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Trace and minor elements in bee honeys produced in Syria

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Abstract: Eleven minerals (K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, and Sr) in 31 honey samples, including 24 Syrian, three imported and four honeys produced from bees fed with sugar were quantified using a dry ashing method for X-ray fluorescence analysis. The search for natural groups in the honey samples was carried out by cluster analysis, using complete linkage and Euclidean distance. The Syrian and imported samples clustered into three honey groups: 1) poor in element concentrations (citrus honey); 2) rich in minor and trace element concentrations (wild plants and jujube honeys); and 3) moderate mineral concentrations (multiflora, eucalyptus, crataegus, and sunflower honeys). Results are discussed in terms of the mineral concentrations in Syrian honeys and in comparison with international values.

1. Introduction

Honey is a natural substance formed when the nectar and sweet deposits from plants are gathered, modified and stored in honeycomb by honey bees (Azeredo *et al.*, 2003; Wei *et al.*, 2010). However, honey needs to satisfy numerous quality and certification criteria before commercialization (Devillers *et al.*, 2004; Laube *et al.*, 2010). Different methods based on parameters, such as nutritious, prophylactic properties, pollen and unique flavors analyses were applied to specify the quality of honeys. Although these methods have many advantages, they are not recommended for the fast routine procedure because their applications required for highly specialized personnel; furthermore, they are laborious and time-consuming (Chudzinska and Baralkiewicz, 2010; Wei *et al.*, 2010).

Several researchers found the physicochemical analysis method as a most prevalent tool that could be used for detecting the origin of honey (Adebiyi *et al.*, 2004; Felsner *et al.*, 2004; Serrano *et al.*, 2004; Corbella and Cozzolino, 2006; Cantarelli *et al.*, 2008). For instance, Lachman *et al.* (2007) classified Czech Republic honey samples by combining between the mineral content and the electrolytic conuctivity analyses.

The elemental content of honeys is closely related to the soil and vegetation in the area where the raw material for honey was collected (Caroli *et al.*, 1999; Bilandžić *et al.*, 2012). For instance, Tuzen *et al.* (2007) determined the levels of several trace elements in honey from different botanical origins in Turkey and established a correlation between the content of trace elements and the botanical and geographical origin of honey. Pisani *et al.* (2008) showed the influence of botanical origin on the chemical composition of honey through analysis of various elements in 51 Italian honey samples. Likewise, Grembecka and Szefer (2012), using flame atomic absorption spectrometry, estimated honey quality from different locales in Poland and Europe in light of their mineral composition.

Syria has various flora-rich regions that have been considered suitable for apiculture. Unfortunately, data dealing with element concentrations in Syrian honeys has been ignored. Thus, the present work focuses on determining several elements in different types of honey from different natural and artificial sources using a dry ashing method for X-ray fluorescence (XRF) analysis. In addition, cluster analysis (CA) is also applied in the present study to group the analyzed samples with regard to their botanical origin. The ability of CA to discriminate between natural honeys and those produced from bees fed with sugar was also studied.

2. Materials and Methods

Honey samples

A set of 24 Syrian natural honey samples were analyzed. In addition to the local samples, three jujube honey samples (200 g each) imported from India (two samples)

