

FINGERPRINTING ANALYTICAL STRATEGY USED FOR AUTHENTICATION OF HONEY

Oana Romina DINCA^{a,b}, Roxana Elena IONETE^{a*}, Raluca POPESCU^a, Radu TAMAIA^a, Diana COSTINEL^a, Gabriel Lucian RADU^b

^aNational R&D Institute for Cryogenics and Isotopic Technologies- ICIT Rm. Valcea, 4 Uzinei St., 240050 Rm. Valcea, Romania

^b Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu Str., 011061, Bucharest, Romania

*Corresponding author: roxana.ionete@icsi.ro

INTRODUCTION

To find the most reliable methods for authentication of food or food ingredients has always been a challenging issue.

The authenticity of honey has two different aspects, one related with its content (e.g. 100% real honey and not adulterated with inverted molasses, sugar syrups, sugar cane, sugar beet and syrups of natural origin or with synthetic honey - based on C₄ plant sugars) and second with its geographical and botanical origin.

Our research is of particular interest in the both geographical and botanical discrimination of honey from different floral sources and different regions of Romania as support for quality assessment and classification activities.

METHODS

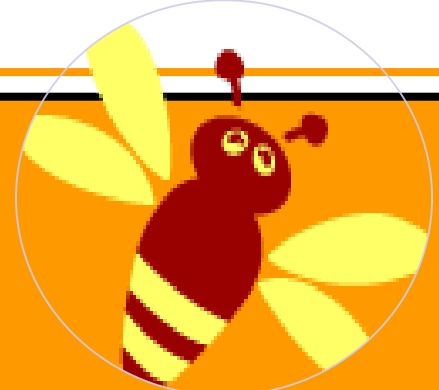
○ *Isotope Ratio Mass Spectrometry* (Deuterium, oxygen 18 and carbon 13 isotope ratio determination) to discriminate honey geographical and botanical origin

○ *Matrix Assisted Laser Desorption Ionization Time-of-flight Mass Spectrometry* (MALDI-TOF MS) for the determination of the botanical origin of honey based on peptide mass fingerprinting (PMF).

