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Quality evaluation and determination of heavy metals (Fe, Zn, and Pb) in Libyan sidr honey by Atomic Absorption Spectroscopy

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ABSTRACT

This work aimed to evaluate four samples of honey collected from the area extending from the city of Misrata in the east to the city of Tripoli in the west and up to the city of Bani Walid in the south of Libya. Various tests (pH estimation, moisture content estimation, ash content, and electrical conductivity) were applied to confirm the quality of honey samples**.** The pH values were 4.4 to 5.8, the moisture content was 12% to 17%, while the ash content was 0.10% to 0.2%, and the electrical conductivity was 0.32 to 0.50 mS/cm. However, there is a variation in the results obtained due to differences in regions. By comparing the obtained results with international standards, all honey samples were found to be acceptable and lower than the maximum level of FAO limits. The concentration of zinc was less than the maximum level of 20 (µg/g) in the Bani Walid and Zliten samples (12.8 and 18.6 µg/g, respectively), while Misrata and Tripoli samples were higher than the WHO limit, with 21.7 for the former and 29.58 for the latter. However, the lead content was slightly higher than the WHO limit of 2 (µg/g) in the Zliten sample with 2.1 (µg/g), while the other three samples were within acceptable limits with 1.15 µg/g for the Bani-Waleed sample, 1.35 µg/g for the Tripoli sample, and 1.49 µg/g for the Misurata sample. Nevertheless, the Misurata sample had the highest iron level with 50 µg/g among the four samples. It was found to be higher than the WHO limit (40 µg/g), while the other three samples were lower than the maximum level with 37 µg/g, 35 and 40 µg/g for Bani-Waleed, Tripoli, and Zliten samples, respectively. Honey can be used as a biosensor of environmental pollution with heavy metals.

Keywords: Honey, biosensor, heavy metals, atomic absorption.

1. Introduction

Libya has a special geographic location and a large space of 1.6 million Km^2, which provides various ecosystems (El-Hajaji, 2017). The eastern and middle parts of the country have the most plant cover, such as Wadi alkuf and Wadi majer. Different kinds of flowers can be found there, which are considered the main food for honeybees (Al-Traboulsi & Alaib, 2021; Requier et al., 2015). Honeybees feed on nectars of vegetation or plants and produce honey by collecting, transforming, and combining the plant extract with specific substances stored in honeycombs (Rikohe, 2023; Singh, 2022). Honey has various properties (nutritional and medicinal) because of its special chemical composition, which contains carbohydrates, proteins, vitamins, and minerals (Khan et al., 2014; Tafere, 2021). Heavy metals might pollute honey and cause serious health issues for humans (Islam et al., 2014). The journey of searching for food for honeybees makes the latter cover a circle of 5 $km^{2,}$ and contact with various surfaces during this journey might be considered a biosensor of pollution (Danner, 2017; Porrini et al., 2002). Heavy metal content in Libyan Sidr honey has not been investigated until now in the central district of Libya, which encourages this work to be done. Analyzing honey can indicate the contamination of heavy metals, which reflects environmental pollution (Lazor et al., 2012). Iron and zinc are essential elements that the human body needs for normal health and growth due to the roles of iron and zinc in the immune system (Silva et al., 2019). Iron deficiency leads to anemia and degeneration of the nervous system (Ponka, 2004). Zinc can help the skin against ultraviolet radiation and decrease cancer risks (Rostan et al., 2002). Human activities increase the level of heavy metals circulating in the environment (Mishra et al., 2019). The concentration of heavy metals at the biosphere level is increasing rapidly due to industrial activities, which causes environmental problems (Masindi & Muedi, 2018). Nevertheless, the accumulation of metals in the human body might cause severe damage with longer consumption of honey (Solayman et al., 2016). Lead is another metal that might be found in honey, and even its low content is considered a serious threat because of its toxicity (Islam et al., 2014). This search aimed to evaluate the quality and select heavy metal content in Libyan honey.

2. Materials and methods

Five natural liquid honey samples (50 g) were collected from different Libyan cities (Bani-Waleed, Zliten, Misurata, and Tripoli) in June 2023. The selected location of the study (10, 11, and 14) in Libya can be seen in **Figure 1**.

