NIR detection of honey adulteration reveals differences in water spectral pattern

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INTRODUCTION

Unifloral False Acacia (*Robinia pseudoacacia*) honey (liquid due to the high fructose content, very light colored and flavored) may easily be adulterated with high-fructose corn syrup (HFCS), negatively influencing market growth by damaging consumer confidence [1].

Aquaphotomics considers water as a multi-element system that can be described by its multi-dimensional NIR spectra. Since water's H-bonds are present in most natural samples, this analytical approach, using perturbed water in different environments as a mirror for the rest of the molecules in the sample, can be effectively applied to various fields [2].

OBJECTIVE

- **Developing an applicable NIR model for screening the adulteration of unifloral *Robinia* honey using fiber-optic probe.**
- **Applying recent findings of aquaphotomics to interpret the chemometrics calibration models for measuring the level of fructose syrup adulteration.**
- **Extracting important information about the functionality of *Robinia* honey related to its water structures.**

MATERIALS & METHODS

Pure *Robinia* honey samples
- from four geographic regions of Hungary
- in different periods of False Acacia blossom in 2012.

Isoglucose syrup (High Fructose Corn Syrup, HFCS)
- from high-temperature closed process,
- liquid, cleaned, sterile, ion exchanged and filtered
- 40% fructose , 33% glucose.

Individual honey samples were diluted with HFCS
- random concentrations (n = 40)
- range of honey content = 100-60%
  (honey content mean±SD = 80.79±12.89)

- FOSS NIRSystems 6500 spectrometer (FOSS NIRSystems, Inc., Laurel, MD, USA)
- OptiProbe fiber optic immersion sampling unit, with 2mm layer thickness
- Transflectance spectra, 1100–1800 nm, 2nm step
- Scanning in two rounds, on two successive days
- In random order in both rounds
- Six consecutive spectra for each sample at each time
- Total number of scanned samples: n = 41
- Total number of stored spectra: n = 492

- Data processing with The Unscrambler 9.7 (CAMO Software AS, Oslo, Norway) and MSOffice Excel 2010 (Microsoft Co.)

REFERENCES

[1] Mehryar, L., & Esmaiili, M., 2011. 11th International Congress on Engineering and Food, Athens, Greece

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[3] Kinoshita et al., 2012. Scientific Reports, 2, 856; DOI:10.1038/srep00856