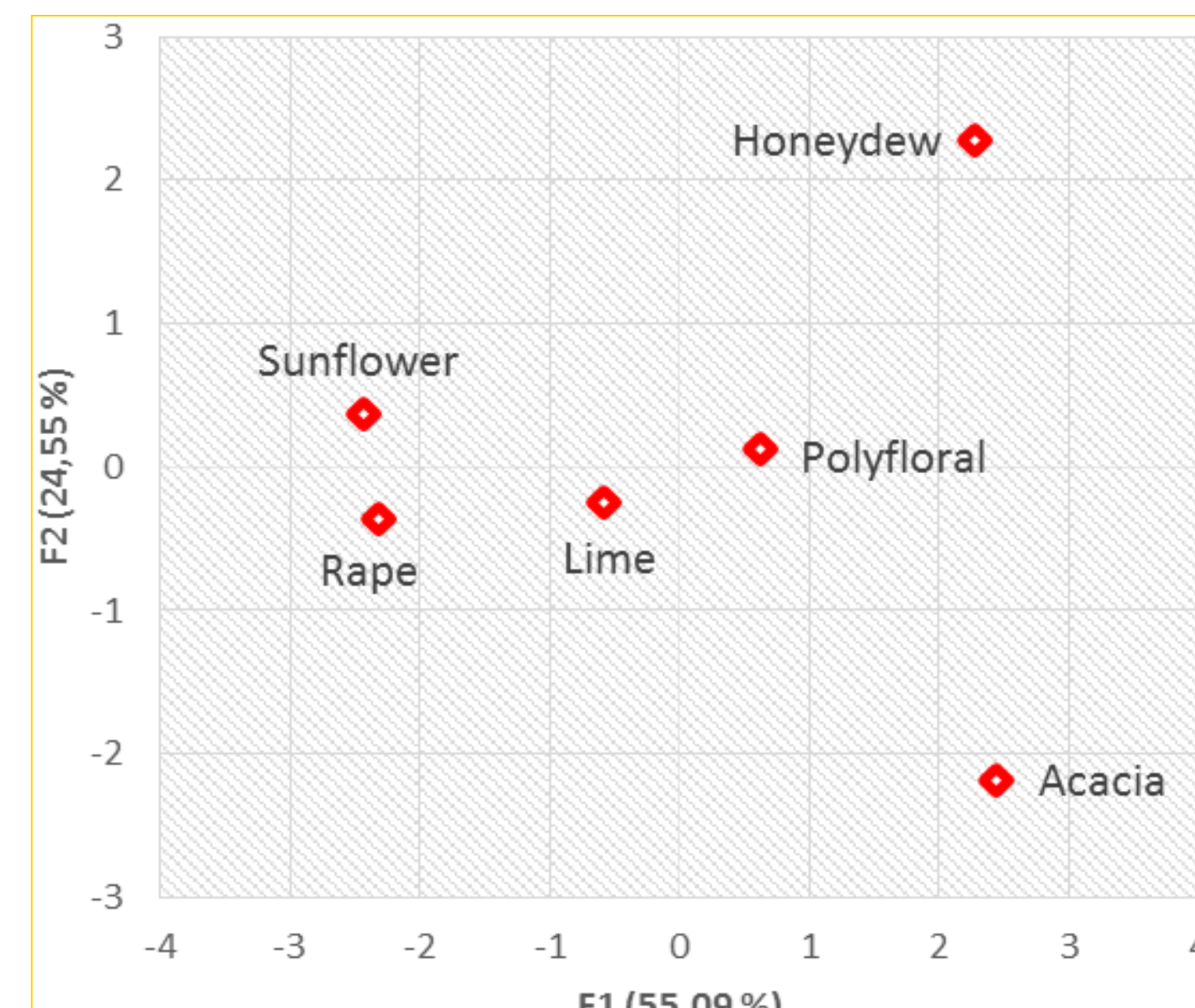
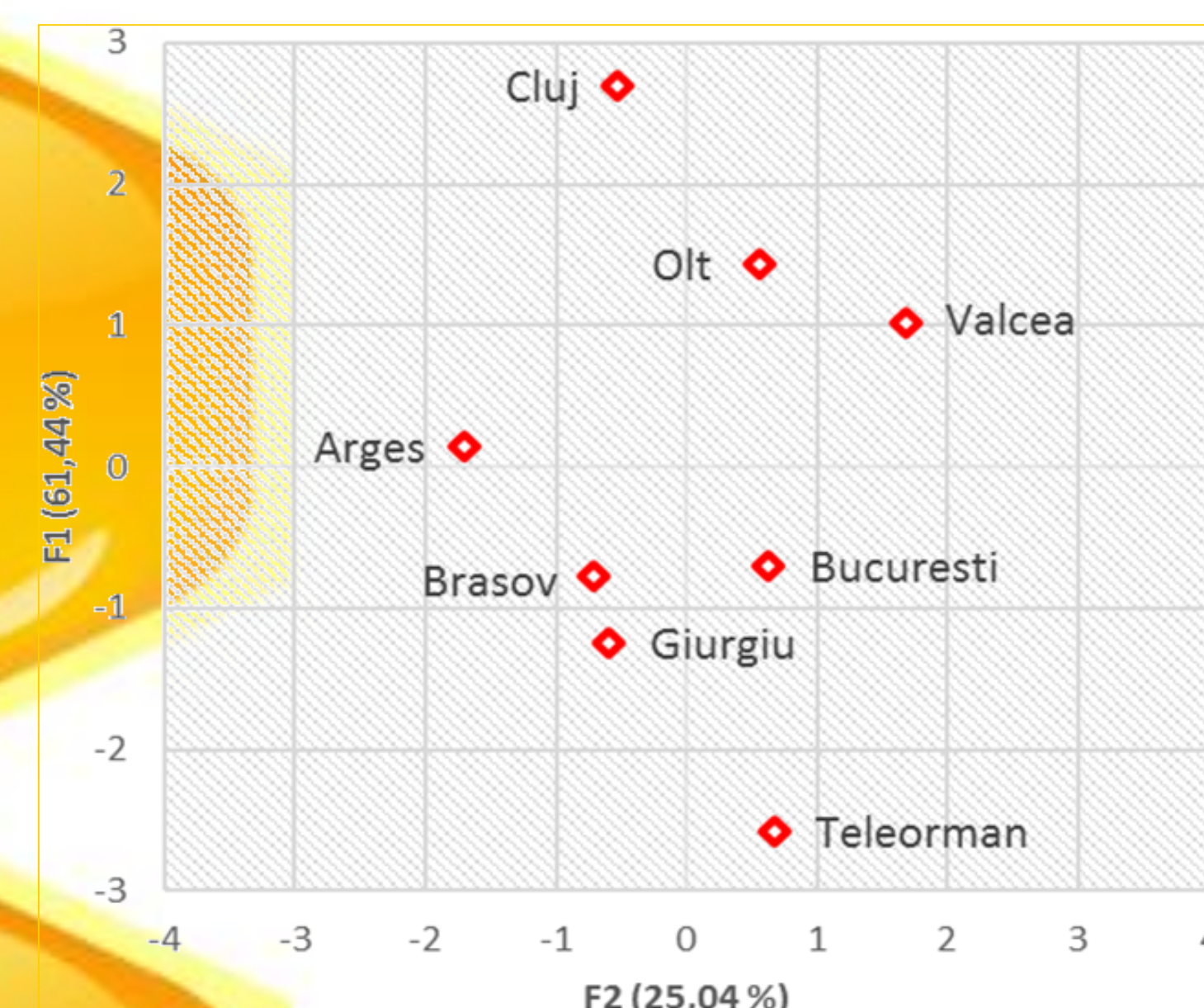
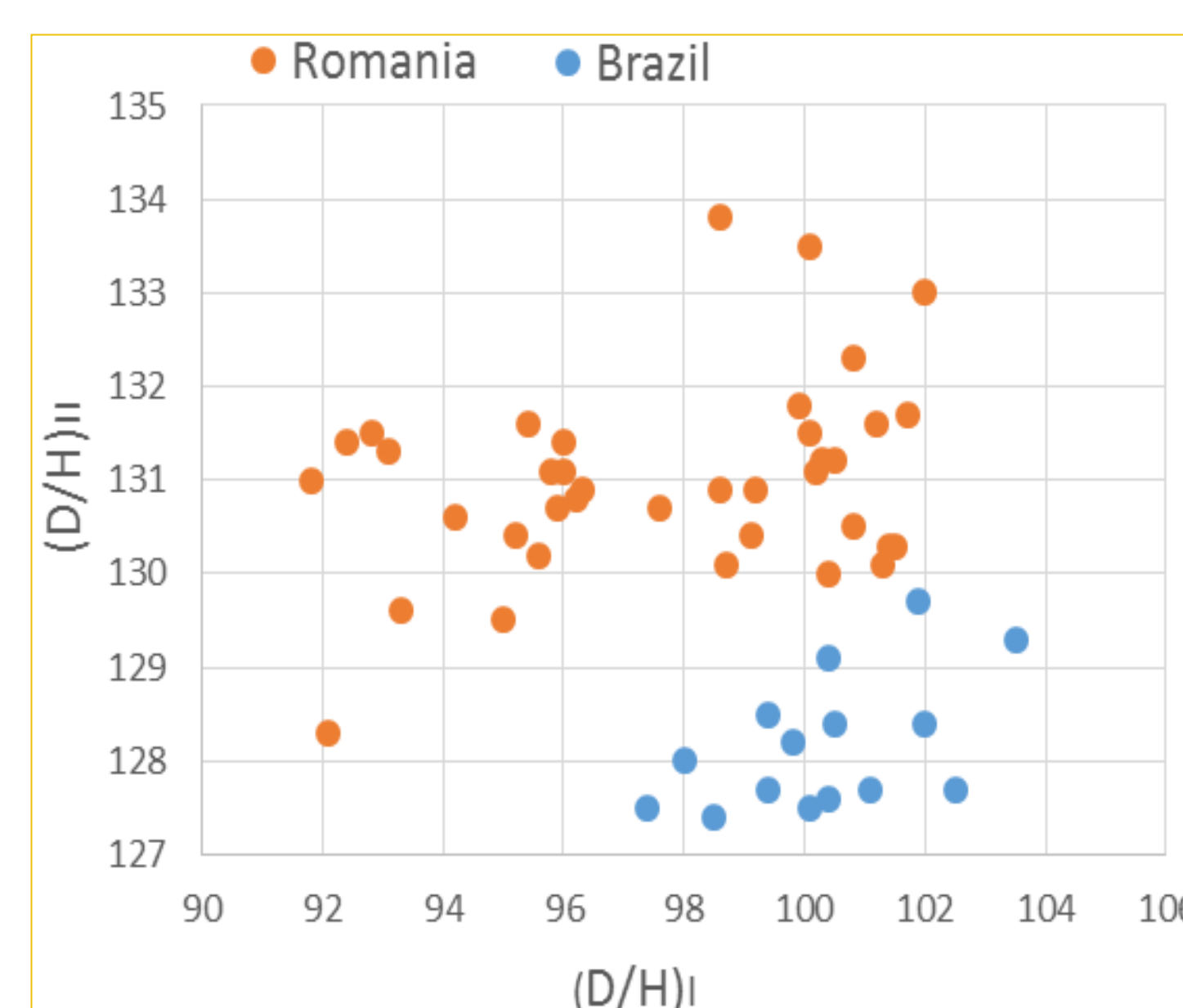