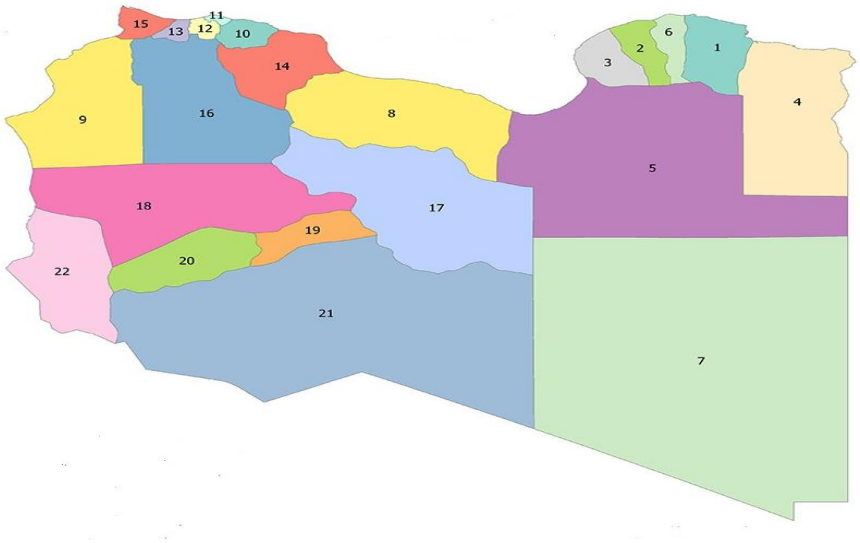

Figure 1. Demonstrates the districts of Libya

2. 1. Samples preparation for AAS measurements

2 g of each honey sample were weighed and placed in a dry oven at 105 °C for 24 h then cooled down. After that, 1 g of each sample was taken into a 100 ml flask and 20 ml of an acidic mixture of 1:1 (HNO_3 and $HCLO_4$) was added to the flask and heated at 70 °C for 2 h and cooled down. 5 ml of concentrated HCl was added and the volume continued to 50 ml with distilled water (Ploegaerts et al., 2023).

2. 2. Physiochemical properties of honey samples

pH, moisture, ash content, and electrical conductivity were measured to estimate the quality of the honey.

2. 3. Determination of (Fe, Zn, and Pb) by AAS

Atomic absorption spectroscopy model varian spectra 220Z at Delta Scientific Laboratory was used to determine the heavy metal content in honey samples.

3. Results and discussion

3. 1. pH measurements

2g of each honey sample was dissolved in 10 ml of hot distilled water, and a pH400 portable pH meter was used.

Table 1. Shows the pH values for the honey samples and FAO standard.

Honey samples	pH values
Bani Waleed	4.4
Misurata	5
Zliten	4.8
Tripoli	5.8
FAO	5

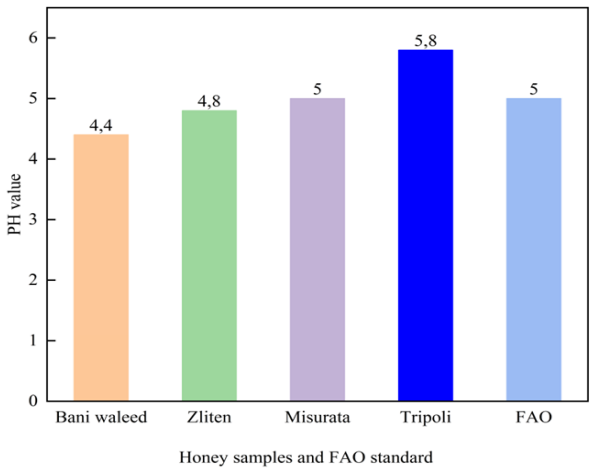

Figure 2. Illustrates the pH values for honey samples and FAO standards.

Figure 2 shows that the pH values for all samples ranged from 4.0 to 6.0. The Bani-Waleed sample had the lowest pH value (4.4), followed by Zliten (4.8) and the Misurata sample (5.0). However, Tripoli had the highest pH value (5.8). When compared with the FAO standard, only the Tripoli sample was higher, and the three others were under the limit and acceptable.

3. 2. Moister content

1 g of each honey sample was weighed in a Teflon container and placed in the oven at 105 °C for 3 hours, and then the ash percentage was measured for each sample.

Table 2. Demonstrates the moister content in honey samples

Honey samples	Moister%
Bani Waleed	16
Misurata	17
Zliten	16
Tripoli	12
FAO	21

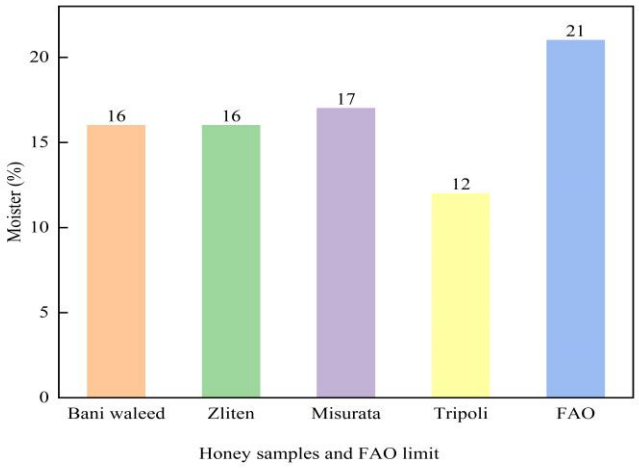

Figure 3. Shows the moister content in honey samples and FAO standard.

