# ESSENTIAL MINERALS DISTRIBUTION IN SOME HONEY TYPES FROM BANAT COUNTY

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## Abstract

*It were analyzed the total minerals contents for different types of honey from Banat County. The analysed minerals were: Na, K, Mg, Ca, Fe, Mn, Zn and Cu. Metals contents were determinated by flame atomic absorption spectrometry (F-AAS) with high-resolution continuum source ContrAA 300 spectrometer. The results were statistically interpreted using multivariate analyses.*
***Keywords:*** *minerals, honey, flame atomic absorption spectrometry, multivariate analyses*

## Introduction

Honey is considered an important source of energy witch contains a complex mixture of carbohydrates, aromatic substances, pigments, amino acids, other organic acids [Terrab et al, 2003], vitamins ($B_1$, $B_2$, $B_5$, $B_6$, C, E, K, A), enzymes and minerals. One kilogram of honey has the same caloric value with 3 liters of milk, 430 grams of butter, 2 kilograms of eggs, 1.7 kilograms beef, 4.5 kilograms of fish, 600 grams chocolate [Socaciu, 2003].

Honey is produced by Apis melifera (bees) using flower nectars and sugar exudation [Bura et al, 2005]. The flower sources used by the bees influence the final chemical composition of honey [Bura et al, 2005]. Many studies have shown that the minerals contents of the honey varied in accordance with the geographical origin.

The aim of this study was to determine the contents in Na, K, Ca, Mg, Fe, Mn, Zn and Cu from different types of honey originating from flowers, acacia, sunflower and lime. This study represents a part of serial researches having like principal subject the minerals contents of honey samples produced in different location from Banat County.

## Experimental

### Samples preparation

The essential metals were determinated in ten honey samples from different location situated in Banat County: Timiş District and Caraş-Severin District. Analyzed honey samples from Timiş District were purchasing from: Timişoara – 1, Conacul Iosif – 2, Berini – 3. Figure 1 present the map of Timiş District:


**Fig 1**: The map of Timiş District [www.travelworld.ro]

Analyzed honey samples from Caraş-Severin District were purchasing from: Domaşnea – 4, Bocşa-Română – 5, Plugova – 6, Cuptoare-7. Figure 2 present the map of Caraş-Severin District:


**Fig. 2**: The map of Caraş-Severin District [www.travelworld.ro]

The ten analysed honey samples from Timiş and Caraş-Severin Districts were the following:
**Sample 1 -** Mixed flowers honey from Timişoara
**Sample 2** - Sunflower honey from Conacul Iosif
**Sample 3** - Acacia honey from Domaşnea
**Sample 4** – Mixed flowers honey from Conacul Iosif
**Sample 5** - Lime honey from Bocşa-Română
**Sample 6** - Acacia honey from Plugova
**Sample 7** – Mixed flowers honey from Berini
**Sample 8** - Sunflower honey from Berini
**Sample 9 -** Acacia honey from Cuptoare
**Sample 10 -** Lime honey from Cuptoare

The heavy metals content from honey samples were analyzed after dry burning of 10 g in the quartz capsules at 650$^{o}$C for 4 hours. After complete burning a nitric acid 0.5 N solution was added up to 50 mL. The solutions obtained were used for total essential metals contents determination by flame atomic absorption spectrometry (F-AAS).

**Reagents**

The standard solutions (1000 mg/L) were analytical grade from Riedel de Haen (Germany). The nitric acid 65% solution used was of ultra pure grade (Merck, Germany). All solutions were prepared using deionized water.

**The essential metals contents determination**

Analysis of essential metals content was made with ContrAA-300, Analytik-Jena device, by flame atomic absorption spectrometry (FASS) in air/acetylene flame. The device working parameters (air, acetylene, optics and electronics) were adjusted for maximum absorption for each element. Acetylene was of 99.99 % purity. Under the optimum established parameters, standard calibration curves for metals were constructed by plotting absorbency against concentration. In a definite range for each metal a good linearity was observed. The correlation coefficient for the calibration curves ($r^2$) ranged between 0.9745 - 0.9891. All analyses were made in triplicate and the mean values were reported. All the values obtained for essential metals contents in analysed samples were calculated in mg/kg honey (ppm).

Statistical interpretation of data obtained using multivariate analyses was performed with Statistica-6 software.

## Results and Discussions

The analyzed essential minerals for human's organism were the macroelements **Sodium**, **Potassium**, **Calcium**, **Magnesium** and the microelements **Cooper**, **Zinc**, **Manganese**, **Iron**.

