Characterization of Nectar Honeys According to Their Physicochemical Parameters and Mineral Content

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The aim of this study was to characterise the nectar honeys (monofloral and multifloral) extracted from beehives placed in the South-Muntenia region of Romania, site where honey production increased in the last years. Physicochemical characteristics (pH, electrical conductivity, ash content refractive index, water content) and minerals content (P, K, Ca, Fe and Zn) were evaluated. The obtained results indicate o good quality level that demonstrates an adequate extracting and processing of honey.

Keywords: honey, physicochemical parameters, mineral content, quality

Honey is a complex foodstuff, a natural sweet substance produced by bees from the nectar of plants (nectar honey) or from honeydew excreted by plant sucking insects (honeydew honey) [1, 2]. This food source for bees in beehive has a very long story for human consumption and for medicinal use [3, 4].Today are very well knows the therapeutical effects of honey and for that reason it is important to include that in our daily foods. Honey contains a complex mixture of proteins, free amino acids, phenolic compounds, vitamins and minerals necessary on the body health, being reported to contain about 200 substances [5]. Honey composition is influenced by the plant species, environmental conditions and by the beekeepers through the type of beehive, honey extraction and processing.

Honey composition is influenced by the plant species, soil resources on growing, environmental conditions and by the beekeepers through the extraction and processing. Honey commercially available in Romanian markets has a high variation in quality, largely assessed by colour, flavour and density. A deep control of the honey quality is necessary and it is very important to verify the compliance with the quality specifications of the European Union [1].

The aim of this study was to investigate the quality of 14 different type nectar honey samples extracted from beehives placed in South-Muntenia region of Romania. For this purpose physicochemical characteristics together with mineral content were evaluated. Physicochemical parameters: pH, electrical conductivity, ash content, refractive index and water content, were analysed using the Harmonised Methods of the International Honey Commission [6]. The mineral content of food and environmental samples is determined using different sensitive analytical techniques [7-10,12]. In this work a rapid and not expensive technique was used: Energy Dispersive X-ray Fluorescence (EDXRF) combined with Internal Standard technique [11,12]. The concentrations of minerals: P, K, Ca, Fe and Zn were determined.

Experimental part

Sample collection

A number of 14 honey samples collected from different sites of South-Muntenia region of Romania (figure 1) during the 2011 harvesting season were provided by individual beekeepers.

Fig. 1. Geographical position of sampling sites

The botanical origin of the honey samples was established based on the information provided by beekeepers. Table 1 shows the botanical and geographical origin of the honey sample. Data indicate that about 78% of honey samples were monofloral (rape, acacia, sunflower and linden) and about 22% were multifloral. *Robinia* sp. (acacia) was the main source used by honeybees in the South-Muntenia region of Romania. Samples were transferred to the laboratory in the original packages, kept at 20-22 ^{0}C and analysed no longer than 48 h after extraction from the beehive by beekeepers.

Physicochemical analysis

Physicochemical parameters were analysed using the Harmonised Methods of the International Honey Commission [6].

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Sample	Botanical origin	Geographic origin
h1	Monofloral - *Brassica (*rape)	Draganesti Vlasca, Teleorman
h2	Monofloral - *Robinia* (acacia)	Valea Bujorului, Giurgiu
h3	Monofloral - *Robinia* (acacia)	Bogati, Arges
h4	Monofloral - *Robinia* (acacia)	Schitu Golesti, Arges
h5	Multifloral - Blossom, blend	Telesti, Dambovita
h6	Monofloral - *Tilia* (linden)	Crevedia Mare, Giurgiu
h7	Monofloral - *Heliantus* (sunflower)	Cosambesti, Ialomita
h8	Monofloral - *Tilia* (linden)	Snagov, Ilfov
h9	Monofloral - *Robinia* (acacia)	Sabareni. Ilfov
h10	Monofloral - *Heliantus* (sunflower)	Dragos Voda, Calarasi
h11	Monofloral - *Robinia* (acacia)	Pucioasa, Dambovita
h12	Multifloral - Blossom, blend	Pucioasa, Dambovita
h13	Multifloral - Blossom, blend	Moreni, Dambovita
h14	Monofloral - *Robinia* (acacia)	Bezdead, Dambovita

Table 1
BOTANICAL AND GEOGRAPHICAL ORIGIN OF HONEY SAMPLES

The *p*H solution of 10 g honey in 75 mL of CO_2 free distilled water was measured by a Consort P501 pH-meter.