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and Pakistan (one sample) were used for comparison purposes. The Syrian honey samples (500 g each) were collected directly from sedentary beehives in different parts of Syria during the late spring and early summer months. All samples were collected in clean, closed glass jars and immediately transferred to the laboratory. The samples were unpasteurized, stored in glass bottles and kept at 4-5°C in the dark until analysis. The Syrian honey samples under study belonged to six representative honey types: citrus (C, n=6), multiflora (M, n=6), *Eucalyptus* (Eu, n=5), crataegus (Crat, n=3), sunflower (Sun, n=2) and wild plants (W, n=2). The botanical origin of some honey samples was confirmed by pollen analysis, according to Louveaux *et al.* (1978). Additionally, two types of artificial honey samples based on honeys produced from bees fed with sugar were collected after feeding a sugar solution to bees in one apiary (one beehive). The two sugar solutions were prepared as follows: the first solution (HIS) was prepared by mixing sugar and water on a 1:1 basis. A total of 1.5 kg commercial sugar was completely dissolved in 1.5 l hot-ultrapure water (18.2 MΩcm specific resistivity) using an electrical heating plate at 60°C. The obtained solution was cooled at room temperature. Then, the following chemical salts were dissolved in the sugar solution: (0.7259 g) $FeCl_3.6H_2O$, (0.0372 g) $Ni(NO_3)_2.6H_2O$, (0.0424 g) $CuCl_2.2H_2O$, (0.1563 g) $ZnCl_2$; the solution was mixed with a glass rod. The final volume of the obtained sugar solution was 2480 ml. The second sugar solution (HSB) was prepared in the same way but no chemical salts were added. For statistical analysis, two indipendent HIS and HSB sugar solutions were prepared. Feeding to bees of the sugar solutions was carried out at seven-day intervals.

Reagents and solutions

All aqueous solutions and dilutions were prepared with ultrapure water obtained from a water purification system (New Human Power II, South Korea) with 18.3 MΩcm specific resistivity. The solutions of 14 N HNO_3 'Analar' (BDH) were used for the honey ash dissolutions. The stock standard solutions of K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, and Sr with concentrations of 1000 μg ml^{-1} each were used for the preparation of the multi-element reference targets for XRF calibration. A pure cellulose powder (AG) for analysis from Seelze (Hannover/Germany) was used as a binder for preparation of the XRF targets.

Analytical procedures

Eleven elements (K, Ca, Ti, Cr, Mn, Fe, Cu, Ni, Zn, Rb, and Sr,) were determined in the honey samples using a dry ashing method for XRF analysis (Khuder *et al.*, 2010). Ten g of each honey sample were put in a 50-ml crucible and dried in an oven at 105°C for 72 h, covered, cooled in a desiccator and weighed. Each crucible-held dried sample was subjected to ashing in an electrical furnace. The temperature was increased in three steps: 200, 300, and 550°C; where the first and second steps lasted for 20 min each, while the third step lasted for 16 h. The ash of each honey sample was weighed and kept in the desiccator. Each obtained ash was dissolved in 1-ml volume of 6 N HNO_3 then removed to a small 5-ml volume vial. A volume of 100 μl of suspended cellulose solution (0.120 g ml^{-1}) was added to each dissolved ash. The obtained mixtures were thoroughly shaken using an electrical shaker (KS 125 basic, IKALABORTECHNIK Co., Japan) for 5 min, then removed to XRF spectro-cups with surface area of 4.91 cm^2 each, and dried under IR lamp. Finally, each obtained honey target was weighed and subjected to XRF analysis using Mo-secondary target for the determination of Fe, Ni, Cu, Zn, Rb, and Sr, and Cu-secondary target for the determination of K, Ca, Ti, Cr, and Mn.

Instrumental measurements

The XRF measurements were performed using an energy dispersive X-ray fluorescence instrument equipped with a 2 kW Mo tube and a Si (Li) semiconductor detector (PGT Co.) with an energy resolution of 140 eV at 5.9 keV. The operating conditions were differed, depending on the mode of the X-ray excitation: 7 mA and 17 kV, and 5 mA and 45 kV by using Cu- and Mo-secondary targets, respectively. The live time was 1000 s for both of the X-ray excitation modes.

The peak areas in the obtained spectra were evaluated using the AXIL-QXAS software package (IAEA, 2005). The XRF results were compared with those obtained by standardized AAS method using hollow cathode lamps (Rashed and Soltan, 2004). The accuracy, precision, and limits of detection (LOD) of the XRF were estimated using the method described by Khuder *et al.* (2010).