**Na** is an alkaline metal essential in many physiological processes. It is present in extra cellular fluids in animals and humans and is responsible for depolarization of cellular membrane and for the water equilibrium in intra- and extra cellular medium. In blood **Na** concentration is about 10 times more than in intracellular medium [Mogos, 1997]. The lower content in **Na** for analyzed honey samples was determinated in sunflower honey from Berini (26.6 ppm). The highest content in **Na** was obtained for sunflower honey from Conacul Iosif (138.8 ppm).

**K** is also an essential macro-element for human. It is important because: is involving in muscles contraction, in lipids metabolism, in proteins synthesis, maintaining the fluid and electrolyte balance in the body and is responsible in the nerve impulses sending. The necessary daily intake is between 2-4 g/day [Mogos, 1997]. For analyzed honey samples the higher **K** concentrations were determinated in acacia and lime honey from Cuptoare (7030.0 ppm, respectively 6570.0 ppm) and the lower in sunflower honey from Berini (25.4 ppm).

**Ca** is an alkaline-earth metal essential for animals and humans, particularly in cell physiology. A deficit in **Ca** can affect the formation of bones and teeth, but the excess retention can cause kidney stones. **Ca** deficiency for a long time is responsible for osteoporosis, when the bones are deteriorated and increased the risk of fractures. The necessary daily intake is between 350 and 1100 mg/day [Mogos, 1997]. In analyzed honey samples the **Ca** contents varied between 2.7 – 592.5 ppm. The highest **Ca** contents were obtained in lime and acacia honey from Cuptoare (592.5 ppm, respectively 382.0 ppm), followed by mixed flowers honey from Conacul Iosif (122.6 ppm). The smaller **Ca** concentration was determinated in acacia honey from Domaşnea (2.7 ppm).

**Mg** is essential to all the cells from humans. It is present in many enzymes involved in proteins, lipids and carbohydrates metabolisms. **Mg** deficiency in humans caused muscle spasms, and has been associated with a high blood pressure, many cardiovascular diseases, diabetes and osteoporosis. The necessary daily intake is 350 mg/day for men and 300 mg/day for women [Mogos, 1997]. The values obtained for **Mg** in analyzed honey samples ranged between 10.2 – 684.3 ppm. The highest contents were

measured in (ppm) and the smallest in lime and acacia honey from Cuptoare (684.3 ppm, respectively 654.3 ppm).

The *Sodium, Potassium, Calcium and Magnesium* contents in analyzed honey samples are presented in Table 1:

**Table 1**: The concentrations in Na, K, Ca and Mg for analyzed honey samples

| Honey samples | Na ppm | K ppm | Ca ppm | Mg ppm |
|---|---|---|---|---|
| 1. Mixed flowers honey from Timişoara | 118.4 | 406.4 | 24.3 | 41.7 |
| 2. Sunflower honey from Conacul Iosif | 138.8 | 2089.0 | 111.2 | 88.6 |
| 3. Acacia honey from Domaşnea | 34.4 | 148.0 | 2.7 | 10.6 |
| 4. Mixed flowers honey from Conacul Iosif | 125.5 | 1492.0 | 122.6 | 53.6 |
| 5. Lime honey from Bocşa-Română | 83.8 | 642.5 | 93.6 | 45.9 |
| 6. Acacia honey from Plugova | 45.2 | 223.5 | 8.6 | 23.2 |
| 7. Mixed flowers honey from Berini | 34.4 | 59.4 | 2.8 | 16.3 |
| 8. Sunflower honey from Berini | 26.6 | 25.4 | 6.0 | 10.2 |
| 9. Acacia honey from Cuptoare | 52.5 | 7030.0 | 382.0 | 654.3 |
| 10. Lime honey from Cuptoare | 82.7 | 6570.0 | 592.5 | 684.3 |

**Cu** is an essential microelement for life. Cu deficiency in humans is a rare exception, and would not occur if Cu content were more than 2 mg in the daily diet. The national accepted limit for Cu in similar products is 2.0 mg/Kg [Ordinance 975/1998]. In analyzed samples the smallest content in Cu was founded for acacia honey from Domaşnea (0.104 ppm), and the highest for acacia and lime honey samples from Cuptoare (6.536 ppm, respectively 4.472 ppm). The Cu contents for acacia and lime honey samples from Cuptoare are up to the national accepted limit (2.0 ppm).

