Geographical characterization of Argentinean honeys by FT-Raman spectroscopy

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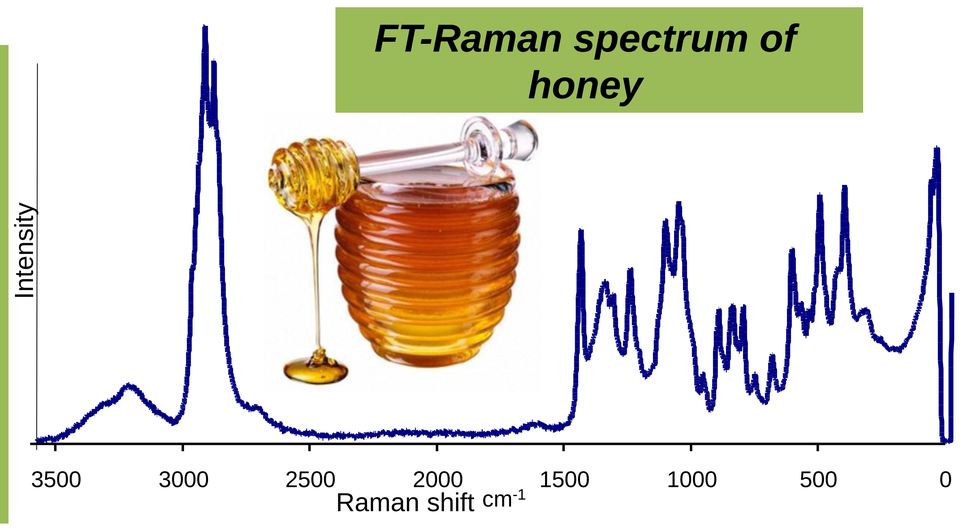
Introduction

Argentina is a major producer of quality honey; 90% of the honey produced in Argentina is acquired by the European Union and the United States. The globalization of the world market makes the authentication and characterization of botanical and geographical origins of honey an important issue. PDO and PGI quality labels are linked to the characteristics of the production systems, geographical origin, cultural and historical practices. Honey is traditionally characterized by performing physicochemical parameter analysis, melissopalynological analysis and sensory analysis; which are costly, tedious, time-consuming, use considerable solvent and reagent amounts and require extensive pollen knowledge and trained honey taste panels. To overcome these drawbacks, vibrational spectroscopy and chemometrics are proposed for the characterization of honeys. The objective of the present work is to develop analytical tools for the protection of honeys coming from three important producer Argentinean regions. **FT-Raman spectra have been treated by multivariate data analysis tools to develop classification models aiming to distinguish honeys according to their geographical origin**.

Optimization of FT-Raman experimental conditions

	Optimised parameters
Sample temperature (-80ºC, -18ºC, 4ºC, RT, 40ºC) →	**40ºC**
Laser power (600 mW, 700 mW, 800 mW) →	**800 mW**
Sample position on the Z axis (100, 105, 110, 120, 140) →	**105**
Resolution (4 cm^{-1}, 8 cm^{-1}) →	**4 cm^{-1}**
Number of scans (8, 16, 32, 64, 128) →	**128 (~ 4 min)**

FT-Raman spectrum of honey



Multivariate data analysis: Partial Least Squares Discriminant Analysis

PLS-DA model	Preprocessing	PLS comp.	Boundary	Class	N	*prior prob.*	% Recognition ability	% Prediction ability
***Buenos Aires* vs non-Buenos Aires**	full MSC + centering	2	0.559	Bue	71	*0.53*	97.2	97.2
				non-Bue	62	*0.47*	91.9	88.7
***Catamarca* vs non-Catamarca**	full MSC + centering	3	0.395	Cat	26	*0.33*	88.5	88.5
				non-Cat	54	*0.68*	85.2	81.5
***Misiones* vs non-Misiones**	full MSC + centering	4	0.411	Mis	36	*0.35*	97.2	94.4
				non-Mis	68	*0.65*	91.2	91.2

Samples: Argentinean honeys from Buenos Aires, Catamarca and Misiones (year 2014)

Data: FT-Raman spectra (3734 variables)

3-fold Cross-validation 3-fold

MSC: multiplicative scatter correction

PLS comp.: number of PLS components

Prior prob.: prior probability

Boundary: defined by the quartiles of box & whisker plot of the classifications in CV

FT-Raman equipment:
Vertex 70 – RAM II Bruker FT-Raman spectrometer, equipped with a Nd:YAG laser with an output at 1,064 nm (9,398.5 cm^{-1}), and a liquid-nitrogen cooled Ge detector. Maximum of laser power is 1.5 W. The measurement accessory is pre-aligned, only the Z-axis of the scattered light is adjusted to set the sample in the appropriate position regarding the local point. OPUS 6.0 software was used for the spectral acquisition, manipulation and transformation. Samples are placed in classical glass tubes of an internal diameter of 12 mm and a length of 75 mm (Schott Duran®), which are introduced into a dedicated sample holder developed at the CRA-W and made of aluminium to assure repeatable position of the sample
in front of the laser beam. The sample holder is placed in the sample compartment.
Multivariate data analysis:
Software: The Unscrambler 9.1 (Camo Process AS, 1986-2004)

Conclusion

- ✓ **FT-Raman spectra** contain useful information to classify honeys according to their **geographical origin**.
- ✓ **Satisfactory binary PLS-DA classification models** are obtained for Argentinean honeys produced in the provinces of **Buenos Aires, Catamarca** and **Misiones**.
- ✓ Recognition ability ≥ prediction ability in CV:
  - → Classes are **well-represented** by the samples in the training set.
  - → Models are **feasible**, not random
- ✓ Better classification results are expected using larger sample sets, including samples from several harvests.

❖ **Further work:** Honey from these Argentinean provinces of next harvests are planed to be analysed by FT-Raman spectroscopy, and further multivariate data analysis will be performed to achieve validated binary classification models providing a tool to guarantee PDO/PGI classification for these honey production regions.

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