TRACE ELEMENT CONTENT OF HUNGARIAN ACACIA HONEYS

Nikolett Czipa[a]*, Zita Burján[a], Dávid Andrási[a] and Béla Kovács[a]

Paper was presented at the 4th International Symposium on Trace Elements in the Food Chain, Friends or Foes, 15-17 November, 2012, Visegrád, Hungary

Keywords: Honey, Trace element content, ICP-MS, ICP-OES

Forty-four acacia honey samples from beekeepers and hypermarkets were collected examined in our laboratory. Five elements (Al, Cu, Fe, Li, Sr, Zn) were analysed by ICP-OES and seven elements (As, Ba, Cd, Cr, Ni) were also determined by ICP-MS. Aluminium, iron and zinc were the most abundant elements found in our samples under study. The concentration was ranging between 100.0 and 4910 μg kg^{-1} for Fe, 319.0 and 4440 μg kg^{-1} for Zn and 242.0 and 3095 μg kg^{-1} for Al. The lowest values were 4.648±4.184 μg kg^{-1} for Cd, 27.12±13.62 μg kg^{-1} for Cr and 42.49±20.37 μg kg^{-1} for As. The element concentration increased in the following order: Cd < Cr < As < Li < Ni < Ba < Cu < Sr < Al < Zn < Fe.

* Corresponding Authors
Fax: +36.52.417574
E-Mail: czipa@agr.unideb.hu
[a] Institute of Food Science, Quality Assurance and Microbiology, Centre for Agricultural and Applied Economic Sciences, University of Debrecen, 138. Böszörményi Str. Debrecen, H-4032, Hungary

Introduction

Honey is a very important and healthy food product that is defined by the EU (Eu Council Directive 2001/110/EC) as “The natural sweet product produced by *Apis Mellifera* bees from the nectar of plants from secretions of living plants, which bees collect, transform by combining with specific substances of their own, deposit, dehydrate, store and leave in honeycombs to ripen and mature.” In the year 2010 the honey production of the world was 1.540.242 tons and in EU was 202.871 tons. Hungary was the fourth biggest honey producer in EU with 16.500 tons. Hungarian acacia honey is widely known famous due to his purity.

Quality of honeys depends on various parameters such as sugar, moisture, vitamin, amino acids, element content, enzyme activity, electrical conductivity, solid corpuscles, etc. Mineral content of honey is very low.[1] Some of the metals such as chromium, copper, iron, manganese and zinc are essential for human body,[2] but at the same time these elements can be toxic to human beings in high doses.[3]

Mineral content of a honey may be the indicator of the environment.[4] The collecting area of the honey bees is about 7 km^2. Due to this large surface area the honey bees and their products is suitable to show the status of this area (e.g. chemical pollution).[5]

Methods

Samples

Examined acacia honey samples were collected from beekeeper and hypermarkets, the collecting area was Hungary. Ten samples each collected in the year 2007, 2008 2011 and 14 samples in 2009 respectively and stored in glass jars at room temperature in dark until analysis.

Reagents and solutions

All chemicals were of analytical-reagent grade or better. Nitric acid 69% and hydrogen peroxide 30% were purchased from VWR. Ultrapure water (Milli-Q® Integral 3/5/10/15 System, Millipore, France) was used to the preparation of solutions and dilutions.

Instrumentation

Samples were prepared according to the method of Kovács et al. .[6] Determination of aluminium, copper, iron, lithium, strontium and zinc was carried out by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Thermo Scientific iCAP 6300, England). Measuring of arsenic, barium, cadmium, chrome and nickel concentration was carried out by inductively coupled plasma-mass spectrometry (ICP-MS) (Thermo Scientific X Series 2, England). All measurement was performed in triplicate.

Results and discussion

The results are shown in Table 1. and Table 2. Iron was the most abundant element presented in most of the honey samples where as the cadmium was found at the lowest amount in all samples.

