric flask and completed with distilled water. The blank solution was prepared using the same steps as above but without the samples. The measurement was conducted using an atomic absorption spectrometer and flame photometry.

**Statistical analysis:**

The reported data represent the mean ± standard error (number of analyzed items). A one-way ANOVA was completed, followed by the HOC post hoc test (Least Significant Difference (LSD)) using the SPSS version 17 statistical package for social sciences. The statistical significance was set at ($P<0.05$).

**Results and Discussion**

**Potassium K**

The results of the statistical analysis showed that the (Apple date) variety had a significantly higher potassium content (18136), while the lowest value was for the Saidi Date (6053) table (1) and Figure (1). Our study aligns with a study of 17 varieties of Moroccan dates (1055.26 – 1604.10) [35]. Our results were much higher than those reported for Saudi date varieties [36].

**Table 1.** Primary and secondary metals contents (mg/kg) in the studied date samples.

| Category | Cadmium | Lead | Potassium | Sodium | Iron |
|---|---|---|---|---|---|
| Apple Date | ND | ND | 18136 | 409 | 0.060 |
| Macca Nucleus | 0.008 | ND | 8754 | 404 | 0.045 |
| Saidi Date | 0.005 | ND | 6053 | 379 | 0.106 |
| Dakkla Waddan | 0.001 | ND | 6283 | 256 | 0.092 |
| Dakkla Jafah | ND | ND | 6074 | 223 | 0.043 |

ND: Not detected below delectation limit (0.0001mg/kg)

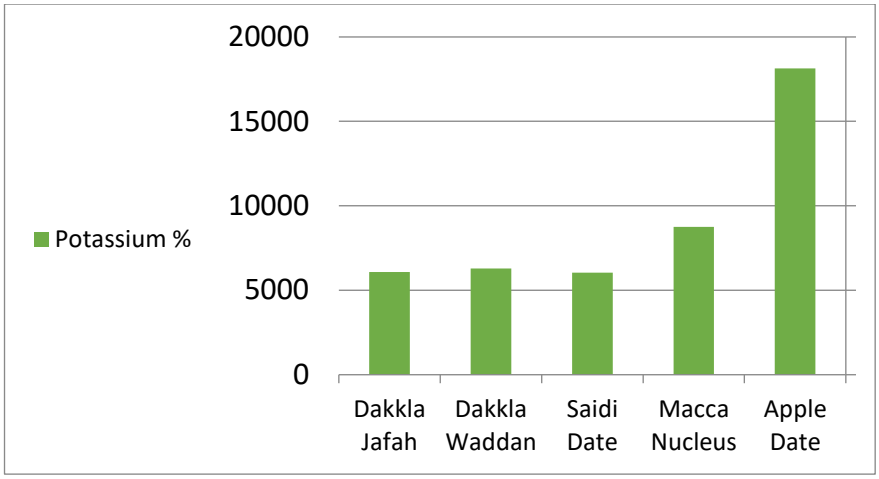


**Figure 1.** Potassium contents in the studied date samples.

**Sodium Na**

The presence of significant differences in sodium content among the studied date samples ,where the sodium percentage in the five studied date samples ranged from (233-409) as in the Table (1) and figure (2). The results showed that highest sodium content was found in the (Apple date) and the lowest in the (Dakkla Jafah date), which is consistent with [37] and [38] for Saudi dates (134-320) and (334-338) respectively.