Statistical analysis

Basic statistics were carried out using the STATISTICA 6.0 statistical package for windows (Statsoft). Prior to chemometric processing, the root square of data was carried out in order to stabilize the variance. CA was used to group the analyzed honey samples with regard to their botanical origin. The Euclidean distance was used to measure the similarity as clustering method single linkage.

3. Results

XRF analysis

A typical XRF spectrum of a honey sample excited by means of Cu- and Mo-secondary targets is shown in figure 1. The spectra confirmed the presence of K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, and Sr in the analyzed samples. The detected elements were calibrated by constructing sensitivity curves (Fig. 2) and quantified using the AXIL-QXAS program. The validity of XRF was examined by estimating the precision, accuracy, and LOD parameters (Table 1). The LOD of K, Ca, Ti, Cr, and Mn were 0.40, 0.09, 0.06, 0.01, and 0.01 μg g^{-1}, respectively; while those of Fe, Ni, Cu, Zn, Rb, and Sr were 0.050, 0.032, 0.031, 0.030, 0.009, and 0.007 μg g^{-1}, respectively. A comparison

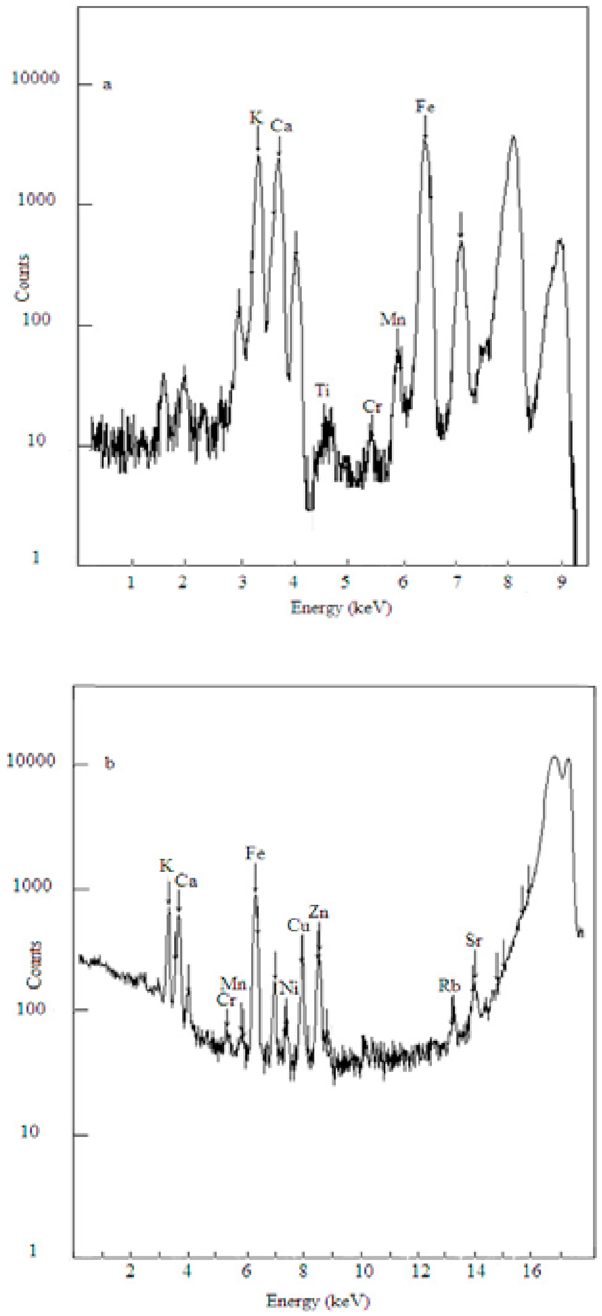

Fig. 1 - Typical spectra of a honey sample excited by X-ray Mo tube with (a) Cu-, and (b) Mo-secondary targets.