The quantity of iron was the highest in samples of the year 2007 and 2008. This value was four times higher in the year 2007 (1787-4913 μg kg^{-1}) as compared to year 2011 (100-1781 μg kg^{-1}). Zinc concentration was very high in 2009 (2190-4440 μg kg^{-1}) and 2011 (319.1-3924 μg kg^{-1}) samples which was two to three times higher than in other years. The zinc concentration in 2009 and 2011 samples was higher than the iron concentration. Aluminium content was nearly same in all years. The content of this element was higher in 2011 than the iron concentration.

Table 1. Trace element content by ICP-OES

	Al	**Cu**	**Fe**	**Li**	**Sr**	**Zn**
2007	1324±262	269.2±56.9	3771±571	56.18±2.13	283.7±22.3	1032±472
2008	1678±273	302.6±42.3	2238±568	56.28±2.08	249.1±41.6	1442±4212
2009	1027±224	406.2±44.3	1696±609	58.53±0.89	350.0±51.8	3294±560
2011	1552±255	358.6±63.9	844±262	54.88±3.04	550.6±161.8	1838±423
Average	1463±211	324.9±59.9	2178±772	56.32±2.41	340.5±119.1	1747±471

Table 2 Trace element content by ICP-MS

	As	**Ba**	**Cd**	**Cr**	**Ni**
2007	40.98±9.46	135.6±40.5	2.294±0.291	34.66±15.44	141.5±32.4
2008	33.97±12.25	97.98±18.91	6.995±0.307	31.56±10.96	123.6±32.8
2009	55.75±11.91	84.60±17.57	10.45±3.94	19.20±6.75	71.88±36.81
2011	17.61±7.71	67.35±9.14	1.773±0.368	17.76±11.21	68.31±26.18
Average	42.49±20.37	98.07±47.37	4.641±4.184	27.12±13.62	98.19±47.69

Concentration of other elements was lower then 1000 µg kg^{-1}. Lithium content wasn't shown any change during the four years. Nickel and barium were found in the samples in the same level**.** Copper concentration was the highest in 2009 (338.2-454.3 µg kg^{-1}) and the lowest in 2007 (210.7-374.5 µg kg^{-1}). Strontium content was two times higher in 2011 (327.2-831.3 µg kg^{-1}) than 2007 and 2008 (261.4-319.3 and 185.2-400.7 µg kg^{-1}).

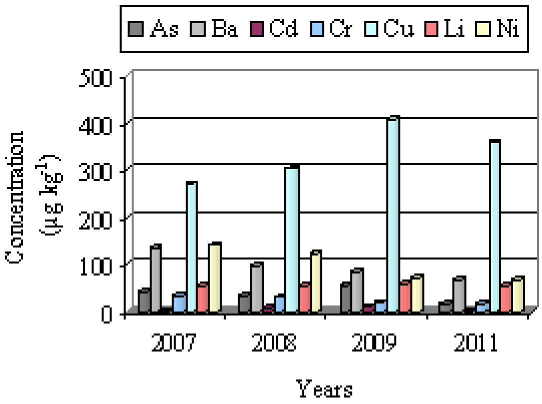

Figure 1. Element content of acacia honeys I.

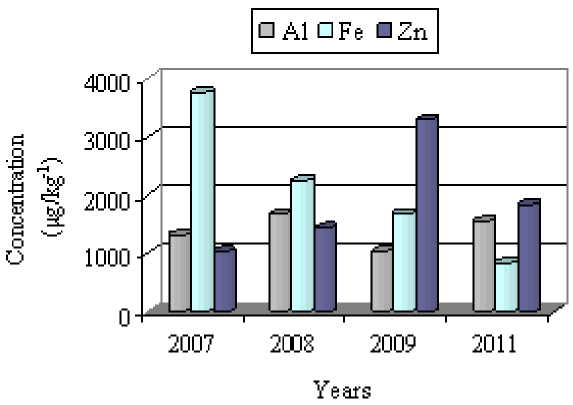

Figure 2. Element content of acacia honeys II.