It can be seen in **Table 2** and **Figure 3** that all four honey samples contained less moist than the FAO limit (21%) where the Tripoli sample was the lowest at 12% followed by Bani-Waleed and Zliten samples with 16% while the Misurata sample was the highest among the four samples with 17%. The reason for that might be the hot weather in Libya. The low content of moister makes the storage of honey easier and stands much longer, and that is why Libyan honey is considered one of the best honey in the world (Chou et al., 2020).

3. 3. Electrical conductivity

5g of each honey sample was dissolved in 100 ml of hot distilled water, and an EC600L Conductivity Meter was used.

Table 3. Shows the electrical conductivity values for honey samples and FAO standards.

Honey samples	Electrical Conductivity mS/cm
Bani Waleed	0.32
Misurata	0.33
Zliten	0.5
Tripoli	0.32
FAO	0.8

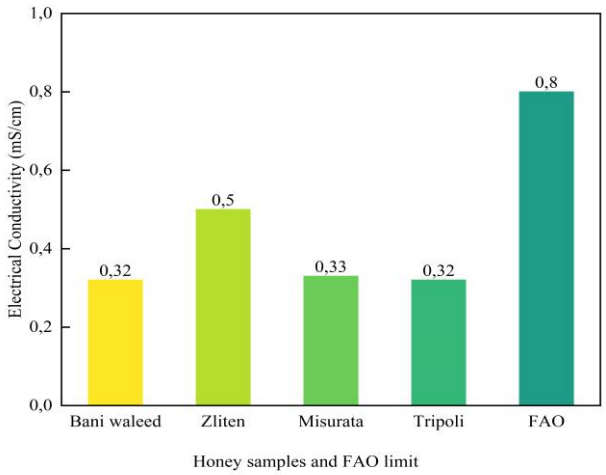

Figure 4. Shows the electrical conductivity for honey samples and FAO standard

According to **Figure 4**, the Tripoli and Bani Waleed samples had the lowest E.C value among the four samples, 0.32 ms/cm, while the Misurata sample was slightly higher, 0.33 ms/cm, and the Zliten sample had the highest E.C value, 0.5 ms/cm. Even though all samples were lower than the FAO standard (0.8 ms/cm), that's a sign of high-quality honey (Gebeyehu & Jalata, 2023; Lim et al., 2022).

3. 4. Ash content

1 g of each honey sample was weighed in a porcelain crucible and placed in the oven at 600 °C for 3 hours then the ash percentage was measured for each sample.

Table 4. Demonstrates the ash content in honey samples and FAO standards.

Honey samples	Ash Content %
Bani Waleed	0.10
Misurata	0.10
Zliten	0.10
Tripoli	0.20
FAO	0.60

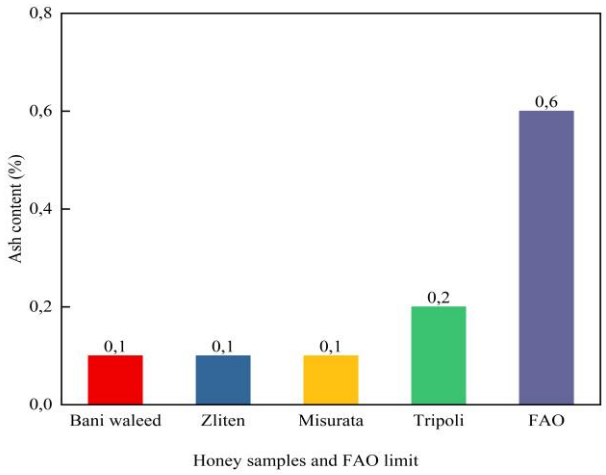

Figure 5. Shows the ash content in honey samples and FAO standards.

It can be seen from **Figure 5** that the Tripoli sample had the highest ash content (0.20%), while the Zliten, Bani Waleed, and Misurata samples had the same ash content (0.10 %). The difference in these results is due to the difference in the type of plant prevailing in the region and the geographical location of each sample. On the other hand, all four samples were significantly lower than the FAO standard (0.80%). As a result, the quality of the honey is considered high, as expected (Gebeyehu & Jalata, 2023; Lim et al., 2022).

3 .5. Heavy metals contents

Table 5. Demonstrates the content of Fe, Zn, and Pb (µg/g) in honey samples and WHO standards.