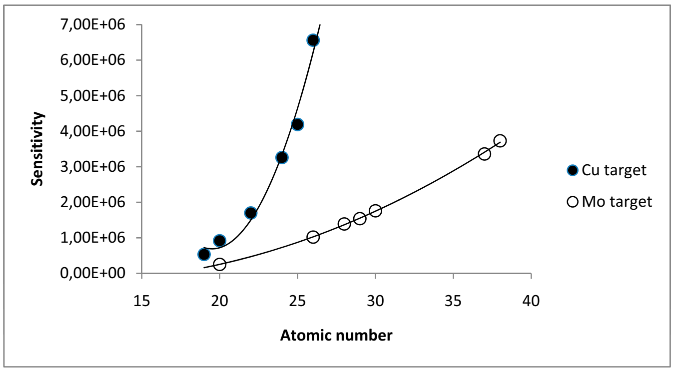

Fig. 2 - Calibration sensitivity curves obtained by X-ray excitation of elements using Cu- and Mo- secondary targets.

between XRF and AAS methods revealed a correlation coefficient above 0.990, indicating that the XRF was reliable and suitable to determine most of the elements in honey samples.

Table 1 - Determination of different elements in multi-element standard sample using Cu- and Mo-secondary targets for XRF analysis (z)

Secondary target	Elements	(Means±SD) (y)	A (%) (x)	RSD (%)(w)
Cu	K	9.68±0.35	-3.2	±3.62
	Ca	10.25±0.25	2.5	±2.44
	Ti	10.22±0.30	2.2	±2.94
	Cr	9.66±0.35	-3.4	±3.62
	Mn	9.72±0.33	-2.8	±3.40
Pooled (rms)(v)			2.85	
Mo	Fe	9.95±0.66	-0.5	±6.63
	Ni	9.50±0.55	-5	±5.79
	Cu	10.44±0.82	4.4	±7.85
	Zn	10.42±0.52	4.2	±4.99
	Rb	9.92±0.11	-0.8	±1.11
	Sr	9.95±0.08	-0.5	±0.80
Pooled (rms)d			3.24	

(z) The ‘dark matrix’ entered for running QXAS-AXIL program with Cu-secondary target mode was C (5%) and H by difference; while, that for Mo-secondary target was Si (1%) and O by difference.

(y) XRF results (µg) were obtained by measuring the multi-element standard three times; SD is the standard deviation.

(x) A is the accuracy calculated by the difference between the obtained and the used amounts (absolute amount is 10 µg).

(w) RSD is the relative standard deviation; RSD=(SD x Mean $^{-1}$) x 100.

(v) is the root mean square of elemental accuracy.

Honey analysis

Chemical analysis data (Table 2) concerning the studied honey samples differentiated two mineral groups: the most abundant and the trace elements. The first group was composed of K and Ca, having concentrations of more than 10 µg g^{-1}. The second mineral group comprised the trace elements: Fe, Cu, Zn, Rb, Ti, Cr, Mn, Ni, and Sr. Of these, two subgroups were noted: the trace elements Fe, Cu, Zn, and Rb with concentrations in the 1-10 µg g^{-1} range, and a second subgroup (Ti, Cr, Mn, Ni, and Sr) with concentrations < 1.0 µg g^{-1}.

The data were clustered in order to find the similarities between analyzed honey samples (Fig. 3) and also the elements (Fig. 4).

4. Discussion and Conclusions

The honey samples in the present work were subjected to an ashing process in order to increase the sensitivity of the XRF analysis, and the concentrations of the elements were much higher than the obtained LOD values.

