

ELEMENTAL PROFILE AND CHEMOMETRICS FOR GEOGRAPHICAL TRACEABILITY OF HONEYS FROM PANTANAL AND CERRADO BIOMES

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The honey of *Apis mellifera* bees presents a chemical composition directly influenced by flora and environmental conditions of the region of origin. The elemental profile can act as a natural marker for authentication and geographical traceability purposes. Spectrometry techniques combined with chemometric methods are promising tools to explore this profile, allowing the differentiation of honeys from different localities, contributing to product valorization, fraud prevention, and the strengthening of the regional beekeeping sector. This work aims to evaluate the elemental profile of honeys from Pantanal and Cerrado biomes in the state of Mato Grosso do Sul, targeting their geographical identity^{1,2}. A total of 35 honey samples were collected in various cities to better represent the reality of production in this state of Brazil. The samples were stored in a temperature and humidity-controlled environment. An aliquot of 300 mg of honey was weighed into PTFE capsules. Two milliliters of concentrated nitric acid (69%) were added, and a pre-digestion was carried out for 2 h. Then, 1 mL of hydrogen peroxide (30%) and 5 mL of ultrapure water were added. The samples were subjected to microwave-assisted digestion (Milestone ETHOS UP) at 195 °C and 1800 W. The digests were diluted to 25 mL with ultrapure water and subsequently analyzed by inductively coupled plasma mass spectrometry (ICP-MS), using calibration curves for Cu, Fe, Mn, Zn, Cr, Ba, Sr, As, Cd, Ni, V, Pb, and Se in the concentration range of 1-500 µg/L, and by inductively coupled plasma optical emission spectrometry (ICP-OES), with calibration curves for Ca, K, Na, Mg, S, P, Mn, Fe, Ba, Cu, and Zn in the concentration range of 0.005-500 mg/L. Certified reference materials (NIST 1549 Non-Fat Milk Powder and CRM-Agro C1004a Tomato Pulp) were employed for analytical quality control. Multivariate statistical tools such as analysis of variance (ANOVA), hierarchical cluster analysis and dissimilarity were applied to the elemental profile of honey samples to identify patterns of similarity and differentiation among them. Significant differences in mass fractions of Ca, K, Mg, Mn and Fe were observed among the honey samples. The applied multivariate tools highlighted clear patterns of dissimilarity and differentiation between the samples, indicating the potential of elemental profile of honeys for geographical traceability.

1 Zoani, S. et al. Honey origin determination by combining Raman spectroscopy and elemental profiling. *Journal of Food Composition and Analysis*, 2014.

2 Al-Awadhi, Mokhtar and Deshmukh, Ratnadeep R., Classification of Honey Botanical and Geographical Sources using Mineral Profiles and Machine Learning (November 23, 2022). Proceedings of the International Conference on Information Systems and Emerging Technologies (ICISET), Available at SSRN: <https://ssrn.com/abstract=4332757> or <http://dx.doi.org/10.2139/ssrn.4332757>