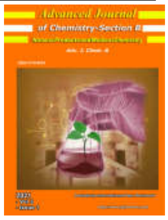
Advanced Journal of Chemistry, Section B, 2021, 3(4), 361-374

Advanced Journal of Chemistry-Section B
Natural Products and Medical Chemistry

Journal homepage: http://www.ajchem-b.com/



Original Research Article

The Contents of some Macro and Trace Elements in Uniflora and Multiflora Honey Samples Collected from Three Regions in East Libya

Nagwa H. S. Ahmida[1*], Najma H. Towier[2], Seham Shaboun[3], Salwa Y. S. Rahil[2], Aziza Ahmida[4], Randa. S. El-zwaeya[1], and Abdelkarem A. Elgazali[2]

[1]*Environmental Health Department, Faculty of Public Health, University of Benghazi, Benghazi, Libya.*
[2]*Chemistry Department, Faculty of Art and Science-Tokra/University of Benghazi, Benghazi, Libya.*
[3]*Department of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Benghazi, Benghazi, Libya.*
[4]*Chemistry Department, Faculty of Science, University of Benghazi, Libya*

ARTICLE INFO

Article history
Submitted: 2021-11-22
Revised: 2021-12-18
Accepted: 2021-12-27
Available online: 2022-01-01
Manuscript ID: AJCB_2111_1099
DOI: 10.22034/ajcb.2021.316305.1099

KEYWORDS
Macro element,
trace elements
flame atomic absorptio spectrometry,
uniflora honey,
multiflora honey

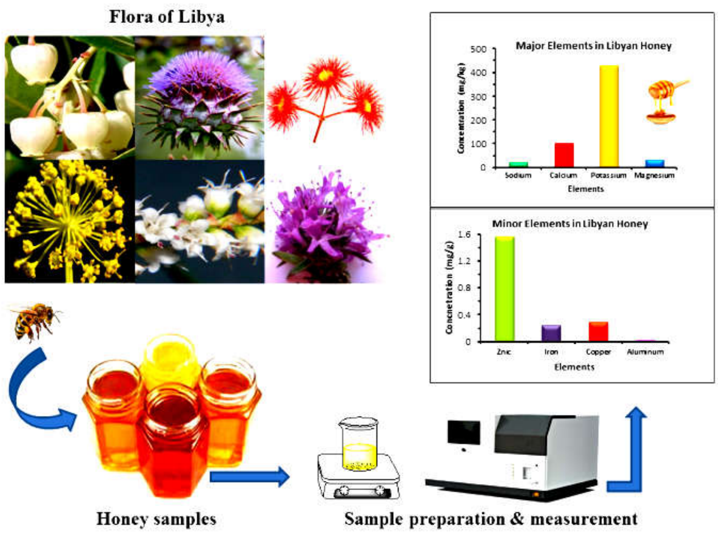
HIGHLIGHT
- Flame Atomic absorption spectrophotometer was used to determine the minerals contents in some uniflora and multiflora Libyan honey samples.
- The results of the essential minerals contents indicated that Libyan honey is a good source of nutrients for both adult and children.
- Based on the contents of trace and toxic minerals, the selected Libyan honey samples are considered to be safe for human consumption.

ABSTRACT

The determination of elements contents in honey has been recently increased as their benefits to human health and as indicator for environmental pollution. In this study, the levels of some macro and trace elements (main mineral contents) and two toxic heavy metals, were evaluated in honey samples. These samples were collected from beekeepers in three different regions in East Libya; including Benghazi, Maraj and Ajdabiya, during 2018. The collected samples included; *uniflora* and *multiflora* honey. The levels of ten elements were measured using flame atomic absorption spectrophotometer (FAAS). The detected metals included; sodium (Na), calcium (Ca), potassium (K), magnesium (Mg), zinc (Zn), iron (Fe), copper (Cu), aluminium (Al) and toxic elements; such as lead (Pb) and cadmium (Cd). The results showed, the ranges of macro minerals, Na, Ca, K and Mg varied from 10.93-32.30,39.14-298.5, 176.24-734.28 and 12.62-55.26mg/kg, respectively. The ranges of trace and toxic elements, Zn, Fe, Cu, Al, Cd and Pb varied from 0.43-2.51, 0.25-0.72, 0.02-0.61, 0.009-0.042, 0-0.011 and 0-0.009 mg/kg, respectively. The concentrations of all elements were statistically significant difference within all samples (P<0.05), except Zn. The levels of macro and trace elements in the selected Libyan honey samples were variable, while Cd and Pb elements were detected in few honey samples and not detected in the rest. This study reveals that Libyan honeys were high quality, rich in minerals and safe with toxic metals that present within permissible limits of the Libyan Standard Legislation.

*Corresponding author: Nagwa H. S. Ahmida
☏Tel.:00218927266974
✉E-mail:najwa.ahmida@uob.edu.ly

GRAPHICAL ABSTRACT



INTRODUCTION

Honey is a complex mixture that contains many elemental components, which depends on the geographical and botanical origin [1]. Based on the origin of plants, honey can be classified to uniflora and multiflora honey. The uniflora honey derived from one flora and it is named on this plant which considers as pollen origin that the pollen comes from. However, the multiflora honey made from numerous plants. Commercially, the multiflora honeys are the most abundant flora honey. The interest in uniflora honeys have been increased recently as it is highly recommended that the medicinal properties of plants can be transported to honey from the flora [2]. An approximately six thousand years ago, the honey was used as a medicine. The reports for using honey as medicine were clearly written on Sumerian and Papyri clay tablets by Egyptians before 1900–1250 BC [3]. Recently, the attention has been focused on apitherapy (the medical of using honey bee products) as part of folk and protective medicine for some diseases. Also, as enhancer of wellbeing and health [4]. Honey has antibacterial, antioxidant, immunity-enhancing and other therapeutic properties. On the other hand, the honey can be threaten the wellbeing health due to the presence of certain metals. The sources of the honey metals are mainly external in origin. These metals can cause serious health problems when accumulate to toxic levels in human body [5]. However, honey in general contains from 0.1% to 1.0% minerals compounds [1], that can be divided into toxic and essential minerals. These toxic minerals are poisonous even at low concentrations. However, essential minerals are very important needs for human health in a specific range, but beyond this range they are consider as poisonous [5].