Table 2 - Element concentrations in Syrian honeys from different botanical origins determined by using X-ray fluorescence analysis

Botanical origins		Element concentrations (µg.g^{-1})										
		K	Ca	Ti	Cr	Mn	Fe	Cu	Ni	Zn	Rb	Sr
M	Mean	138	76.1	0.212	0.029	1.04	5.87	2.34	0.23	1.21	1.03	0.63
	Min.	56.2	44.6	0.102	0.017	0.36	4.0	0.83	0.08	0.21	0.44	0.41
	Max.	183	118	0.285	0.036	1.69	9.42	4.53	0.39	3.82	2.2	1.03
Eu	Mean	121	92.6	0.292	0.016	1.74	8.35	3.82	0.18	2.44	1.05	0.64
	Min.	66.7	50.6	0.145	0.011	0.36	5.72	1.59	0.17	0.53	0.43	0.47
	Max.	228	127	0.401	0.024	3.16	12.4	6.09	0.20	7.16	1.78	0.79
C	Mean	40.3	45.5	0.085	0.026	0.50	1.74	1.14	0.13	2.42	0.32	0.31
	Min.	5.7	7.3	0.052	0.011	0.15	1.04	0.62	0.11	1.01	0.07	0.14
	Max.	84.6	78.5	0.099	0.054	1.06	2.43	1.59	0.14	4.30	0.94	0.70
Crat	Mean	125	43.3	0.103	0.028	0.90	7.57	2.95	0.20	3.50	1.57	0.48
	Min.	47.5	39.1	0.071	0.014	0.46	3.83	1.66	0.15	1.41	0.26	0.44
	Max.	179	46.1	0.125	0.055	1.34	13.1	4.39	0.25	7.33	2.53	0.50
Sun	Mean	107	34.4	0.142	0.024	0.32	4.83	3.10	0.162	3.83	0.81	0.65
	Min.	98.3	33.6	0.115	0.019	0.2	4.68	2.67	0.135	3.75	0.65	0.32
	Max.	115	35.1	0.168	0.029	0.42	4.98	3.53	0.188	3.91	0.98	0.99
W	Mean	198	50.3	0.30	0.029	2.54	17.0	3.4	0.265	2.88	4.52	0.38
	Min.	187	49.1	0.18	0.024	1.81	14.2	1.06	0.109	1.38	1.57	0.36
	Max.	208	51.4	0.42	0.034	3.26	19.7	5.73	0.420	4.37	7.47	0.41
J	Mean	250	58.5	0.17	<0.01	3.37	5.40	1.46	0.083	0.65	3.97	0.49
	Min.	219	38.7	0.12	-	0.60	4.98	0.83	0.081	0.27	2.69	0.13
	Max.	280	78.3	0.22	-	6.13	5.82	2.08	0.084	1.03	5.24	0.85
HSB	Mean	4.1	16.1	0.05	<0.01	0.11	1.35	1.34	0.069	3.19	0.08	0.09
	Min.	3.9	15.3	0.03	-	0.10	1.28	1.27	0.064	3.03	0.07	0.08
	Max.	4.3	16.9	0.07	-	0.20	14.2	1.41	0.074	3.35	0.08	0.10
HIS	Mean	5.1	17.0	0.05	<0.01	0.09	22.0	3.29	1.36	21.6	0.05	0.07
	Min.	4.8	16.1	0.03	-	0.08	20.9	3.12	1.28	20.5	0.04	0.06
	Max.	5.4	17.9	0.07	-	0.12	23.1	3.46	1.44	22.7	0.05	0.07

M, Eu, C, Crat, Sun, W, J, correspond to multiflora, *eucalyptus,* citrus, crataegus, sunflower, wild plants and jujube, honeys respectively. HSB and HIS were honeys produced from bees fed with sugar alone and sugar enriched with salts, respectively.