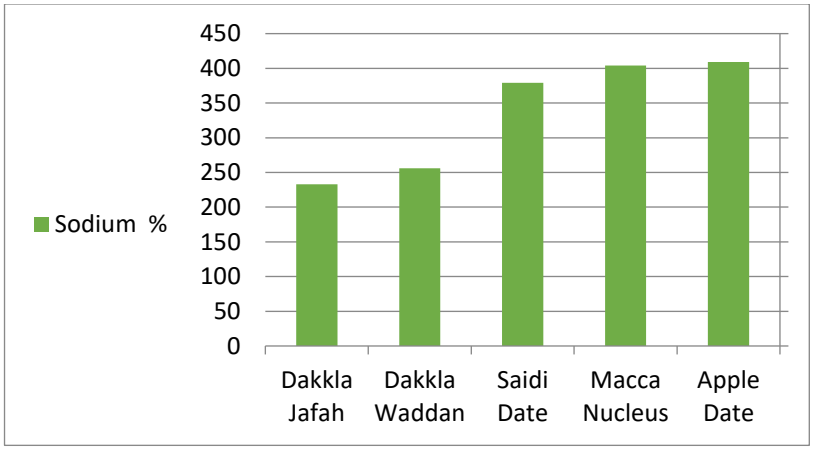


**Figure 2.** Sodium contents in the studied date samples.

**Iron Fe**

Table (1) and Figure (3) displays the iron content in all varieties did not exceed the permissible limits set by the World Health Organization and the Food and Nutrition Organization (0.043 – 0.060), which are comparable to the values of Pakistani dates (0.8 - 0.82) [39]. These values are lower than those obtained for other Libyan dates [24]. There were no statistically significant differences in iron content among the five studied date varieties.

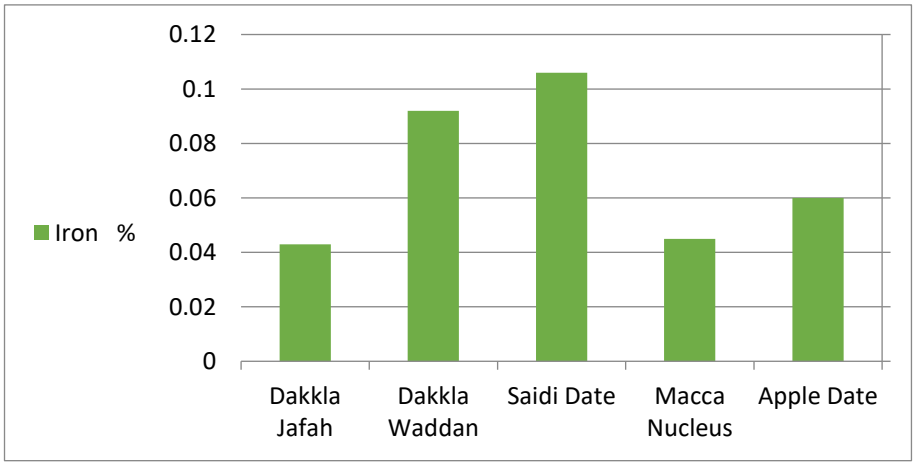


**Figure 3.** Iron contents in the studied date samples.

**Cadmium Cd**

The Cadmium values in the studied date varieties ranged between (0.001– 0.008) and did not exceed the safe limits, while (Apple date) and (Dakkla Jafah date) did not contain cadmium (Figure 4 and Table 1). This is consistent with the values mentioned in study [40] and lower than the values of other Libyan dates (0.00 - 0.58) [24].