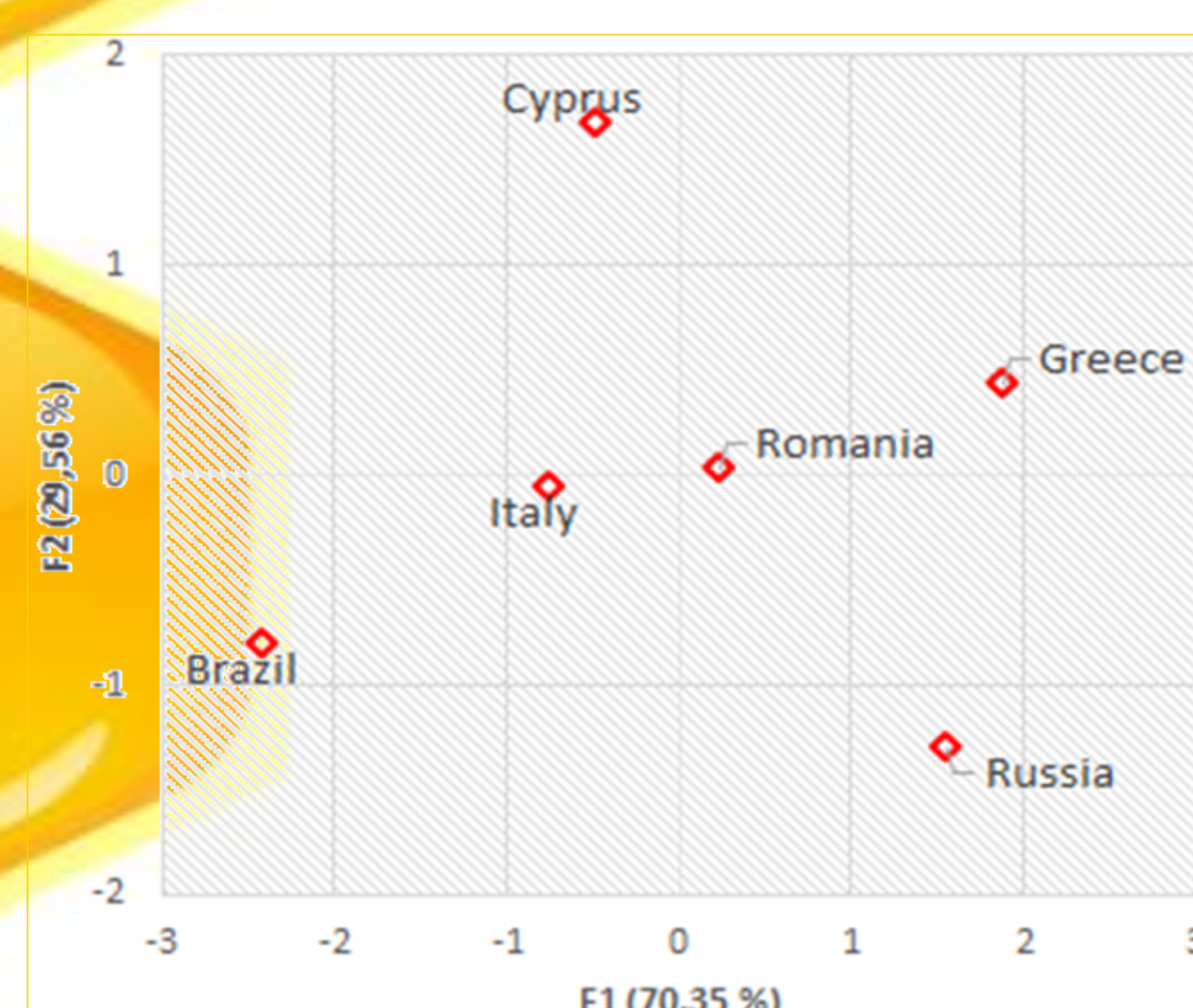
○ *Site-specific Natural Isotopic Fractionation By Nuclear Magnetic Resonance* (SNIF-NMR) to create databases on the isotopic characteristics of the honey of certain floral varieties.

