# Fingerprinting Maple Syrup by Vibrational Spectroscopy and Pattern Recognition

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## ABSTRACT

Maple syrup is prone to be adulterated with cheap cane, beets or corn syrup due to its expensive ingredient – sap of sugar maple, and the simplicity in its chemical composition. Bourbon barrel (BBL) aged maple syrup is the premium maple syrup product produced by aging syrup in oak bourbon barrel for several weeks to months to develop richer bourbon flavor. The high price of BBLs may prompt the potential counterfeit of aging process. Traditional authentication methods include chromatography and stable isotope ratio analysis, which are time-consuming and cost-prohibitive for most companies due to the requirements of expensive instrumentation and trained personnel. Advances in miniaturization of spectroscopy instruments combined with powerful chemometrics have allowed new portable devices to be field deployable for non-destructive and real-time analysis, however, their accuracy and precision have not yet been determined in maple syrups. Our objective was to develop a predictive algorithm to fingerprint the unique compositional make-up of maple syrup, allowing for fast product authentication and detection of potential ingredient tampering. Samples were kindly provided by Bissell Farms (Jefferson, OH) that included pure maple syrups and Bourbon barrel (BBL) aged maple syrup. Also, we purchased commercial maple syrup samples (n=21) and syrup blends (n=5) from local grocery stores. Spectra were collected by modular Raman 1064 spectrometer and Fourier-transform infrared (FTIR) spectroscopy and analyzed by pattern recognition (SIMCA) and partial least square (PLS) regression. Both Raman and FTIR spectra showed interesting signature patterns that the strong fluorescence in corn syrup samples were highlighted while the syrup blends were resembling patterns of maple syrups. All corn/blended syrups were easily discriminated from maple syrup by chemometrics. Furthermore, BBL maple syrups clustered away from “pure” maple syrups (single ingredient with no foreign substances). Interestingly, three BBL maple syrups grouped with the “pure” samples, indicating limited aging process. Our data showed clustering of “pure” maple syrups by geographical origins (US or Canada) and by lignin contents, which is due to variation in oxidation precondition during sap evaporation. Our data supports the application of a classification algorithm based on the unique Raman and FTIR spectra profile of maple syrup.

# INTRODUCTION

Native Americans are widely recognized as the first to discover the sweet sap dripping from the broken maple bark (Chamberlain, 1891). Pure maple syrup has a reputation of wholesome, traditional sweetener, being renowned for its unique taste and flavor. According to USDA (2018), US production of maple syrup in 2018 totaled 4.16 million gallons with an estimated value of $141 million. In addition, Bourbon barrel (BBL) aged maple syrup is a premium maple syrup product produced by aging syrup in oak bourbon barrels for several weeks to months to develop richer bourbon flavor.

Maple syrup manufacture is rather costly. Although sap contents may be various from different maple trees, in general, 1L of pure maple syrup is produced by concentrating around 35L of maple sap to 66 °Brix (Martin et al., 1996). Therefore, economic incentives exist for adulteration of maple syrup by adding cheaper cane, beets or corn syrup to the boiling sap or by blending the syrup with corn syrup. As the taste of a little cane sugar or corn syrup added to maple syrup is virtually undetectable the temptation to increase yields by fraudulent means can be strong (Paradkar, et al., 2003).

The composition of pure maple syrup is relatively simple, with unique characters. In general, pure maple syrups produced in North America are comprised of 68 ± 4% sucrose, 0.43 ± 1.11% glucose, 0.30 ± 0.54 % fructose, small amount of amino acids, phenolic compounds, trace amount of organic acids, including malic and fumaric acids, minerals and salts (Stuckel and Low, 1996).

Traditional authentication methods include chromatography and stable isotope ratio analysis, which are time-consuming and cost-prohibitive for most companies due to the requirements of expensive instrumentation and trained personnel (Da-Wen 2018). Advances in miniaturization of vibrational spectroscopy instruments combined with powerful chemometrics can overcome those problems by offering fast product authentication, non-destructive and real-time analysis (Santos and others 2013), however, their accuracy and precision have not yet been determined in maple syrups. Fourier transform infrared spectroscopy (FTIR) is one type of vibrational spectroscopy that measures the absorbance and transmittance of infrared light. Raman spectroscopy is another type of vibrational spectroscopy by using an intense light beam, like laser, to excite the sample molecules through inducing Raman-active vibrational modes (Paradkar et al, 2003). Therefore, Raman measures inelastically scattered photons.

## OBJECTIVE

The objective of this research was to generate predictive algorithms based on Raman and mid-infrared spectral fingerprints to characterize unique compositional traits of maple syrup, allowing for fast product authentication and detection of potential ingredient tampering.

## MATERIALS AND METHODS

### Samples

Maple syrup samples were kindly provided by Bissell Farms (Jefferson, OH) and also purchased from local grocery stores (Columbus, OH) that included maple syrups (n=18) and Bourbon barrel (BBL) aged maple syrup (n=9). In addition, inexpensive syrups (corn, cane or mixture) (n=5) were evaluated. All samples were kept in room temperature to equilibrate before FTIR and Raman measurements.