**Zn** is a constituent in 300 enzymes and proteins that participate in all major metabolic processes. As an essential trace element Zn can influence the vital function by deficiency or excess. The national accepted limit for Zn in similar products is 5.0 mg/Kg [Ordinance 975/1998]. The highest content for Zn was determinated in honey samples from Cuptoare (22.40 ppm for

acacia honey, respectively 20.12ppm for lime honey) and the smallest for acacia honey from Domaşnea (1.008 ppm). The content in Zn for lime honey from Bocşa-Română (5.45 ppm) is very closely to the national accepted limit. The contents in Zn for mixed flowers honey from Timişoara (14.97 ppm), acacia and lime honey samples from Cuptoare (22.40 ppm, respectively 20.12) are highest than national accepted limit (5.0 ppm).

**Mn** is both a constituent and an activator of several enzymes and proteins in plant, animal and humans, and has around 20 identified functions. The highest content in Mn for analyzed samples was obtained for acacia and lime honey from Cuptoare (20.68 ppm, respectively 18.72 ppm). Sunflower honey from Berini has the smallest Mn concentration (0.055 ppm).

**Table 2**: The concentrations in Cu, Zn, Mn and Fe for analyzed honey samples

| **Honey samples** | **Cu ppm** | **Zn ppm** | **Mn ppm** | **Fe ppm** |
|---|---|---|---|---|
| 1. Mixed flowers honey from Timişoara | 0.438 | 14.97 | 0.169 | 5.782 |
| 2. Sunflower honey from Conacul Iosif | 0.337 | 1.433 | 1.325 | 6.072 |
| 3. Acacia honey from Domaşnea | 0.104 | 1.008 | 0.079 | 1.467 |
| 4. Mixed flowers honey from Conacul Iosif | 0.175 | 1.833 | 0.64 | 2.923 |
| 5. Lime honey from Bocşa-Română | 0.324 | 5.45 | 0.356 | 8.632 |
| 6. Acacia honey from Plugova | 0.294 | 1.474 | 0.109 | 2.182 |
| 7. Mixed flowers honey from Berini | 0.217 | 3.427 | 0.129 | 4.849 |
| 8. Sunflower honey from Berini | 0.111 | 1.112 | 0.055 | 1.130 |
| 9. Acacia honey from Cuptoare | 6.536 | 22.40 | 20.68 | 33.187 |
| 10. Lime honey from Cuptoare | 4.472 | 20.12 | 18.72 | 46.232 |
| **National limit, ppm** | **2.0** | **5.0** | **-** | **-** |

**Fe** is an essential element for humans. Approximately 60% of Fe is bound in hemoglobin, 10% in Fe-dependent tissue enzymes, 20% are stored as ferritin and 10% in hemosiderin [Schümann and Elsenhaus, 2004]. The honey samples from Cuptoare have the greatest content in Fe (46.232 ppm for lime honey, respectively 33.187 ppm for acacia honey). The smallest content in Fe (1.130 ppm) was determinated in sunflower honey from Berini.

The *Cooper, Zinc, Manganese and Iron* contents in analyzed honey samples are presented in Table 2:

For cluster analysis it was used Statistica-6 software. Cluster Analysis (CA) was used to group a number of cases witch present similarities into clusters. It was used the Euclidean distance, a geometrical distance in the multidimensional space calculated as:

$$\mathbf{distance(x,y) = \{\Sigma i\ (xi - yi)^2\}^{1/2}}$$

Using Na, K, Ca and Mg like variables it was performed the calculation of cases - dendrogram, presents in figure 3:

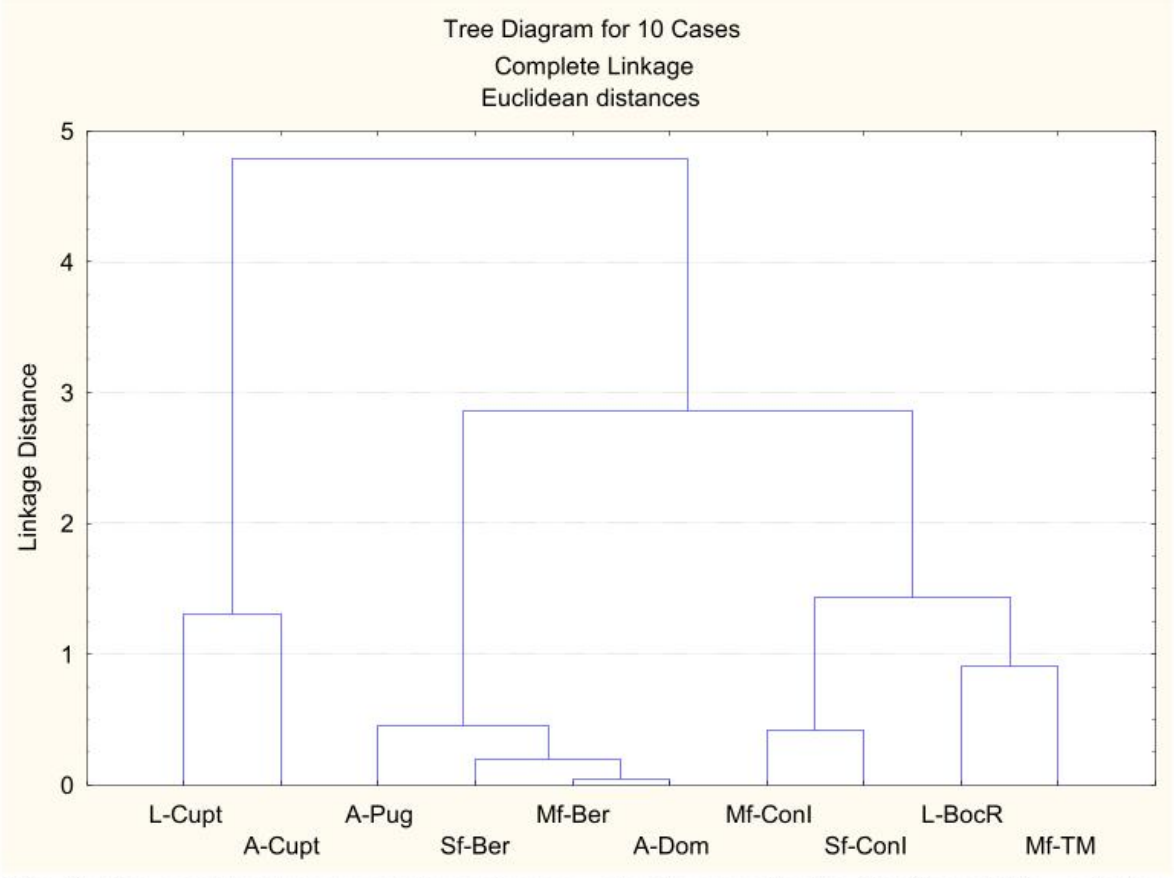


**Fig. 3**: The graphical representation of cases – dendrogram for Na, K, Ca and Mg variables

The graphical representation of cases - dendrogram from figure 3 shows that honey samples can be group in three main groups, each of them characterized by the appropriate macroelements (Na, K, Ca and Mg) contents.

The first group is formed by acacia and lime honeys from Cuptoare witch have the highest contents in K, Ca and Mg between all the samples. Both samples are from the same location: Cuptoare.

The second group is formed by: acacia honey from Domaşnea, mixed flowers honey from Berini, Sunflower honey from Berini, acacia honey from Plugova, witch have generally smaller Na, K, Ca and Mg concentrations. The honey samples from Domasnea present similitude in essential macroelements contents with those from Plugova and Berini. Domasnea is situated in Caras-Severin District, very closed to Plugova. Berini is situated in Timis District.

The third group presents two subgroups: one is formed by mixed flowers honey from Timişoara and lime honey from Bocşa-Română and other formed by mixed flowers and sunflower honeys from Conacul Iosif. The subgroup formed by honeys from Timisoara and Bocsa-Romana have an appropriate Magnesium content. The other subgroup is formed by honeys from the same location Conacul Iosif, witch present the highest contents in Na.

Using Cu, Zn, Mn and Fe like variables it was performed the calculation of cases - dendrogram, presents in figure 4:

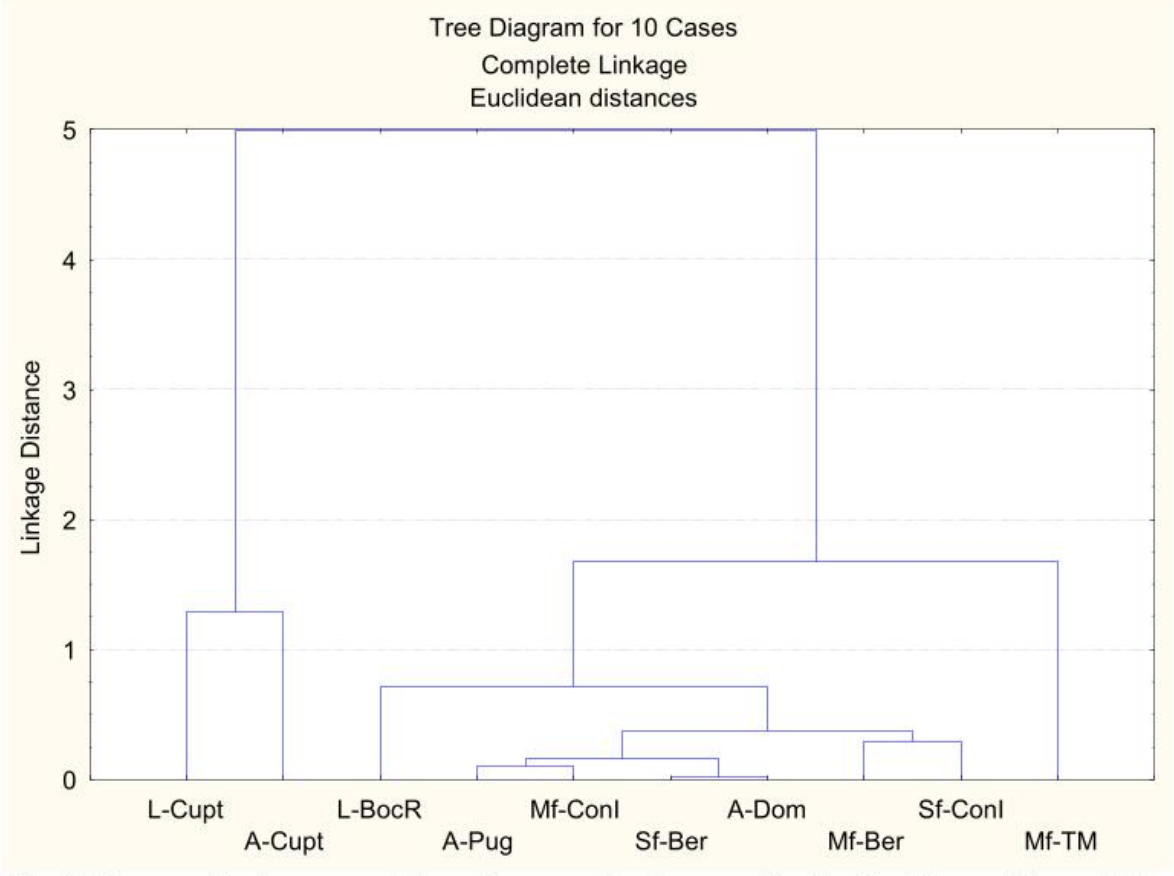


**Fig. 4**: The graphical representation of cases – dendrogram for Cu, Zn, Mn and Fe variables

The graphical representation of cases - dendrogram from Figure 4 using microelements like variables shows that honey samples can be differentiate in two main groups.

The first group is formed by acacia and lime honeys from Cuptoare witch have the highest contents in Cu, Zn, Mn and Fe between all the analyzed honey samples.

The second group is formed by three subgroups: one subgroup contains lime honey from Bocşa-Română characterized by medium contents in Zn and Fe; other subgroup is formed by acacia honey from Plugova, mixed flowers honey from Conacul Iosif, sunflower honey from Berini, acacia honey from Domaşnea, mixed flowers honey from Berini and sunflower honey from Conacul Iosif. Berini is a village situate in Timiş County, closely to Conacul Iosif village. Domasnea is situated in Caras-Severin District, very closed to Plugova. The last subgroup is represented by mixed flowers honey from Timişoara witch contains a high Zn content.

## Conclusions

The major essential macroelement in analyzed honey samples was Potassium, followed by Sodium, Calcium and Magnesium. Iron was found the major microelement in selected honey samples, followed by Zinc, Manganese and Cooper.

**Zn** content determinated for mixed flowers honey from Timişoara, acacia and lime honey samples from Cuptoare are highest than national accepted limit (5.0 ppm). Also the **Cu** contents for acacia and lime honey samples from Cuptoare are up to the national accepted limit (2.0 ppm).

Cluster analysis can be used to discriminate the honey samples from different location situated in Banat County, because the macro- and microelements contents in honey depend on the soil metals concentration.

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*** Excerpt from Romanian Ministry of Public Health *Ordinance no 975/1998*. Maximum limits accepted for heavy metal in foods.