In fact, Libya like other neighbourhoods countries in Africa, where there is no a pollination service for honey production. Thus the wild plants in different parts of Libya are the main source for honey production through migratory beekeeping [6]. In Libya the honey plants are mainly of the following types: *Acacia spp.*, *Citrus spp.*, *Eucalyptus spp.*, *Thymus capitatus* L., *Prunus spp.*, *Lantana camara*, *Medicagosativa*, *Hibiscus rosasinensis*, and many other wild plants that can be also found in North Africa countries [7],[8]. It is important to note that the Mediterranean element's species are mainly present in the Al-Jabal Al-Akhder region (East Libya) by ninety percent. Some of these element's species were used in honey production including; *Arbutus pavarii*, *Thymus capitatus*, *Ziziphus lotus*, *Ballotapseudodictamnus*, *Rosmarinus officinalis* and *Cynaracyrenaica* [9]. The habitants in Libya mainly use honey for medical purposes and as a natural sweetener in sweets and foods. In our studied, the samples were collected from special types of Libyan honeys; included *Zizaphus lotus* (locally named Sider) which considered as one of the most important plants for honey production [10], *Arbutus pavarii*, growing mainly in Al-Jabal Al-Akdar region, it's a special type of honey with bitter taste, locally named Hanon [9]. *Thapsiagarganica* (Diryas), is an inedible and toxic plant to grazing animals, but it is very important medicinal plant that has been recorded in the green mountain heterogeneous landscape by numerous investigators that were studied the plant distribution in Al-Jabal Al-Akdar region [11]. *Tamarixaphylla* L. (Athel) is a tree frequently planted on roadside and included in our large and common species. This tree is distributed in Middle East, Africa including Libya, Afghanistan, Pakistan and India. *Tamarix spp*. can grow in hot and dry places, and it is a sandy habitat [12]. In Africa and Asia, it is used by local people traditionally to treat a number of diseases. However, the therapeutic activities of *Tamarix spp*., were not clearly approved in which there are no clinical trials on human being. Also, the efficacy and safety of this plant were not confirmed [13].

Recently, the determination of minerals` concentrations in honey has been increased as their benefits to human health and as an indicator of any pollution in the environments [14]. The concentrations of minerals in honey depend on the geographical origin of the flowers composition [15]. As well as, the presence of these minerals can increase the nutritional values of honey, especially for children [16]. Although some of these minerals are essential, they cause serious health problems when accumulate to toxic levels in human body [15].

In this work, twenty-one honey samples have been collected from beekeepers in three different geographical regions in east Libya, The samples include fourteen samples of uniflora honeys (*Eucalyptus*, *Ziziphus louts*, *Thymus capitatus*, *Thapsiagarganica*, *Arbutus pavarii*, *Cynaracyrenaica*, *Tamarixaphylla*) and seven samples of multifora honeys, analyze for macro elements; including sodium (Na), calcium (Ca), potassium (K), magnesium (Mg) and some trace elements including zinc (Zn), iron (Fe), copper (Cu), aluminium (Al) and two toxic elements including; cadmium (Cd) and lead (Pb). The obtained results of each elements will compared with the recent reference values of minor and major elements in honey samples collected from different parts of the world.

EXPERIMENTAL

Material and Methods

All reagents were of analytical grade. Double deionized water was used for all chemical preparations and dilutions. Nitric acid (65%), hydrogen peroxide (30%) and the stock standard solutions (1000mg/L) of each element were supplied from Merck (Darmstadt, Germany).

Honey Samples

Twenty-one different samples of uniflora and multiflora Libyan honey (about 250 g for each) were collected during 2018 seasons from three different beekeepers in east Libya. All the samples placed in clean and dry glass bottles and kept at room temperature away from direct light until analysis. The information concerning botanical data; location; local name and periods of collection were recorded and expressed in Table 1.

Table1. Types and Regional data of the selected Libyan Honey Samples

Flora source (Local name)	Sample Code	Region	Flowering season
Multiflora (Elrabee)	M1- M5	Benghazi	1st March -31st September
	M6	Maraj	
	M7	Ajdabiya	
*Eucalyptus (*Elkafoor)	E1- E2	Benghazi	1st July-30th August
	E3	Maraj	
	E4	Ajdabiya	
*Ziziphus louts (*Sidr*)*	Z1	Benghazi	15th May-15th June
	Z2	Maraj	
	Z3	Ajdabiya	
*Thymus capitatus (*Zaatar*)*	T1	Benghazi	15th June-30th June
	T2	Maraj	
	T3	Ajdabiya	
Thapsiagarganiaca, (Diryas)	D1	Maraj	1stMarch-30thJune
Arbutus pavarii(Hanon)	H1	Ajdabiya	Late October -February
Cynaracardnulculus (Qahmoul)	C1	Ajdabiya	15th March-15th April
*Tamarixaphylla (*Athel*)*	A1	Ajdabiya	1st July-31st July

Procedures

One gram of honey sample was placed in a small beaker and 10 mL of nitric acid was added. The sample was heated on electric hot plate at 90°C and the temperature of this mixture was gradually increased to 120°C, until the evolving of brown fumes was stopped. Then, 2.5mL of hydrogen peroxide was added and the digest was transferred to 100mL volumetric flask with deionized water. After treatment of the solution sample, the filtrate was used to determine macro elements (Na, Ca, K and Mg) and other trace elements (Zn, Fe, Cu, Al, Cd and Pb) using flame atomic absorption spectrophotometer (FAAS) equipped with a deuterium lamp for background correction and hollow-cathode lamps for each of the studied element. The metals contents were determined using calibration curves of different metal ions. The calibration curves were constructed by plotting the absorbance values versus the concentrations of different standard solutions of each element [17, 18].

Statistical Analysis

The data were analyzed using Statistical Package for the Social Sciences (version 21; SPSS Inc., Chicago, IL, USA) software program. All the determinations were done in duplicate. The data were presented as mean ±standard deviation (mean ±SD) and range (min-max). The multiple comparisons one-way analysis of variance using Duncan's test, were used to determine the significant difference among the concentrations of minerals and heavy metals in honey samples (n=21). The level of significance $P<0.05$, was considered for all tests.

RESULTS AND DISCUSSION

The results of elemental analysis in uniflora and multifora Libyan honey were summarized in Table 2 for macro elements and Table 3 for trace and toxic elements. Some metals were found in extensive amounts, some in very small amounts and others were not detected in some of the analyzed honey samples. The concentrations of elements in our selected honey samples from East Libya, were compared with others research articles on honey conducted locally in Libya and in different countries as shown in Table 4 and Table 5.