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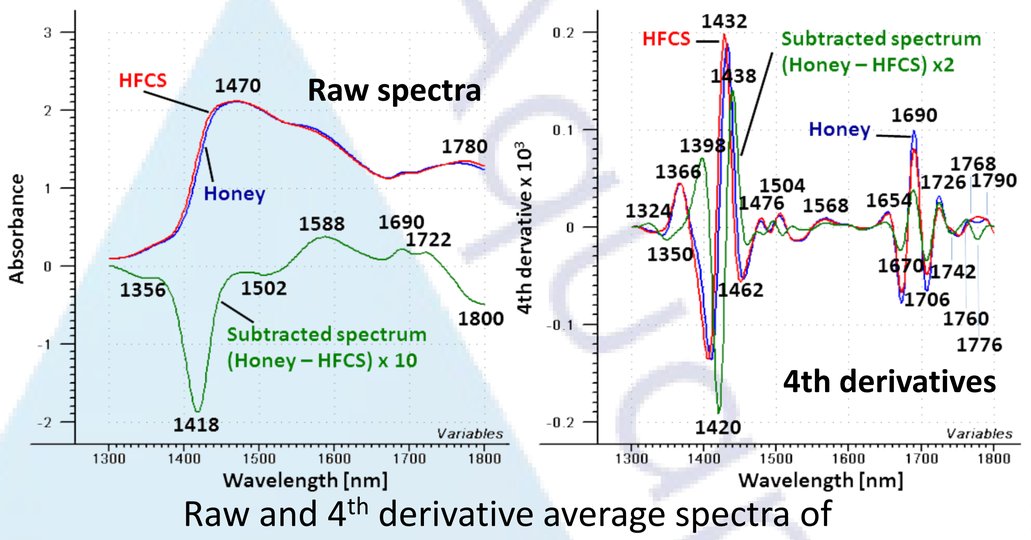
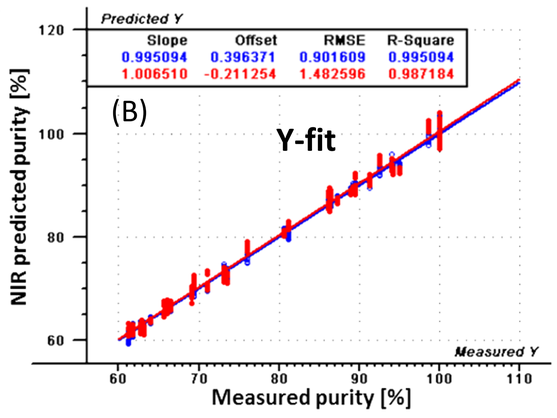
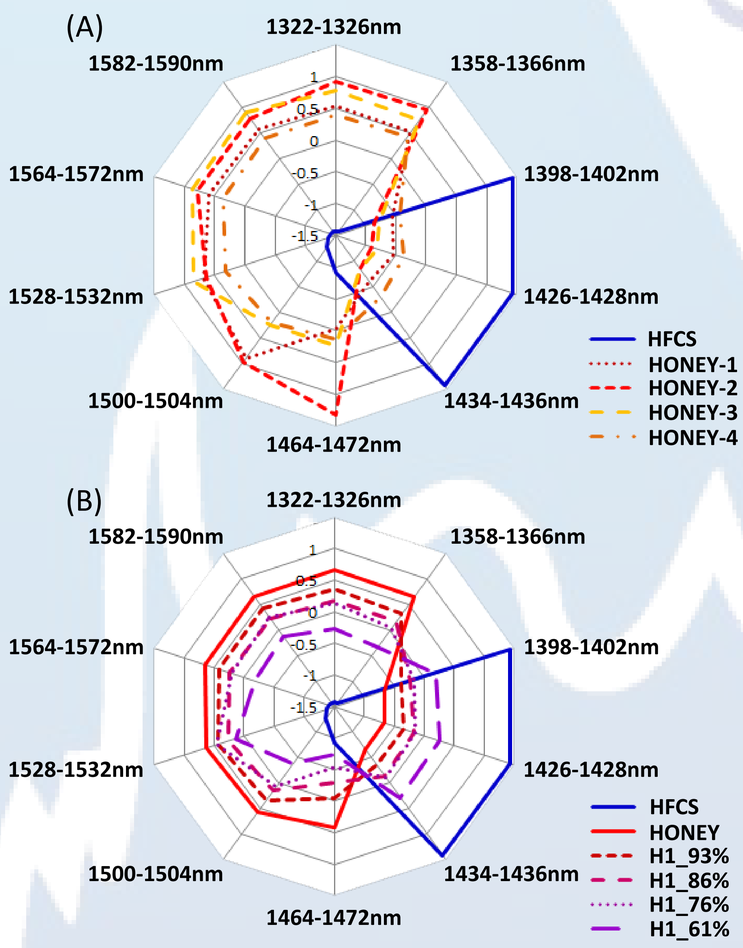
RESULTS



Raw and 4th derivative average spectra of pure honeys and HFCS, and their subtracted spectra.



(A) Regression vectors of PLSR models with (B) the results of calibrations and cross-validations on purity (honey percentage against HFCS) of adulterated honey samples.



(A) Aquagram of the investigated pure *Robinia* honeys and HFCS presenting water spectral pattern.
(B) Aquagram of adulterated mixtures of one honey (H1-purity%) plotted with the mean graph of the pure honeys and graph of HFCS.