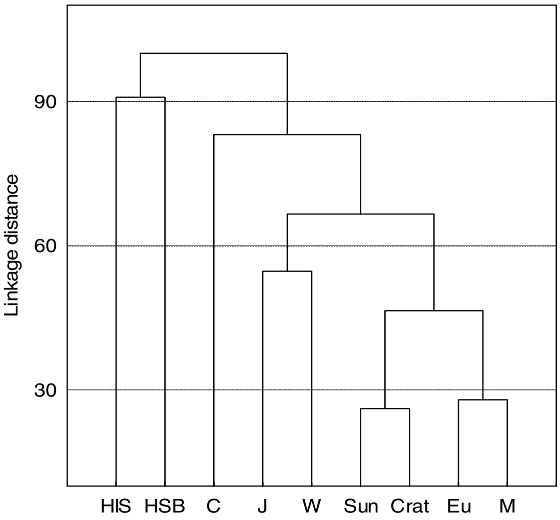

Fig. 3 - Dendrogram of cluster analysis of elements in different types of honeys (root square of data was treated by the linkage method with Euclidean distance as measure of similarity).
HIS and HSB= honeys produced from bees fed with sgar enriched with salts and sugar alone, C= citrus, J= jujube, W= wild plants, Sun= sunflower, Crat= crataegus, Eu= eucalyptus, M= multiflora.

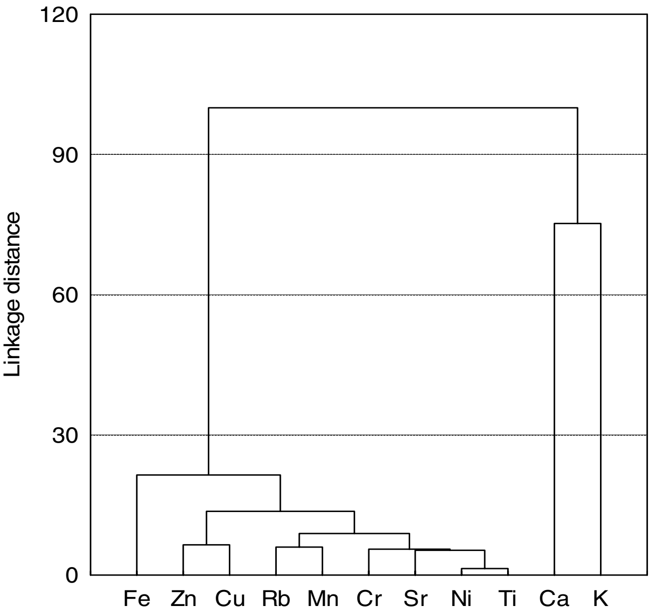

Fig. 4 - Dendrogram of 11 analyzed elements in different types of honey samples (root square of data was treated by the linkage method with Euclidean distance as measure of similarity).

Based on our data the minerals in Syrian natural, artificial, and imported honeys fell into two groups: the first group was composed of K and Ca, while the other included the trace elements Fe, Cu, Zn, Rb, Ti, Cr, Mn, Ni, and Sr.

Potassium represented the most abundant element in the Syrian honey samples with a mean concentration of 107 µg g^{-1}. This finding coincides with most other authors who consider this element to be the most quantitatively important in honey (Terrab *et al.*, 2004; Fernandez-Torres *et al.*, 2005; Nozal Nalda *et al.*, 2005; Pisani *et al.*, 2008). The highest and lowest K concentrations were found in Jujube (250 µg g^{-1}) and citrus (40.3 µg g^{-1}) honeys, respectively; the mean concentrations of K in Syrian honeys were very similar to those in honeys from Brazil (Sodré *et al.*, 2007) and less than values obtained for Turkish honeys (Cantarelli *et al.*, 2008). Calcium in Syrian honeys was the second most abundant element with a mean concentration of 61.9 µg g^{-1}; the values found for this element in Syrian honeys were similar to those of jujube honeys imported from Pakistan and India, as well as for honeys from other countries (Cantarelli *et al.*, 2008; Chudzinska and Baralkiewicz, 2010).