Macro Elements Contents Analysis

The measured macro elements were Na, Ca, K and Mg. According to previous studies, the honey samples mainly contain potassium, sodium, calcium, manganese, chlorine, iron, phosphorus, zinc, manganese, copper, chromium and others. The mineral contents of honey depend mainly on climate conditions, botanical origin and to some extent on soil type [19]. The results in this work shows that the order of macro-elements according to quantity in descending order were K>Ca>Na>Mg.

This order came in accordance with the order of minerals detected in honey samples from Misrata-Libya and Tripoli-Libya as reported by Elbagermi *et al*., and Awad&Elgornazi [20, 21].

The Na contents in the Libyan honey samples ranged from 10.93mg/kg to 32.30mg/kg, with the mean concentration 24.07 ±7.5mg/kg, in which the highest sodium mean concentration (32.30 ±16.8mg/kg) was detected in multiflora honey. Indeed the lowest sodium concentration (10.93 ±1.1mg/kg) was detected in *Cynaracardnulculus* honey.

The maximum concentration range of Na in our honey samples was lower than the Na maximum concentration range in honeys samples collected from East Libya (Al-Jabal Al-akhdar) (24.5-60.0mg/kg) [22] and much lower than the mean concentration of Na in two honey samples collected from different regions in West Libya (Tripoli) [21] in which, the average values of Na concentrations in Garaboli, KasrKhiar and Misurata [20] were 2466mg/kg, 1675mg/kg and 465.1-792.3mg/kg, respectively. While, the minimum Na concentration range of our honey samples fall within the Na concentration range of honey samples collected from Egypt (2.70–17.0mg/kg) [23] and Brazil (1.80–47.20mg/kg) [15].

Table 2. The contents of the Macro minerals (mg/kg) in Selected Libyan honey

Flora Sources of Honey Sample	No.	Minerals Concentrations			
		Na	**Ca**	**K**	**Mg**
Multiflora	7	32.30 ±16.8	96.58 ±39.5	509.60 ±304.1	19.91 ±14.3
Eucalyptus	4	24.25 ±7.9	125.32 ±94.8	540.86±297.3	32.18 ±21.4
Ziziphus louts	3	23.11 ±5.4	59.32 ±42.6	413.73 ±166	20.77 ±8.6
Thymus capitatus	3	29.72 ±24.3	110.32 ±70.6	436.11 ±328.5	12.62 ±5.1
Thapsiagarganiaca	1	15.14 ±0.2	298.5 ±1.5	176.24 ±1.3	48.91 ±0.3
Arbutus pavarii	1	29.46 ±0.5	60.80 ±0.4	302.99 ±1.6	55.26 ±0.1
Cynaracardnulculus	1	10.932 ±1.1	52.31 ±0.3	325.55 ±0.6	33.74 ±0.5
Tamarixaphylla	1	27.61 ±2.2	39.14 ±1.02	734.28 ±1.2	51.651 ±0.6
Mean ±SD		24.07 ±7.5	105.28 ±83.7	429.92 ±170.3	34.38 ±16.1
(Range)		(21.37)	(259.34)	(558.04)	(42.64)
Min-Max		10.93-32.30	39.14-298.5	176.24 -734.28	12.62 -55.26
P-Value		0.000	0.000	0.000	0.000

Values for individual honey samples were the means of duplicate determinations

As well as, the Na mean concentration of our samples (24.07 ±7.51mg/kg) was much lower than the concentration range of Na in honey samples collected from Morocco(367.52-855.24mg/kg), (38.3-263.8mg/kg) [24],]25], Iraq (51.0-120.8 mg/kg) [14], Palestine(41.80-360.30mg/kg) [26],and Malaysia (83.17–732.16mg/kg) [27]. Whereas, the concentration range of Na that detected in our honey samples was fall in the Na concentration ranges of honey samples collected from different regions in United Arab Emirates (UAE) (6.76-531.77mg/kg) [28], Australia (3.7-382.7mg/kg) [29] and NewZealand (1.10–109.90mg/kg) [30]. Although, their maximum ranges were much higher than ours. The opposite for Na concentration range in honeys samples collected from Saudi Arabia (15.69-26.93mg/kg) [31] in which their range nearly fall in ours.

The proportion of Ca in all honey samples had a very wide concentration range started from 39.14 to 298.5mg/kg, with a mean concentration value equal to 105.28 ±83.7mg/kg. The highest Ca mean concentration (298.5 ±1.5mg/kg) was detected in *Thapsiagarganiaca* honey. While, the lowest Ca mean concentration (39.14 ±1.0 mg/kg) in our honey was detected in *Tamarixaphylla* honey. The Ca concentration ranges of our studied honey samples were nearly comparable with the concentration range of Ca in honey samples from Brazil (14.58–304.82mg/kg) [15], Australia (21-270mg/kg) [29]. Actually, Ca concentrations measured in honey samples from three region in Libya, two in Tripoli (named Garaboli and KasrKhiar) and Misurata were, 2110mg/kg, 1005mg /kg and 927.79-1186.6mg /kg, respectively [20],[21]. The concentrations of Ca metal in these regions were much higher than our results. Whereas, the concentration ranges of Ca detected in honey samples from Saudi Arabia (60.75-99.95mg/kg) [31], East Libya (Al-Jabal Al-akhdar) (52.6-97.1mg/kg) [22], Palestine (44.50-150.70mg/kg) [26], Pakistan (46.1-98.1mg/kg) [32] and New Zeeland (50.92-94.31mg/kg) [30], were lower than our Ca concentration range. Our Ca maximum concentration range fall in the Ca concentration ranges detected in honey samples collected from Iraq (140.8-2480mg/kg) [14], Morocco(129.35- 688.43mg/kg) [24], Egypt (156.20–568.06mg/kg) [23], and Malaysia (74.60– 567.2mg/kg) [27]. While, our Ca minimum concentration range fall in the Ca concentration ranges of honey samples from UAE (7.87–183.90mg/kg) [28] and Morocco (22.1-202.7mg/kg) [25].