Honey samples	Zn (µg/g)	Pb (µg/g)	Fe (µg/g)
Bani Waleed	12.8	1.15	37
Misurata	21.7	1.49	50
Zliten	18.6	2.19	40
Tripoli	29.58	1.35	35
WHO	20	2	40

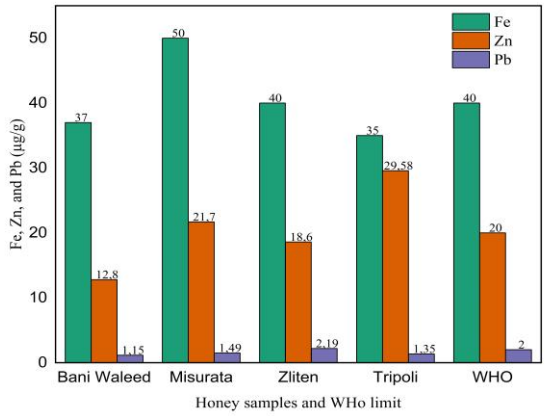

Figure 6. Shows the content of Zn, Pb, and Fe (µg/g) in honey samples and the WHO

The limits bar chart in **Figure 6**. demonstrates the heavy metal contents in the four honey samples, where the X axis shows the average concentration of the three heavy metals (µg/g), and the Y axis represents the honey samples and the maximum level according to the World Health Organization. From the chart above in **Figure 6**, it can be seen that the Bani-Waleed sample had the lower concentration of zinc at 12.80 (µg/g), followed by the Zliten sample with 18.60 (µg/g) and the Misurata sample at 21.70 (µg/g) while the Tripoli sample had the highest content of zinc with 29.58 (µg/g). By comparing zinc content in the four samples with the WHO limit, the Tripoli sample was much higher than the acceptable limit. In comparison, the Misurata sample was slightly higher than the maximum level. On the other hand, Bani-Waleed and Zliten samples were within the acceptable limit (20 µg/g). In terms of lead, the Bani-Waleed sample had the lowest content of lead with 1.15 (µg/g), followed by the Tripoli sample with 1.35 (µg/g) and the Misurata sample with 1.49 (µg/g) and all three samples were within the acceptable limit of lead (2 µg/g) while the Zliten sample was containing the highest concentration of lead among the four samples with 2.1 (µg/g) and that's slightly above the maximum level of lead according to the World Health Organization. Nevertheless, the Misurata sample had the highest iron level among the four honey samples, with 50 (µg/g). That content was much higher than the maximum level of iron 40 (µg/g). However, Bani-Waleed, Tripoli, and Zliten samples were within acceptable standards 37, 35, and 40 (µg/g), respectively. The lead content in this study was lower than the study conducted (Al-Hadar, 2006) on 20 honey samples from different regions of Libya, where the concentration of lead in some samples was 50.0 (µg/g). In addition, the study (Rashed & Soltan, 2004) in samples of honey showed the lead contamination in Egyptian honey was (4.2-9.3 µg/g). This study agreed with the results of (Atrouse et al., 2004) on Jordan honey in about 75% of the samples, where the lead concentration was (0.853-1.234 µg/g). Therefore, the results of this study can be used as a biosensor of environmental pollution (Atrouse et al., 2004; Rashed & Soltan, 2004).

4. Conclusion

This study was carried out on the geographical area extending from Misrata to Tripoli to Bani Walid. This area was chosen due to the large number of beekeepers and the abundant production of honey of all types. Four physicochemical parameters were estimated on honey samples: moisture content, pH, electrical conductivity, and ash content.

The obtained results for the honey samples were compared to international honey specifications. All the studied samples conformed to international specifications and were of high quality. The variation in the result among the four samples reflects the different regions from where the samples were taken. Moisture content in the four samples was very low compared to the maximum allowed content, and due to the low pH, it is possible to store the honey from these areas for a long period without fermentation. The higher the moisture content of the honey, the more likely it is to ferment. The pH values were low for all samples within the acceptable level, and this is why honey can eliminate all microorganisms. Electrical conductivity is one of the most important tests used to measure the quality of honey due to its direct relationship to moisture and ash content. By comparing the obtained results with the FAO standard, honey samples were found to be lower than the maximum level of E.C.

The concentration of zinc in the Bani Walid and Zliten samples was less than the maximum level of 20 (µg/g), while the Misrata and Tripoli samples were higher than the WHO limit. On the other hand, the lead contamination was found to be in the Zliten sample 2.1 (µg/g), which was slightly higher than WHO limit 2 (µg/g), while the other three samples were within acceptable limits. In contrast, the Misurata sample had the highest iron level (50 µg/g) among the four samples and even compared with the WHO limit (40 µg/g), while the other three samples were lower than the maximum level. Honey can be used as a biosensor or an indicator of environmental pollution with heavy metals.

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Competing Interests

The author declares no competing interests.

Abbreviations

AAS: Atomic Absorption Spectroscopy.
EC: Electrical Conductivity.
FAO: Food and Agriculture Organization.
WHO: World Health Organization.

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