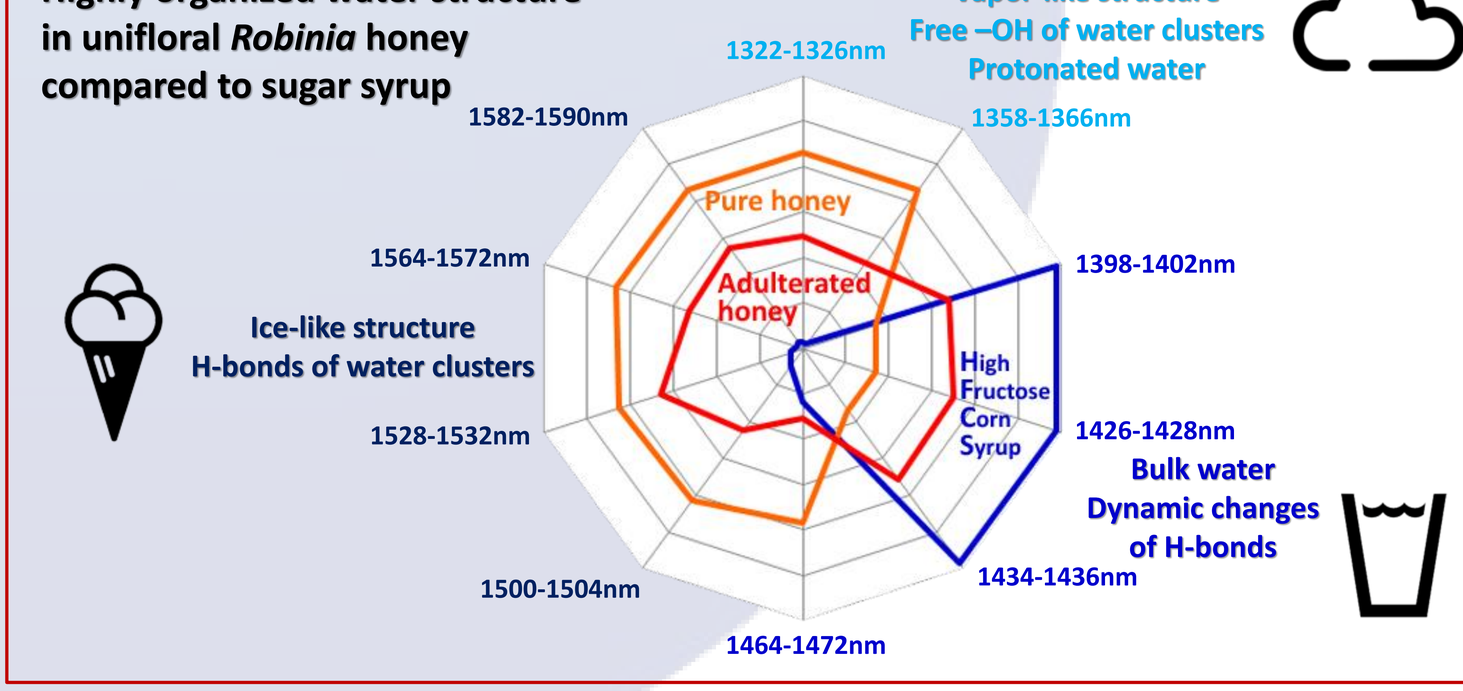
Characteristic changes at water matrix coordinates describe the water spectral pattern.

Visualization with aquagrams [3]:

$$A = \frac{a - \mu}{\sigma}$$

A = Aquagram value
a = absorbance after MSC
μ = average of all spectra
σ = SD of all spectra

Highly organized water structure in unifloral *Robinia* honey compared to sugar syrup



SUMMARY & CONCLUSIONS

- **Quick analytical tests were developed for detecting HFCS adulteration of *Robinia* honeys.**
- **The most accurate NIR models for predicting adulteration level with the lowest cross-validation error ($RMSE_{CV}$ = 1.48%) were achieved within the whole spectral range of 1300-1800nm, containing the absorption bands of both water and carbohydrates.**
- **Investigated unifloral *Robinia* honeys contained larger amount of water having highly organized molecular structure, than industrial sugar syrup (HFCS).**
  - **larger variety of molecules dissolved in the multicomponent system of honeys**
  - **simpler matrix of HFCS has relatively large amount of unstructured water**
- **Adulteration caused gradual reduction of water trimers, molecular structures facilitating the interactions with other molecules.**