Potassium was the dominant mineral in all honey samples, this high concentration can be owned to high K concentration in the tissue of plants [20]. In this study, K concentration ranged from 176.24mg/kg to 734.3mg/kg with the mean concentration value equal to 429.92 ±170.3mg/kg. The highest K mean concentration (734.3 ±1.2 mg/kg) was detected in *Tamarixaphylla* honey. While, the lowest K mean concentration (176.2±1.2mg/kg) was detected in *Thapsiagarganiaca* honey. The concentration ranges of K in honey samples collected from three regions in Libya two in Tripoli (Garaboli; 1414 mg/kg and KasrKhiar; 961.0mg/kg) [21] and Misurata (1100.8-1781.6mg/kg) [20], were higher than our range of honey samples. The mean concentration of K in our honey samples fall within the K concentration ranges of honey samples collected from Saudi Arabia (298.60-491.410mg/kg) [31], Iraq (93.80-712.8mg/kg) [14], East Libya (Al-Jabal Al-akhdar) (482-640mg/kg) [22], Pakistan (225–439 mg/kg) [32], and Palestine (42.80-585.00mg/kg) [26]. Even more, for honey samples from Egypt (36.67–73.13mg/kg) [23] and New Zealand (200.07mg/kg) [30], that our K mean concentration were much higher than their K concentrations. The maximum concentration range of K in our studied honey samples fall within the K concentration ranges in honey samples from Morocco (644.02-1883.15 mg/kg) (350.3-1047.7mg/kg) [24] [25], UAE (86.00–2690.29mg/kg) [28], Malaysia (413.63-

2417.43mg/kg) [27], and Australia (202-4600mg/kg) [29], although the maximum K concentration range in the last three honey samples were much higher than ours.

The magnesium contents in all analysed honey samples ranged from 12.62mg/kg to 55.26mg/kg with the mean concentration value equal to 34.38 ±16.1mg/kg. The highest Mg mean concentration (55.26 ±0.1mg/kg) was detected in *Arbutus pavarii* honey. Meanwhile, the lowest Mg mean concentration (12.62 ±5.1mg/kg) was detected in *Thymus capitatus* honey.

The Mg concentration range of our selected honey samples fall within the concentration range of Mg in honey samples from UAE (2.28–92.99mg/kg) [28], Morocco (8.9-101.8mg/kg) [25], Australia(6.0-190mg/kg) [29] and New Zealand (7.52–86.33mg/kg) [30]. The concentration range of Mg in our samples was lower than Mg concentration range of honey samples from Saudi Arabia (80.70-199.30mg/kg) [31], and were much higher than the Mg concentration range of honey samples collected from Iraq (0.260-0.721mg/kg) [14] and Brazil **(**2.48–28.33mg/kg) [15]. On the other hand, our maximum Mg concentration rang fall in the Mg concentration range in honey samples collected from Morocco (18.42-131.21mg/kg) [24], Malaysia (21.83-199.33mg/kg) [27], and Pakistan (31.3–71.8mg/kg) [32]. All the analysed macro elements in our studied uniflora and multiflora honey samples were fall within the limits set by Codex Alimentarius for nutrients in honey [33].

Trace and toxic elements Contents Analysis

The concentration of trace elements, included Zn, Fe, Cu, Al, and two toxic elements; included, Pb and Cd, were determined in all honey samples (Table 3). The order of these elements according to quantity in descending order were Zn>Fe>Cu>Al>Cd>Pb. Zinc contents in all honey samples ranged from 0.43mg/kg to 2.51mg/kg, with the mean concentration value equal to 1.57±0.6mg/kg. The highest Zn mean concentration (2.51 ±0.01mg/kg) was detected in *Cynaracardnuculus* honey. Whereas, the lowest zinc mean concentration (0.43 ±0.02mg/kg) was detected in *Arbutus pavarii* honey. The concentration range of Zn element in Libyan honey samples was accordance to the concentration ranges of Zn in honey samples from Egypt (0.28-2.41mg/kg) [23] and New Zealand (0.37-2.46mg/kg) [30].

As well as, the Zn concentration range in our selected honey samples was much lower than the Zn concentration range in honey samples collected from different regions in West Libya (Misurata) (3.677-7.430mg/kg) [20], East Libya (Al-Jabal Al-akhdar) (0.06-8.1mg/kg) [22], Morocco (1.41-4.26mgkg) [24], Saudi Arabia (3.44-5.72mg/kg) [31], Palestine (1.00-19.90mg/kg) [26], Malaysia (4.70-173.77mg/kg) [27] and Romania (15.0-3640mg/kg) [34]. Whereas, the concentration range of Zn in our samples was higher than the concentration range of Zn of honey samples collected from Ethiopia (0.062-0.336 mg/kg) [35] and Bangladesh (0.0208mg/kg) [36]. The minimum Zn concentration of our honey samples fall within the Zn concentration range of honey samples collected from Iran (0.122-6.638 mg/kg) [37]. The proportion of Fe as an essential metal in the selected Libyan honey samples ranged from 0.25mg/kg to 0.72mg/kg, with the value of mean concentration equal to 0.25 ±0.01mg/kg. The highest Fe mean concentration (0.72 ±0.9 mg/kg) was detected in *Thymus capitatus* honey. While, the lowest Fe mean concentration (0.25 ±0.01mg/kg) was detected in *Tamarixaphylla* honey. The Fe concentration range of our samples fall within the concentration range of Fe in honey samples collected from Australia (0.2–99.0 mg/kg) [29].

Table 3. Trace and Toxic elements contents of the analysed Libyan honey samples (mg/kg)