- Combine different techniques and a multicriteria interpretation to improve available knowledge of the product.
- Improve understanding of the problems of honey authenticity.
- Discriminating Romanian honey from other countries based on geographical and botanical origin
- Separate the Romanian honey samples into their individual provenance regions
- Clearly distinguish between certain types of honey.

SPECIFIC TARGETS



RESULTS



Discriminating Romanian polyfloral honey, based on geographical origin, from other countries using three discriminant functions.

	Samples	(D/H)I ppm	(D/H)II ppm	R
Means of isotopic values by SNIF-NMR after polyfloral honey fermentation	Romania	97.30 (95-102)	131.08 (129.5-133)	2.700 (2.61-2.758)
	Italy	98.8 (98.6-99.2)	130.23 (129.8-130.9)	2.655 (2.631-2.715)
	Greece	95.40 (93.84-96.81)	132.75 (130.77-135.54)	2.783 (2.751-2.855)
	Russia	93.78 (93.3-94.2)	130.08 (129.3-130.8)	2.774 (2.767-2.780)
	Cyprus	100.28 (92.69-105.53)	132.94 (130.23-135.37)	2.654 (2.511-2.891)
	Brazil	100.04 (97.1-103.5)	128.15 (127.4-129.3)	2.563 (2.492-2.655)

Principal component analysis (PCA) was used for visualization and as a tool for differentiation between different geographical origin of Romanian honey samples into their individual provenance regions.

In order to confirm and reinforce distinctions between the various different monofloral honeys, we performed a principal component analysis using the mean values.

