Rapid screening of clover honey adulteration with infrared spectroscopy and chemometrics.

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INTRODUCTION

- Honey and maple syrup, olive oil, seafood, juice and spices are among food ingredients subject to economically motivated adulteration (EMA) according to the FDA food fraud website[1].
- 2019 Canadian Gov report found that 22% of 240 honey products investigated were adulterated[2].
- NMR, MS, stable carbon isotope ratio analysis (SCIRA), etc. can flag honey adulteration with other sweeteners but require lengthy analysis[3].
- Coupling of chemometric tools and IR affords simplicity and efficiency.
- This work: Developed non-targeted chemometric models from ATR-FTIR spectra to separate authentic USDA honey samples from those that have been adulterated with either corn syrup or rice syrup at 7~16% (w/w) concentration ranges.

1. https://www.fda.gov/food/compliance-enforcement-food/economically-motivated-adulteration-food-fraud].
2. Canadian Government Report: Enhanced honey authenticity surveillance (2018 to 2019). (2019).
3. Başar, B. & Özdemir., D. (2018), J. Sci. Food & Agr. 98, 5616-5624.

MATERIALS & METHODS

Authentic and Commercial Honey Samples

Product Type	# of Test Samples	Comments
Authentic USDA Honey	46	From USDA in Louisiana, Maryland, Utah, and Arizona.
Commercial Clover Honey (ORA)	39	From 15 states and 23 companies.
Honey test samples adulterated with Rice Syrup	90	Adulterated 3 USDA test samples and 6 commercial products with 2 rice syrups at 5 concentrations (1-16%, w/w)
Honey test samples adulterated with Corn Syrup	89	Adulterated 3 USDA test samples and 6 commercial products with 2 corn syrup at 5 concentrations (3-15%, w/w)

ATR-FTIR Spectrometer

- Nicolet 6700 benchtop FTIR spectrometer equipped with a single bounce diamond ATR crystal.
- 128 replicate IR scans per sample collected at 4 cm^{-1} resolution.
- Takes <4 min per test sample.
- Five replicate datasets of the test samples.

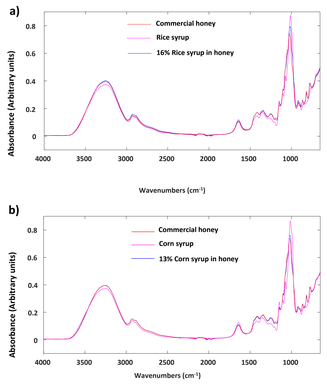
Chemometrics Analyses

- Principal Component Analysis (PCA)
- Soft Independent Modelling of Class Analogy (SIMCA)
- PLS_Toolbox_8.0.1 (Eigenvector Research Inc.) in MATLAB
- Limit for the Q residuals = 0.95 to separate “typical” honey from “atypical” honey.

RESULTS & DISCUSSION

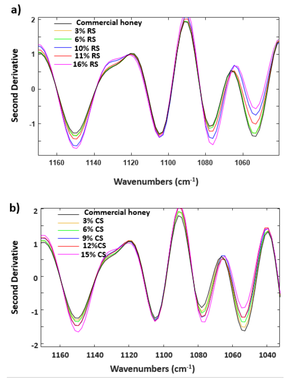
ATR-FTIR Spectral Features

- Raw ATR-FTIR spectra separate both rice syrup and corn syrup adulteration at 16% (w/w) and 13% (w/w), respectively.



Figures 1a & 1b.

- Second derivative band intensities better illustrates correlations among syrup concentrations.



Figures 2a & 2b.

Principal Component Analysis (PCA)

- Unsupervised exploratory analysis based on PCA to differentiate adulterants (Fig. 3)
- PC 1 accounts for 94.4% of the spectral variance, while PC 2 accounts for 2.6% of the spectral variance
- Authentic USDA samples and commercial clover honey are similar.

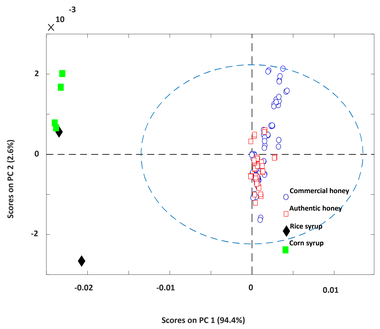


Figure 3. Unsupervised PCA score plots for the FTIR data collected for commercial honey labeled clover, authentic honey test samples from USDA, and pure rice and corn syrup adulterants.

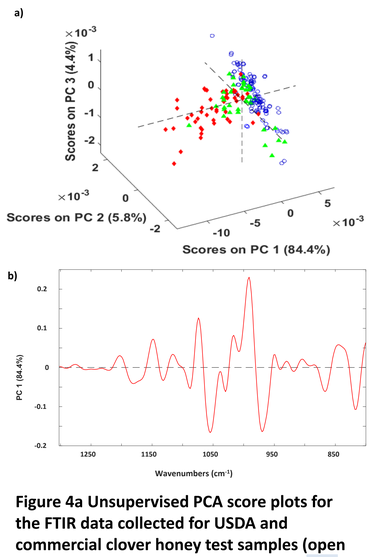


Figure 4a Unsupervised PCA score plots for the FTIR data collected for USDA and commercial clover honey test samples (open blue circles for both sample types) and rice syrup spiked test samples [green triangles for 1-6% (w/w) levels; red diamonds for 7-16% (w/w) levels].

Figure 4b Plot of the first principal component (PC1) as a function of wavenumbers.

Non-targeted Screening by SIMCA

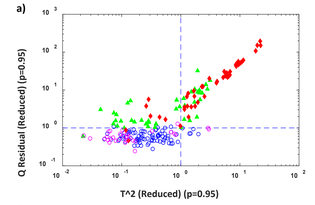


Fig. 5a: Rice syrup adulterated test samples.
Q Residual (reduced) versus Hotelling's T2 (reduced) plots for the non-targeted SIMCA model developed with USDA and commercial honey test samples (open blue circles).
Tested with USDA and commercial honey test samples (open pink squares) and rice syrup spiked test samples [green triangles for 1-6% (w/w) levels; red diamonds for 7-16% (w/w) levels];

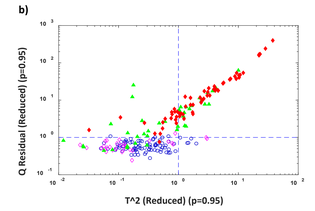


Fig. 5b: Corn syrup adulterated test samples.
Similar plot of the previous SIMCA model developed with USDA and commercial honey test samples (open blue circles) was tested with USDA and commercial honey (open pink squares) and corn syrup spiked test samples [green triangles for 1-6% (w/w) levels; red diamonds for 7-15% (w/w) levels].

Product Type	Predicted “Typical” and “Authentic”	Predicted “Adulterated”	% Specificity
Authentic and Commercial honey control	53	7	88.3%
Honey test samples adulterated with Rice Syrup			
1-6% (w/w)	18	48	72.7%
7-16% (w/w)	2	82	97.6%
Honey test samples adulterated with Corn Syrup			
1-6% (w/w)	21	45	68.2%
7-15% (w/w)	5	91	94.8%

CONCLUSIONS

Developed chemometric models for infrared spectra of commercial clover honey samples adulterated with either rice syrup (C-3 plant syrup) or corn syrup (C-4 plant syrup).

A rapid non-targeted screening approach based on a single class SIMCA produced 97.6% and 94.8% correct classification rates for test samples adulterated with rice and corn syrups, respectively, at 7 ~ 16% (w/w) concentration ranges.

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