Honey Sample	Minerals Concentration (mean ±SD)					
	Zn	**Fe**	**Cu**	**Al**	**Pb**	**Cd**
M1	1.90±0.06	0.32±0.01	0.073±0.01	0.010±0.001	BLD	BLD
M2	2.16±0.02	0.14±0.03	0.24±0.01	0.031±0.003	0.009±0.001	0.0085±0.001
M3	2.36±0.08	0.67±0.06	0.11±0.01	0.026±0.001	0.007±0.001	BLD
M6	1.10±0.04	0.34±0.01	0.13±0.01	0.013±0.001	BLD	BLD
M5	1.72±0.04	0.88±0.02	0.78±0.02	0.012±0.000	BLD	0.0035±0.005
M6	1.59±0.01	0.10±0.01	0.87±0.03	0.078±0.000	BLD	BLD
M7	0.36±0.01	0.29±0.01	1.00±0.01	0.005±0.000	BLD	0.005±0.000
Multiflora	**1.60 ±0.7**	**0.39 ±0.3**	**0.46 ±0.4**	**0.025 ±0.02**	**-**	**-**
E1	1.64±0.02	1.16±0.05	1.20±0.13	0.043±0.002	BLD	BLD
E2	2.25±0.06	0.11±0.01	0.04±0.01	0.01±0.001	BLD	BLD
E3	1.31±0.02	0.64±0.04	0.24±0.003	0.02±0.000	BLD	BLD
E4	1.46±0.04	0.21±0.01	0.22±0.005	0.01±0.001	BLD	BLD
Eucalyptus	**1.66 ±0.4**	**0.53 ±0.48**	**0.43 ±0.53**	**0.02 ±0.02**	**-**	**-**
Z1	2.16±0.05	0.22±0.005	0.26±0.022	0.032±0.003	BLD	BLD
Z2	1.74±0.04	0.08±0.013	0.50±0.001	0.017±0.000	BLD	BLD
Z3	0.82±0.02	0.50±0.004	0.18±0.004	0.027±0.001	BLD	BLD
Ziziphus louts	**1.57 ±0.7**	**0.27 ±0.2**	**0.31 ±0.2**	**0.025±0.008**	**-**	**-**
T1	0.84±0.01	0.34±0.03	0.032±0.005	0.03±0.000	BLD	BLD
T2	3.22±3.6	1.75±0.2	0.49±0.005	0.053±0.004	BLD	BLD
T3	2.03±0.02	0.079±0.001	0.56±0.03	0.044±0.003	BLD	0.0110±0.001
Thymus capitatus	**2.030 ±1.2**	**0.72 ±0.9**	**0.36 ±0.3**	**0.042 ±0.01**	**-**	-
Thapsiagargan iaca (D1)	**1.094±0.010**	**0.26±0.03**	**0.14±0.014**	**0.014±0.000**	**BLD**	**BLD**
Arbutus pavarii (H1)	**0.43±0.02**	**0.34±0.004**	**0.04±0.004**	**0.018±0.001**	**BLD**	**BLD**
Cynaracardnul culus (C1)	**2.51±0.01**	**0.37±0.009**	**0.61±0.001**	**0.009±0.001**	**BLD**	**BLD**
Tamarixaphyll a (A1)	**1.66±0.03**	**0.25±0.01**	**0.02±0.003**	**0.027±0.000**	**0.007±0.001**	**BLD**
Mean ±SD	1.57 ±0.6	0.25 ±0.01	0.30 ±0.2	0.023 ±0.01	-	-
(Range)	(2.08)	(0.47)	(0.59)	(0.033)	(0.009)	(0.011)
Min-Max	0.43-2.51	0.25-0.72	0.02-0.61	0.009-0.042	0-0.009	0-0.011
P-value	0.174*	0.000	0.000	0.000	0.000	0.000

BLD: Below Limit of Detection, * statistically not different.

However, the Fe concentration range in various honey samples from East of Libya (Al-Jabal Al-akhdar) (1.7—2.5 mg/kg) [22], Brazil (0.31–8.76 mg/kg) [15], Kosovo(1.670 mg/kg) [38], Morocco (0.71-4.68) [24], New Zealand (0.67-3.39 mg/kg) [30], Palestine (2-10.8mg/kg) [26], Egypt (2.57-14.01mgkg) [23] and Pakistan (2.98-16.2mg/kg) [32], were higher than the concentration of Fe in our honey samples. Even more, the Fe concentration ranges in honey samples from Saudi Arabia (67.18-98.13 mg/kg) [31] and Malaysia (55.83-233.0mg/kg) [27], were much higher than the Fe concentration range in our samples. On other hand, Fe concentration ranges in honey samples from Iraq (0.0024-0.0348 mg/kg) [14] and Bangladesh (0.205 mg/kg) [36] were lower than the Fe concentration range in the honey samples collected in this study.

The concentration of Cu metal in the Libyan honey samples ranged from 0.02mg/kg to 0.61mg/kg, with the mean concentration value equal to 0.30 ±0.2mg/kg, in which the highest Cu mean concentration (0.61 ±0.001mg/kg) was detected in *Cynaracardnuculus* honey. Meanwhile, the lowest Cu mean concentration (0.02 ±0.003mg/kg) was detected in *Tamarixaphylla* honey. Copper concentration range and the mean concentration of our selected honey samples fall in the concentration range of Cu in honey samples collected from Ethiopia (0.02-1.15 mg/kg) [39], Malaysia (N.D-2.93mg/kg) [27], New Zealand (0.009-0.70mg/kg) [30] and Palestine (0.0-1.52 mg/kg) [26]. The maximum concentration of Cu in our honey samples was lower than Cu concentration range in honey samples collected from East Libya (Benghazi) (0.8-10.40mg/kg) [40], Malaysia (ND–2.93 mg/kg) [27] and Iran (0.276-2.872mg/kg) [37]. As well as, the Cu concentration range in our samples was much lower than the Cu concentration ranges of samples collected from Romania (2.00–33.00mg/kg) [34]. On the opposite, the Cu concentration range of our samples was higher than the Cu concentration ranges in honey samples collected from East of Libya (Al-Jabal Al-akhdar) (0.04-0.05mg/kg) [22], West of Libya (Misurata) (0.004-0.032mg/kg) [20], Ethiopia (0.027-0.0696mg/kg) [35], Bangladesh (0.0427mgkg) [34], Egypt (ND-0.28mgkg) [23] and Pakistan (0.08-0.33mg/kg) [32].

Aluminium metal was detected in all the honey samples, and ranged from 0.009mg/kg to 0.042mg/kg, with the mean concentration value equal to 0.023±0.01mg/kg. The highest Al mean concentration (0.042 ±0.01mg/kg) was detected in *Thymus capitatus* honey. While, the lowest Al mean concentration (0.009 ±0.001mg/kg) was detected in *Cynaracardnuculus* honey. Honeybees exposed to Al metal during foraging for nectar. Exposure the human body to high levels of Al leads to neurotoxicity, Alzheimer disease, and breast cancer [41]. Few researchers were determined this metal in honey samples; including honeys collected from Australia (0.05-14.0mg/kg) [29] and New Zealand (0.21-21.32mg/kg) [30]. The concentration ranges of Al in these honey samples were higher than the concentration range of the honey samples in this study.