The three elements in the lowest concentration were cadmium, chromium and arsenic. Cadmium level was very low, its value ranged between 0.112 and 15.5 µg kg^{-1}. The concentration of this element was more times higher in 2009 (6.49-15.5 µg kg^{-1}) than 2011 (0.11-4.07 µg kg^{-1}). Chrome content was higher in 2007 and 2008 than 2009 and 2011, this value was nearly duplex. The lowest arsenic concentration (5.65-26.5 µg kg^{-1}) was measured in 2011 and the highest (33.8-69.1 µg kg^{-1}) in 2009

The average concentration of the examined elements decreased in the following order: Fe>Zn>Al>Sr>Cu>Ni≥Ba>Li>As>Cr>Cd. In 2009 the barium concentration of the honey samples was higher than the nickel content (Figure 1.). The iron concentration was the highest in 2007 and 2008 but in 2009 and 2011 the zinc content was the higher. In 2007 and 2008 the zinc content was followed by aluminium concentration that was lower than the iron content in 2009. The concentration of aluminium and iron was inverse of the previous year (Figure 2.).

Among the elements examined so far there was no significant relation found. The nearest correlation was r^2=0.536 between the cadmium and arsenic content. This was followed by cadmium and lithium concentration with r^2=0.511.

Table 3. Comparison of trace element content of honey types from different country

	Tuzen et al.	**Pisani et l.**	**Terrab et al.**	**Our results**
Al	83-325	No data	445-25400	242-3095
As	No data	2.78-20.20	0.00-1930	5.65-69.12
Ba	No data	218-2634	280-1116	18-302
Cd	0.90-17.90	1.00-15.30	0.00-50.00	0.11-15.52
Cr	No data	No data	20.0-440.0	3.3-48.4
Cu	230-2410	172-5900	2620-7800	139-552
Fe	1800-10200	970-13700	4920-24100	100-4912
Li	No data	No data	11700-27700	53-61
Ni	5.3-29.9	77.0-2760.0	170.0-660.0	4.5-392.6
Sr	No data	850-2010	0-1010	185-831
Zn	1100-12700	720-3660	70-16800	319-4440

 DOI: 10.17628/ECB.2012.1.446

Compared to our results Terrab et al.[7] reported higher element concentrations of avocado honeys from Spain. Tuzen et al.[1] measured lower aluminium concentration in the multifloral honeys from Turkey, but determined iron, nickel and zinc content was higher than our values. The barium, copper, iron, nickel and strontium content in the honey samples from Siena County[8] showed higher concentrations (Table 3).

The lithium content in Spain honeys samples was more than two times higher than our values. In case of cadmium concentration, the difference among the countries was not very important.

From our results it can be concluded, that the concentration of some element may alter year after year, but in case of main toxic elements (As, Cd) this alteration does not mean much as regards to food-safety instance - these elements are found in a very low concentration.

Acknowledgements

The research work was supported by the TÁMOP 4.2.1./B-09/1/KONV-2010-0007 and TÁMOP-4.2.2/B-10/1-2010-0024 projects. The project was co-financed by the European Union and the European Social Fund.

References

[1]Tuzen, M.; Silici, C.; Mendil, B.; Soylak, M. *Food Chem.* **2007**, *103*, 325-330.

[2]Falco, G.; Gomez-Catalan, C.; Llobet, J.M.; Domingo, J.L. *Trace Elements and Electrolytes* **2003**, *20*, 120-124.

[3]Domingo, J.L. *J. Toxicol. Environ. Health* **1994**, *42*, 123-141.

[4]Przybylowski, P.; Wilczynska, A. *Food Chem.* **2001**, *74*, 289-291.

[5]Leita, L.; Muhlbachova, G.; Cresco, S.; Barbattini, R.; Mondini, C. *Environ. Monitoring and Assesment* **1996**, *43*, 1-8.

[6]Kovács, B.; Győri, Z.; Prokisch, J.; Loch, J.; Dániel, P.; *Commun. soil sci. plant anal.,* **1996** , *27*(5-8), 1177-1198.

[7]Terrab, A.; Recamales, A.F.; González-Miret, M.L.; Heredia, F.J. *Food Chem.,* **2005**, *92*, 305-309.

[8]Pisani, A.; Protano, G.; Riccobono, F. *Food Chem.,* **2008**, *107*, 1553-1560

Received: 15.10.2012.
Accepted: 12.11.2012.