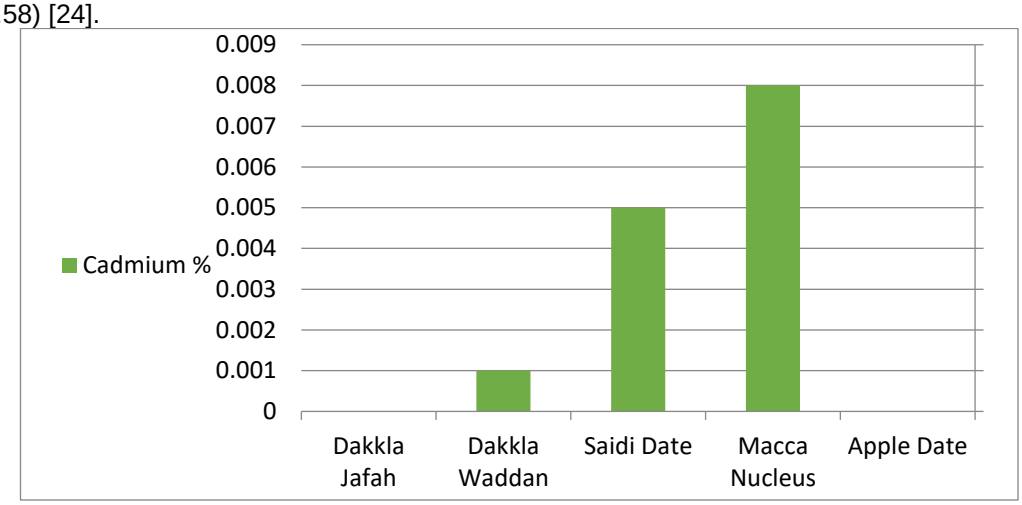


**Figure 4.** Cadmium contents in the studied date samples.

**Lead Pb**

The analysis did not show any lead values in all the samples studied. This could be due to the samples not containing lead or the levels being below the sensitivity of the device. Studies have shown the absence of lead in date varieties in a study of Nigerian dates [41] and Sudanese dates [42]. There is no significant difference between lead (Pb), cadmium (Cd), iron (Fe), and the other studied chemical elements, because iron (Fe) has the highest P.value, which equals (0.522) or (52%), and is greater than the significance level, therefore there is no statistical significance. Table 2 shows the correlation coefficients for the chemical elements in the date samples that were analyzed in this study. It is worth noting that the highest correlation value observed in the study (including all positive and negative correlations) was between potassium and sodium (0.541*) with a statistical significance level (0.05). It was also observed that the P. Value equals (0.037) which is 3.7%, and is higher than the significance level, indicating a positive direct relationship. The Pearson correlation analysis shows that iron has a weak positive relationship with cadmium and sodium, and that cadmium and potassium have a negative relationship as indicated in the table (2). There is no correlation between lead and sodium. And cadmium, as well as potassium and iron.

**Table 2.** The Pearson correlation coefficient for the five elements

| Category | Lead | Cd | K | Na | Fe |
|---|---|---|---|---|---|
| **Lead** | 1 | -0.437- | 2.550 | -0.065- | -0.338- |
| **Sig** | | 0.104 | 0.360 | 0.817 | 0.218 |
| **Cd** | -0.437- | 1 | -0.225- | -0.119- | 4.390 |
| **Sig** | 0.104 | | 0.420 | 0.674 | 0.102 |
| **K** | 0.255 | -0.225- | 1 | 5.41*0 | -0.134- |
| **Sig** | 0.360 | 0.420 | | 0.037 | 0.635 |
| **Na** | -0.065- | -0.119- | 5.41*0 | 1 | 2.830 |
| **Sig** | 0.817 | 0.674 | 0.037 | | 0.307 |
| **Fe** | 0.338-- | .4390 | -0.134- | .2830 | 1 |
| **Sig** | 0.218 | 0.102 | 0.635 | 0.307 | + |

*correlation is significant at the 0.05 level (2-tailed)

**Conclusion**

Many studies conducted on palm fruits have revealed the nutritional and medicinal importance of dates due to their content of various minerals and other chemicals. The mineral analysis of the varieties used in this study (Dekkla Jafha, Dekkla Waddan, Macca Nucleus, Saidi, and Apple Date) showed that they are good sources of essential nutrients such as potassium, sodium, and iron. Potassium was considered the most abundant mineral in all the studied varieties, and the iron levels in any of them did not exceed safe limits. There is a variation in the mineral content among the studied date varieties, which can be attributed to climatic and environmental factors such as soil type, fertilizer dosage, irrigation volume, and ripening stage. This study provides insight into the safety of these dates concerning lead and cadmium, which are among the most hazardous heavy metals. There is no potential public health concern from consuming these dates.

Since the dust adhering to edible plants may be contaminated with heavy metals, it is recommended to wash the fruit before consumption.

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