The presence of toxic metals, such as Pb and Cd, in honey predicted a local pollution [42]. In this study, the concentrations of Pb and Cd were below the detection limits of spectrophotometric method of analysis in all honey samples, except in few samples. Actually, Pb was detected in three honey samples. Two honey samples were *multiflora* honeys from Benghazi city and the third honey sample was *Tamarixaphylla* honey from Ajdabiya. The Pb mean concentrations in these three honey samples were (0.009±0.001mg/kg), (0.007±0.001mg/kg) and (0.007±0.001mg/kg) respectively. In the other hand, the Cd was detected in four honey samples. Two of these honey samples were *multiflora* honeys from Benghazi, with Cd mean concentrations detected at 0.0085 ±0.001mg/kg and 0.0035 ± 0.005mg/kg respectively The other two honey samples were *multiflora* honey and *Thymus capitatus* honey from Ajdabiya. The Cd mean concentrations in these two honey samples were 0.005±0.000mg/kg and 0.011±0.001mg/kg, respectively. The levels of both toxic metals in our honey samples were less than the maximum authorized limits that set by Libyan Standard Legislation [43]. The concentration ranges of both Pb and Cd in honey samples collected from different regions in Libya, included; Misurata (Pb: 0.0029-0.024mg/kg, Cd: 0.0033-0.017mg/kg) [20], Al-Jabal Al-akhdar (Pb: 0.007-0.3mg/kg, Cd: 0.003-0.2 mg/kg) [22] and Benghazi (Pb: ND-0.06 mg/kg, Cd: N.D 0.005 mg/kg) [39], were higher than the concentration ranges for our honey samples, except the concentration of Cd metal in honey samples collected from Benghazi (ND-0.005mg/kg), which was lower than ours. Also, the concentration ranges of Pb and Cd metals in our collected samples were lower than the concentration ranges of both metals in honey samples collected from Egypt (Pb: ND-0.75mg/kg, Cd: ND-0.03mg/kg) [23], Australia (Pb: 0.0025-0.69mg/kg, Cd: 0.0025-0.053mg/kg) [29], Kosovo (Pb: 0.880mg/kg, Cd: 0.050mg/kg) [36], Pakistan (Pb: 0.01-0.14mg/kg, Cd 0.01-0.38 mg/kg) [32], Bangladesh (Pb: 0.0560, Cd: 0.0107) [36], Saudi Arabia (Pb: 0.06-0.23mg/kg, Cd: 0.00-0.16mg/kg) [31], and much lower than the concentration range of Pb and Cd in the honey samples collected from Ethiopia (Pb: N.D-2.53mg/kg, Cd: ND-0.017mg/kg)[39], Malaysia (Pb: ND-1.017mg/kg, Cd: ND-1.03 mg/kg) [27], Iraq (Pb: 0.10-0.73mg/kg, Cd: 0.108-0.820mg/kg) [14], Iran (Pb: 0.117-1.628mg/kg, Cd: 0.0136-0.1258mg/kg) [37] and Romania (Pb: 0.05-3.81mg/kg, Cd: 0.76-3.41mg/kg) [34].

Table 4. The contents of some macro elements in honey samples from different countries

Country (year)	Macro Elements` Concentration				
	Na	**Ca**	**K**	**Mg**	**Ref.**
Egypt (2020)	2.70-17.0	156.20-568.06	36.67-73.13	97.02-267.92	23
Australia (2020)	3.7-382.7	21-270	202- 4600	6.0 – 190	29
Libya (Misurata) (2019)	465.1-792.3	927.79-1186.6	1100.8-1781.6	-	20
Pakistan (2019)	77.5-200	46.1-98.1	225-439	31.3 – 71.8	32
Morocco (2018)	367.52- 855.24	129.35-688.43	644.02-1883.15	18.42-131.21	24
Palestine(2017)	41.80- 360.30	44.50-150.70	42.80-585.00	12.30-46.70	26
Libya (Tripoli) (2016)	2466& 1675	2110&1005	1414 &961.0	-	21
Libya (Al-Jabal Al-Akhdar) (2016)	24.5-60.0	52.6-97.1	482-640	21-41.9	22
Iraq (2015)	51.0-120.8	140.8-2480	93.80-712.8	0.260-0.721	14
Saudi Arabia(2014)	15.69-26.93	60.75-99.95	298.60-491.410	80.70-199.30	31
UAE. (2014)	6.76 –531.77	7.87–183.90	86.00–2690.29	2.28 –92.99	28
Morocco (2014)	38.3- 263.8	22.1-202.7	350.3-1047.7	8.9-101.8	25
Malaysia(2014)	83.17-732.16	74.60-567.2	413.63-2417.43	21.83-199.33	27
Brazil (2013)	1.80-47.20	14.58-304.82	21.30- 1513.30	2.48 – 28.33	15
New Zealand (2011)	1.10 -109.90	50.92-94.31	200.07	7.52 – 86.33	30

*The number of significant figures recorded according to the reference

Table 5. The contents of some Trace and Toxic elements in honey samples from different countries.

Country (year)	Minerals Concentrations (mg/kg)					
	Zn	**Fe**	**Cu**	**Pb**	**Cd**	**Ref**
Egypt (2020)	0.28-2.41	2.57-14.01	ND-0.28	**ND-0.75**	ND-0.03	23
Australia (2020)	0.16 – 120	0.2 –99.0	0.05- 4.8	0.0025-0.69	0.0025-0.053	29
Ethiopia (2020)	9.96-16.03	-	0.02-1.15	N.d- 2.53	N.d-0.017	39
Romania (2020)	15.00 –3640	-	2.00 – 33.00	0.05 – 3.81	0.76–3.41	34
Kosovo (2020)	-	1.670	0.360	0.880	0.050	38
Libya (Misurata) (2019)	3.677-7.430	-	0.004-0.032	0.0029-0.024	0.0033-0.017	20
Pakistan (2019)	1.11-41	2.98-16.2	0.08-0.33	0.01-0.14	0.01-0.38	32
Ethiopia (2018)	0.062-0.336	-	0.027-0.0696	-	-	35
Morocco (2018)	1.41-4.26	0.71-4.68	0.41-1.82	ND	ND	24
Palestine(2017)	1.00-19.90	2.00-10.80	0.00-1.52	-	-	26
Libya (Al-Jabal Al-akhdar) (2016)	0.06-8.1	1.7-2.5	0.04-0.05	0.007-0.3	0.003-0.2	22
Iraq (2015)	-	0.0024-0.0348	< 0.1	0.100-0.730	0.108-0.820	14
Iran (2015)	0.122-6.638	-	0.276- 2.872	0.117-1.628	0.0136-0.1258	37
Bangladesh (2015)	0.0208	0.2050	0.0427	0.0560	0.0107	36
Saudi Arabia(2014)	3.44-5.72	67.18-98.13	-	0.06-0.23	0.00-0.16	31
Malaysia(2014)	4.70-173.77	55.83-233.0	ND-2.93	ND-1.017	ND-1.03	27
Brazil (2013)	0.11-1.85	0.31-8.76	0.07-1.29	-	-	15
Libya (Benghazi) (2012)	-	-	0.8-10.40	ND-0.06	ND-0.005	40
New Zealand (2011)	0.3-2.46	0.67-3.39	0.009-0.70	ND-0.04	0.01-0.28	30

*The number of significant figures recorded according to the reference. ND Not Detected.