Electrical conductivity was measured at 20°C with the conductivity meter HACH CO15 using a solution of 20 g dry matter of honey in 100 mL deionised water. Before the measurements the calibration of the conductivity meter was made using a 0.1 M KCl solution. Through the electrical conductivity measurements the ash content was determined.

The refractive index and water content was determined using the NOVEX ABBE refractometer, thermostated at 20°C and calibrated with distilled water. Each honey sample was measured twice and the average value was considered.

Determination of mineral elements

P, K, Ca, Fe and Zn concentrations were determined using Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometry combined with Internal Standard technique, using the ElvaX spectrometer having a X-ray tube with Rh anode, operated at 45 kV. An amount of 3 g of honey was mixed with yttrium internal standard (100 μL, from Y_2O_3 nitric solution of 160.78 mg Y/L). Honey samples were excited for 1800 s and the characteristic X-rays were detected by a multichannel spectrometer based on a solid state Si-pin-diode X-ray detector with a 140 μm Be window and a energy resolution of 165 eV at 5.9 KeV. ElvaX software was used for data acquisition and for the EDXRF spectra processing.

The minerals concentration (C_{min}) was determined using the Castaing's approximation [11]:

$$C_{min} = \frac{I_{min}}{I_{st}} C_{st} \quad (1)$$

where I_{min} and I_{st} are the X-ray intensities measured for mineral and for standard respectively and C_{st} is the concentration of the internal standard.

The accuracy of the measurements was checked by using NIST SRM 1085b Wear-Metals in Lubricating Oil and was obtained a recovery between 98.7% and 102.5%.

Results and discussions

The results obtained for physicochemical parameters determined are presented in table 2. The *p*H values ranged from 3.61 to 4.72. These values are in concordance with the *p*H acceptable range for honey [2]. The observed variation of honey pH can be given by different honey extraction conditions.

The electrical conductivity of honey depends on botanical origin and can give information about mineral salts and proteins content of honey. The values obtained for honey samples under study range between 97.7 and 431.0 μS cm^{-1} and are under maximum values admitted by European honey directive [1].

Through the electrical conductivity measurements ash contents of honey samples were determined. All the values obtained for ash content in analysed honey samples are under the admitted maximum value (0.6%). It was observed a linear relationship, characterised by a correlation coefficient R=0.9969, between the ash content and electrical conductivity (fig. 2), situation reported also by others [13-15].

The refractive index depends on solids content of honey and default on the water content. A linear relationship based on the correlation coefficient R=0.9982 was observed (fig. 3). A value greater than maximum admitted values (20%) by international legislations [2] can be a proof of honey adulteration. For two acacia honey samples (i.e. h9 and h11) collected from Sabareni-Ilfov and Pucioasa-Dambovita, the water content exceeded the maximum admitted values.

The concentrations of P, K, Ca, Fe and Zn determined in honey samples under this study by EDXRF measurements, are given in table 3.

The most abundant mineral was K with an average content of 251.49 mg/kg, followed by Ca with an average content of 61.82 mg/kg and P with an average content of 28.07 mg/kg.

Fe and Zn were present in moderate amounts in the honey samples, with average content of 6.67 mg/kg and 2.88 mg/kg. The mineral content of honey depends on the environmental conditions and the geographical origin.

Sample	pH	Electrical conductivity [μS cm^{-1}]	Ash content [%]	Refractive index	Water content [%]
h1	3.93	159.5	0.0711	1.4975	17.40
h2	3.65	97.7	0.0441	1.4990	16.80
h3	3.96	101.2	0.0450	1.4960	18.00
h4	3.87	99.9	0.0446	1.4985	17.00
h5	4.29	251.7	0.1114	1.4940	18.80
h6	3.84	202.0	0.0897	1.4980	17.20
h7	3.67	188.0	0.0830	1.4985	17.00
h8	4.25	334.0	0.1494	1.4940	18.80
h9	4.72	109.4	0.0439	1.4835	22.80
h10	4.09	206.0	0.0920	1.4950	18.40
h11	4.58	162.2	0.0728	1.4900	20.60
h12	4.12	259	0.1163	1.4950	18.40
h13	4.08	431.0	0.1934	1.4955	18.20
h14	3.61	114.0	0.0464	1.4995	16.40
RSD*	0.14-0.92	2.8-9.5	0.004-0.018	0.08-0.12	0.25-1.30
*Relative Standard Deviation					