The mean concentration of Fe and Cu in Syrian honeys was estimated to be 6.33 and 2.49 µg g^{-1}, respectively. Our value for Fe is very similar to that obtained by Cantarelli *et al.* (2008) for Turkish honeys, but higher than for honey from Argentina, Brazil and Switzerland (Bogdanov *et al.*, 2007; Sodré *et al.*, 2007; Cantarelli *et al.*, 2008). It is worth mentioning that the concentrations of Cu in Syrian honeys were much higher than those for honeys from Poland, Switzerland, the Czech Republic, Brazil and Argentina (Bogdanov *et al.*, 2007; Lachman *et al.*, 2007; Sodré *et al.*, 2007; Cantarelli *et al.*, 2008; Chudzinska and Baralkiewicz, 2010). The mean concentration of Zn and Rb was 2.27 and 1.50 µg g^{-1}, respectively; the value for the former was comparable to those obtained for the imported honeys (1.89 µg g^{-1}), as well as for honeys from Poland, Argentina, Spain, Italy and Turkey (Cantarelli *et al.*, 2008; Chudzinska and Baralkiewicz, 2010). The mean concentration of Rb in Brazilian honey was much lower than that obtained in the present work (Sodré *et al.*, 2007). Latorre *et al.* (1999) reported a mean value of 1.5 µg.g^{-1} in Spain, which is similar to the mean Rb concentration found in Syrian honeys.

Titanium was found in the honey samples with a mean value of 0.184 µg g^{-1}, and Cr was identified in 20 samples (87% of the total) with a mean concentration of 0.025 µg g^{-1}. Sodré *et al.* (2007) found Ti in Brazilian honey samples (mean value 0.112 µg g^{-1}) while the mean concentrations of Cr in different honeys from Switzerland, Chile, and Brazil were 0.005, 0.070 and 0.038 µg g^{-1}, respectively (Fredes and Montenegro, 2006; Bogdanov *et al.*, 2007; Sodré *et al.*, 2007). Manganese and Ni were found in 21 and 14 honey samples, respectively, with mean concentrations of 1.29 and 0.204 µg g^{-1}. The mean concentrations of Mn in honeys from Argentina and the Czech Republic varied from 0.33 to 2.87 µg g^{-1} (Lachman *et al.*, 2007; Cantarelli *et al.*, 2008), and a mean value of 1.0 µg g^{-1} was found in Turkish honey (Tuzen *et al.*, 2007). Concentrations of Ni in Syrian honeys were comparable to those obtained for honeys from Chile, the Czech Republic and Switzerland (Fredes and Montenegro, 2006; Bogdanov *et al.*, 2007; Lachman *et al.*, 2007). Strontium was verified in all samples with a mean concentration of 0.518 µg g^{-1}. Our data showed that the highest Sr concentration (1.03 µg g^{-1}) came from a multiflora honey obtained from a beehive placed near highways. Results similar to ours have been recorded previously: Fredes and Montenegro, (2006) found that the highest concentrations of Sr in Chilean honeys were noted in honeys harvested from beehives close to roads and highways.

Cluster analysis was applied to the data of the 11 elements in the nine types of studied honeys. At a similarity level of 60%, the natural honey samples were grouped into three clusters (Fig. 3). The first cluster contained only the citrus honey, the second Jujube and wild plant honeys, and the third the remaining honey types (sunflower, crataegus, eucalyptus, and multiflora). At the same similarity level, the two artificial honey samples (HIS and HSB) were well discriminated in two clusters. The hierarchical dendrogram (Fig. 4) discriminated between the elements according to their concentrations. The elements Zn, Fe, Rb, Cu, Mn, Ni, Sr, Cr, and Ti represented a group of elements with concentrations ≤10 µg g^{-1}; while K and Ca represented a group of elements with concentrations ≥10 µg g^{-1}. The hierarchical dendrogram shown in figure 4 could suggest a potential relationship between the samples' origin and the clusters of particular elements, which reflects the chemical composition of the botanical origin of honey.

In conclusion, cluster analysis grouped the natural honeys into different clusters with regard to their botanical origin. Citrus honeys, which were poor in element concentrations, formed an individual group while wild plants and jujube honeys formed the second group, which were rich in the determined minor and trace elements. Samples of mutiflora, eucalyptus, crataegus, and sunflower honeys formed the third natural group with moderate elemental concentrations. CA technique also revealed a very good discrimination between natural honeys and those produced from bees fed with sugar.

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