In opposite, the concentration ranges of Pb and Cd in our selected samples were higher than the concentration ranges of both metals in honey samples collected from Morocco (Pb& Cd: ND) [24].

Finally, there was a statistically significant difference (*P*=0.000) in concentrations of all studied macro, trace and toxic elements between all Libyan honey samples, except the concentrations of Zn element, which was a statistically not different (*P*=0.174) between all honey samples.

CONCLUSION

This study showed that, there were wide variations in the levels of measured elements contained in all twenty-one studied Libyan honey samples with high levels of K and Ca. Relatively, the total mineral contents in all analysed honey samples were sometimes higher, lower or/and similar to the previous studies which conducted locally in Libya and internationally in different countries. In addition, the levels of macro and trace elements including toxic heavy metals were with the permission limits of Codex and Libyan Standard specification, respectively. Also, the honey samples collected from different regions in East Libya were rich in the essential elements which can be considered as a good source of nutrients for both adult and children.

ACKNOWLEDGMENTS

The authors of this work would like to thank the technician at the Food Analysis Laboratory, Nutrition Department, Faculty of Public Health, Benghazi University, for providing the Standards of metals and analyzing the digestion honey samples using FAAS.

REFERENCES

[1] Y. Yücel,P. Sultanoğlu, Characterization of Hatay honeys according to their multi-element analysis using ICP-OES combined with chemometrics. *Food Chemistry*, *140*(2013) 231-237.

[2] O. Bobis, A.R. Moise, I. Ballesteros, E.S Reyes, S.S. Durán,J. Sánchez-Sánchez, S. Cruz-Quintana, F. Giampieri, M. Battino, J.M. Alvarez-Suarez, Eucalyptus honey: Quality parameters,chemical composition and health-promoting properties. *FoodChemistry*,325(2020)126870.

[3] S.U Khan, S. I. Anjum, K. Rahman, M. J. Ansari, W. U. Khan, S. Kamal, B. Khattak, A. Muhammad,&H. U. Khan, Honey Single food stuff comprises many drugs.*Saudi journal of biological sciences*, 25(2018) 320-325.

[4]R. K. Gupta, & S. Stangaciu, Apitherapy: holistic healing through the honeybee and bee products in countries with poor healthcare system. *Beekeeping for poverty alleviation and livelihood security*, (2014) 413-446.

[5] Q. M. Ru, Q. Feng,&J. Z. He, Risk assessment of heavy metals in honey consumed in Zhejiang province, southeastern China, *Food and Chemical Toxicology*,53 (2013) 256-262.

[6] M.Keshlaf,The past and present status of beekeeping in Libya. *Journal of Apicultural Research*, 56(2017) 190-195.

[7] F.B. Abdelkader, Situation of Beekeeping in North Africa, *Journal of Apitherapy and Nature*, 3(2020)
1-9.

[8] N. Elmarbet, M. B. Shaban, B. Doro, B. A. Lwaleed, S. Fouch, & M. Elemam, The Antibacterial Activity of Libyan Honey against Gram Negative Bacilli: Potential Treatment Agent for Infectious Diseases?. *Journal of Advances in Medicine and Medical Research*, (2018) 1-10.

[9] F. M.El-Mokasabi, Floristic composition and traditional uses of plant species at WadiAlkuf, Al-Jabal Al-Akhder, Libya. *American-Eurasian Journal of Agricultural &Environmental Sciences*, 14(2014) 685-697.

[10] S.Zerrouk, O. Escuredo, M. S. Rodríguez-Flores, & M. C. Seijo, Palynological characterisation of Sedra honeys (Ziziphus lotus) produced in Algeria. *Grana*, 60(2021) 69-80.

[11] A. E. Al Borki, A. K. Alzerbi, H. F. Kabiel, A. K. Hegazy, Variations in phenological and functional traits in Thapsiagarganica populations in Al Jebel Al Akhdar, Libya. *African Journal of Ecology*,58(2020) 639-648.

[12] M. Tariq,M.A. Wazir, W. Hussain, S. Safadr, A. S Sial, K. Shehzadi,and A. Usman., Phytochemical and Biological Screening of Tamarixaphylla L.(Tamaricaceae). *Acta Scientific Pharmaceutical Sciences*,
3 (2019) 77-84.

[13] R. Bahramsoltani, M. Kalkhorani, S. M. A. Zaidi,M. H. Farzaei,& R. Rahimi, The genus Tamarix: Traditional uses, phytochemistry, and pharmacology, *Journal of ethnopharmacology*,246 (2020) 112245.
Doi: https://doi.org/10.1016/j.jep.2019.112245.

[14] S. A. Dhahir, & A. H. Hemed, Determination of heavy metals and trace element levels in honey samples from different regions of Iraq and compared with other kind. *American Journal of Applied Chemistry*, 3 (2015) 83-92.

[15] M. D. C. T. C. Liberato, S. M. D. Morais, C. E. D. C. Magalhães, I. L. Magalhães, D. B. Cavalcanti, &M. M. D. O. Silva, Physicochemical properties and mineral and protein content of honey samples from Ceará State, Northeastern Brazil. *Food Science and Technology*,33(2013) 38-46.

[16] S. V.Kulkarni, Isolation of trace elements from winter honey samples of umrertehasil. *International journal of researches in*

biosciences, agriculture and technology, 1(2014) 673-677.

[17] W. Horwitz, Official methods of analysis of AOAC international,(17th ed).,Gaithersburg, Md. Washington (2000)

[18] P.L. Buldini, L. Ricci, J. L. Sharma,Recent applications of sample preparation techniques in food analysis. *Journal of Chromatography* A 975(2002) 47-70.

[19] N. Uršulin-Trstenjak, D. Levanić, L. Primorac, J. Bošnir, N. Vahčić, & G. Šarić, Mineral profile of Croatian honey and differences due to its geographical origin. *Czech Journal of Food Sciences*, 33(2015) 156-164.

[20]M.Elbagermi, J. Mayouf, T. Twaish, &H. Edwards, Analysis of Trace and Essential Elements, Phenolic and Flavonoid Compounds in Libyan Honey Samples Collected from Misurata Markets. *To Chemistry Journal*, 4 (2019) 37-46.

[21] M. H. Awad, & A. M. Elgornazi,Physicochemical characterization of honey from KasrKhiar and Garaboli areas-Libya. *Asian Journal of Plant Science and Research*, 6(2016) 8-12.

[22] R. E. Abd-Elkader, A. A. Bellail, A. I. Attia, M. M. Mousa, & I. A. Hamied,Mineral Content and Antioxidant Activity of Different Sample of Libyan Bees Honey. *J. Nucl. Tech. Appl. Sci*, 4(2016) 123-135.