Table 2
DISTRIBUTION DATA FOR PHYSICOCHEMICAL PARAMETERS IN HONEY SAMPLES

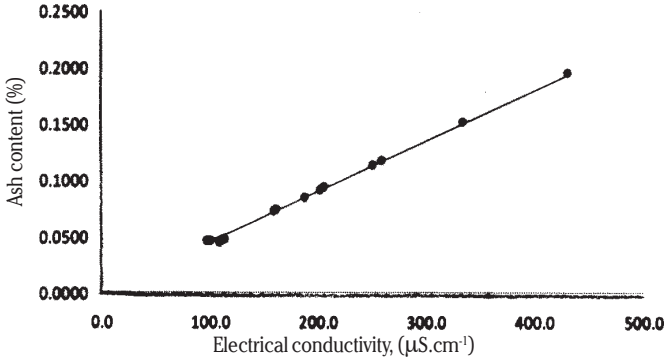

Fig. 2. Linear regression of electrical conductivity (μS cm^{-1}) and ash content (%).

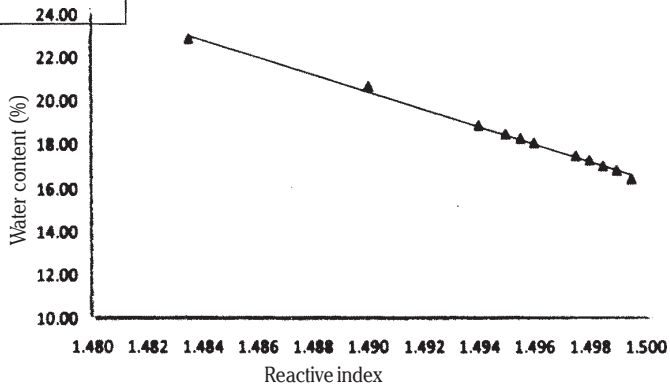

Fig. 3. Linear regression of refractive index and water content (%)

Sample	P	K	Ca	Fe	Zn
h1	45.78	207.84	46.20	11.52	4.89
h2	21.05	258.92	64.12	5.63	1.60
h3	24.40	187.22	58.37	6.35	1.84
h4	21.94	193.95	62.85	6.57	2.47
h5	28.07	433.74	92.21	4.86	3.65
h6	32.34	305.81	37.94	6.92	2.75
h7	48.65	192.25	50.37	10.20	3.58
h8	35. 21	327.06	33.94	7.25	3.02
h9	22.84	211.68	60.79	7.91	2.21
h10	51.02	172.50	49.58	11.04	4.15
h11	28.70	244.07	95.04	6.78	3.85
h12	32.45	370.51	89.70	5.70	3.13
h13	26.05	289.05	64.80	5.89	2.39
h14	27.68	368.53	86.90	5.06	1.77
RSD*	1.3-4.7	1.5-12.1	2.5-9.1	0.8-2.3	0.2-0.9
Mean	28.07	251.49	61.82	6.67	2.88
Minimum	21.05	172.5	33.94	4.86	1.60
Maximum	51.02	433.74	95.04	11.52	4.89
*Relative Standard Deviation					

Table 3
MINERAL CONCENTRATIONS (mg/kg) IN HONEY SAMPLES DETERMINED BY EDXRF MEASUREMENTS

This study will be extended to establish a correlation between the environmental pollution degree and the mineral content together with heavy metals content. *Honey shall be free from heavy metals in amounts which may represent a hazard to human health,* according to the Revised Codex Standard for Honey, Codex STAN 12-1981 [2]. That means that a presence of heavy metals in large amount can be attributed to environmental pollution.

Conclusions

Honeys from the South-Muntenia region of Romania generally present a good quality level, according to the European honey directive. Only two honey samples did not fit within European standards relative to water content, reflecting a poor honey adulteration by beekeepers. The most abundant mineral in honey samples is K, followed by Ca and P. This study demonstrate that basic physicochemical parameters and mineral content, determined by using rapid, cheaper but sensitive and reliable methods, give essential information about the honey quality.

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