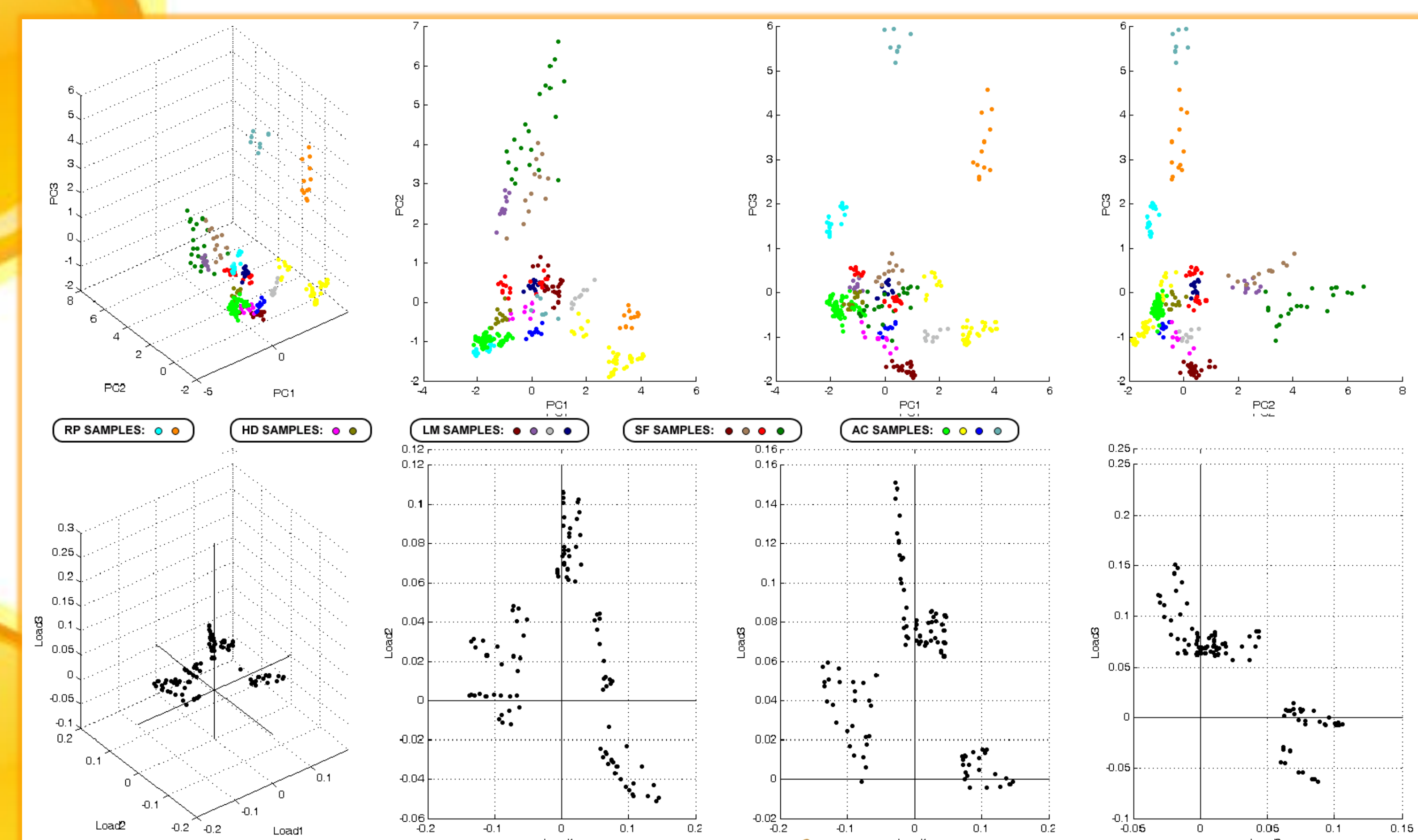
PCA on peptide mass fingerprints show a clear separation of samples based on their botanical origin (RP = rape, HD = honeydew, LM = lime, SF = sunflower, AC = acacia), with a small overlapping between some LM and SF samples perhaps due their small abundance in pollen from the dominant species.

Acknowledgments

This work was supported by the project PN 09 19 02 05, grant No. 19N/2009 – Add. No. 1/2013 from the Romanian Ministry of Education and with the support of the doctoral School “Faculty of Applied Chemistry and Materials Science” Politehnica University of Bucharest.

Bibliography

1. Kropf U., et al. (2010). Determination of the geographical origin of Slovenian black locust, lime, and chestnut honey. Food Chemistry, 121, 839–846.
2. Lolli M., et al. (2008). Classification of Italian honeys by ²D HR-NMR. Journal of Agricultural and Food Chemistry, vol. 56, no. 4, pp. 1298–1304.
3. Schellemborg A., et al. (2010). Multielemental stable isotope ratios (H, C, N, S) of honey from different European regions. Food Chemistry, 121, 770-777.



CONCLUSIONS

Stable isotope analysis of honey proved to be useful for geographic region-of-origin assignment.

SNIF-NMR combined with chemometrics allows correct classification for Romanian honey.

MALDI-TOF MS system is an excellent method for creating protein profiles of honeys in order to identify botanical origin.