[23] G. M. Hamad, E. E. Hafez, N. M. Abdelmotilib, K. M. Abdel Hmeed, S. H. Ali, &A. M. Darwish, Quality Assessment, Functional Potentials, and Safety Evaluation of Stored Egyptian Honey as an Environmental Pollution Bio-indicator. *Environmental Toxicology and Chemistry*, 39(2020)1894-1907.

[24] R. El-Haskoury, W. Kriaa, B. Lyoussi, & M. Makni.Ceratoniasiliqua honeys from Morocco: Physicochemical properties, mineral contents, and antioxidant activities. *Journal of food and drug analysis*, 26(2018) 67-73.

[25] S. Aazza, B. Lyoussi, D. Antunes, &M. G. Miguel, Physicochemical characterization and antioxidant activity of 17 commercial Moroccan honeys. *International Journal of Food Sciences and Nutrition*, 65(2014)449-457.

[26] A. Abdulkhaliq, & K. M. Swaileh, Physico-chemical properties of multi-floral honey from the West Bank, Palestine.*International Journal of Food Properties*, 20 (2017) 447-454.

[27] M. Moniruzzaman, M. A. Z. Chowdhury, M. A. Rahman, S. A. Sulaiman, &S. H. Gan), Determination of mineral, trace element, and pesticide levels in honey samples originating from different regions of Malaysia compared to Manuka honey. *BioMed research international*, 2014 (2014)1-10. http://dx.doi.org/10.1155/2014/359890

[28] H. M. Habib, F. T. Al Meqbali, H. Kamal, U. D. Souka, &W. H. Ibrahim, Physicochemical and biochemical properties of honeys from arid regions. *Food Chemistry*, 153 (2014) 35-43.

[29] N. L. Hungerford, U. Tinggi, B. L. Tan, M. Farrell, &M. T. Fletcher, Mineral and Trace Element Analysis of Australian/Queensland Apismellifera Honey. *International journal of environmental research and public health*, 17(2020) 6304.

[30] L. P. Vanhanen, A. Emmertz, &G. P. Savage, Mineral analysis of mono-floral New Zealand honey. *Food Chemistry*, 128 (2011) 236-240.

[31] A. S. Alqarni, A. A. Owayss, A. A. Mahmoud, M. A. Hannan. Mineral content and physical properties of local and imported honeys in Saudi Arabia .*Journal of Saudi Chemical Society*.18 (2014) 618-25.

[32] M. F. Lanjwani,&F. A. ChannaMinerals content in different types of local and branded honey in Sindh, Pakistan. *Heliyon*, *5* (2019) e02042.

[33] Codex Alimentarius Commission. (2001) Codex standard for honey. Codex-Stan-12-1981. Food and Agricultural Organization of the United Nations, Rome, Italy; World Health Organization, Geneva, Switzerland.

[34] S. Bartha, I. Taut, G. Goji, I. A.Vlad, & F. Dinulică. Heavy Metal Content in Polyfloral Honey and Potential Health Risk, A Case Study

of CopșaMică, Romania. *International journal of environmental research and public health*, 17 (2020) 1507. Doi:10.3390/ijerph17051507

[35] Teka, A. E. (2018). Levels of some selected trace and essential elements in honey from selected wore as of sidamazone, southern region, Ethiopia. *J AgricSci*, *2*(1), 12-18

[36] M. Asaduzzaman, M. S. Rahman, S. Munira, M. M. Rahman, M. Islam, M. Hasan, M. A. Siddique, S. Biswas, M. H. Khan, & M. Rahman, M. A. Islam, Analysis of biochemical composition of honey and its anti-oxidant, Phytochemical and anti-bacterial properties. *J Biomed Pharm Res*, 4(2015) 69-81. Available Online at www.jbpr.in.

[37] H. M. Aghamirlou, M. Khadem, A. Rahmani, M. Sadeghian, A. H. Mahvi, A. Akbarzadeh, & S. Nazmara, Heavy metals determination in honey samples using inductively coupled plasma-optical emission spectrometry. *Journal of Environmental Health Science and Engineering*, 13(2015) 1-8.
DOI 10.1186/s40201-015-0189-8.

[38] M. Fadil, D. Krasniqi, &M. Ahmet, Heavy Metals In Honey Produced In Some Localities In Kosovo. *Rasāyan J . Chem*, 13(2020), 2036-2044. http://dx.doi.org/10.31788/ RJC.2020.1345811.

[39] E. Adugna, A. Hymete, G. Birhanu, & A. Ashenef, Determination of some heavy metals in honey from different regions of Ethiopia. *Cogent Food & Agriculture*, *6*(2020), 1764-182. https://doi.org/10.1080/23311932.2020.1764182.

[40] N. H. Ahmida, M. Elagori, A. Agha, S. Elwerfali,& M. H. Ahmida ,Physicochemical heavy metals and phenolic compounds analysis of Libyan honey samples collected from Benghazi during 2009-2010.*Food and Nutrition Sciences*, 4(2012) 33-40. http://dx.doi.org/10.4236/fns.2013.41006

[41] K. klotz, W. weistenhöfer, F. Neff, A. Hartwig, C. van thriel, H. Drexler. The Health Effects of Aluminium Exposure. *Dtscharzteblint*, 114 (2017) 653-659. Doi:10.3238/arztebl.2017.0653

[42] M. Perugini, M. Manera, L. Grotta, M. C. Abete, R. Tarasco, & M. Amorena, Heavy metal (Hg, Cr, Cd, and Pb) contamination in urban areas and wildlife reserves: honeybees as bio-indicators. *Biological trace element research*, 140 (2011)170-176. DOI 10.1007/s12011-010-8688-z

[43] Libyan National Center for Standardization and Metrology, Ministry of Commerce, "Libyan Standard Concerning Honey," *Libyan Standard Legislation for Industrial and Non Industrial Food*, *Concerning Honey*, No. 281 (1995) 47-52.

HOW TO CITE THIS ARTICLE

Nagwa H. S. Ahmida, Najma H. Towier, Seham Shaboun, Salwa Y. S. Rahil, Aziza Ahmida, Randa. S. El-zwaeya, and Abdelkarem A. Elgazali, The Contents of some Macro and Trace Elements in Uniflora and Multiflora Honey Samples Collected from Three Regions in East Libya, , Ad. J. Chem. B, 3 (2021) 361-374.

DOI: 10.22034/ajcb.2021.316305.1099
URL: http://www.ajchem-b.com/article_142677.html