### FTIR Analysis

The Aligent 4500 Series Portable Fourier-transform Infrared Spectroscopy (CA, USA) equipped with a 3-reflection attenuated total reflectance ZnSe crystal (FTIR-ATR) was used for FTIR analysis. Single-beam spectra (4000 – 650 $cm^{-1}$) of the samples were obtained. The crystal was cleaned with ethanol and water between measurements and completely air-dry after each experiment. Spectra were collected in triplicate and used for pattern recognition (SIMCA) and partial least square (PLS) regression.

### Raman Analysis

A Wasatch Photonics Raman 1064 spectrometer (NC, USA) with laser operating at 1064 nm was used for Raman analysis. A laser output power of 1.492W was used. Spectra (250 – 1850 $cm^{-1}$) were collected at 10 $cm^{-1}$ resolution with 3 seconds integration time and 3 scans averaging. Spectra were collected in triplicate and analyzed by SIMCA and PLS regression.

### Multivariate Analysis

Multivariate analysis was used for qualitative and quantitative analysis. Pattern recognition (SIMCA) and partial least square (PLS) regression were used in this study. Discriminant analysis was used to classify samples based on their unique chemical composition.

## RESULT AND DISCUSSION

Authentication of maple syrup and potential adulterants by using pattern recognition was shown in Figure 1. Both Raman and FTIR spectra showed complementary signature patterns allowing to characterize the different maple syrup products based on their unique chemical composition. The strong fluorescence in corn syrup samples were highlighted in their Raman spectrum while the syrup blends resembled patterns of maple syrups. From the figure 1 shown, all corn/blend syrups were easily discriminated from maple syrup by chemometrics.

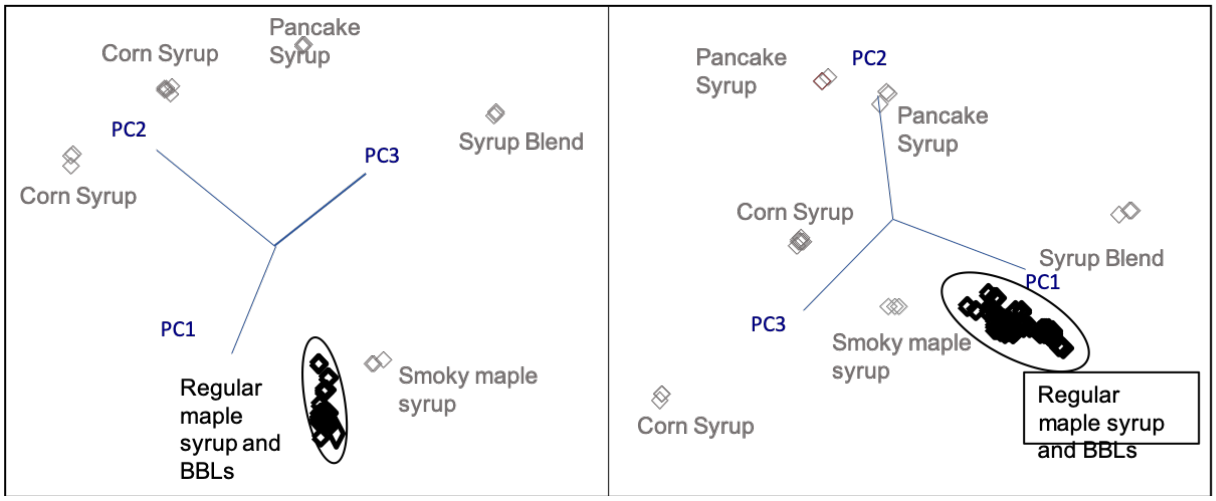


Figure 1. Soft independent modeling of class analogy (SIMCA) 3D projection plots authentication of maple syrup by FTIR (left) and Raman (right)

After excluding all potential adulterants, pure maple syrup exhibited interesting grouping pattern from both Raman and FRIT spectra by using SMICA. In FTIR spectra, pure maple syrup divided into two cluster with strong discriminating power at 1139 and 1490 $cm^{-1}$ wavelength. Those spectrum peaks correspond to lignin constituents in maple syrup (Jerkovic et al., 2010). The compositional differences of lignin in maple syrup might due to the various oxidation conditions during maple syrup evaporation, like foam control, which could have an important impact on the surface area of contact with air (Ho et al., 1992). From Raman spectrum, maple syrups were clustered according to their geographical origins, either Canada origin only, or having a mixture of US origin. Noticing that there were three maple syrup samples separating out from both clusters in both FTIR and Raman spectrum. After generating sugar profile of all samples by HPLC, the

maltose contents of those three samples were shown to be significantly higher than all the other samples.

In addition, BBL maple syrups clustered away from pure maple syrups in both fingerprinting techniques. Discriminating power showed 875 and 1033 $cm^{-1}$ in FTIR, 826 and 882 $cm^{-1}$ in Raman were the most important wavenumbers, indicating differences in ethanol contents. Both techniques showed the vast compositional diversity of BBLs associated with residual ethanol, amino acids and phenolic compounds. Interestingly, some commercial BBLs grouped with the pure maple syrup samples, indicating limited aging process.

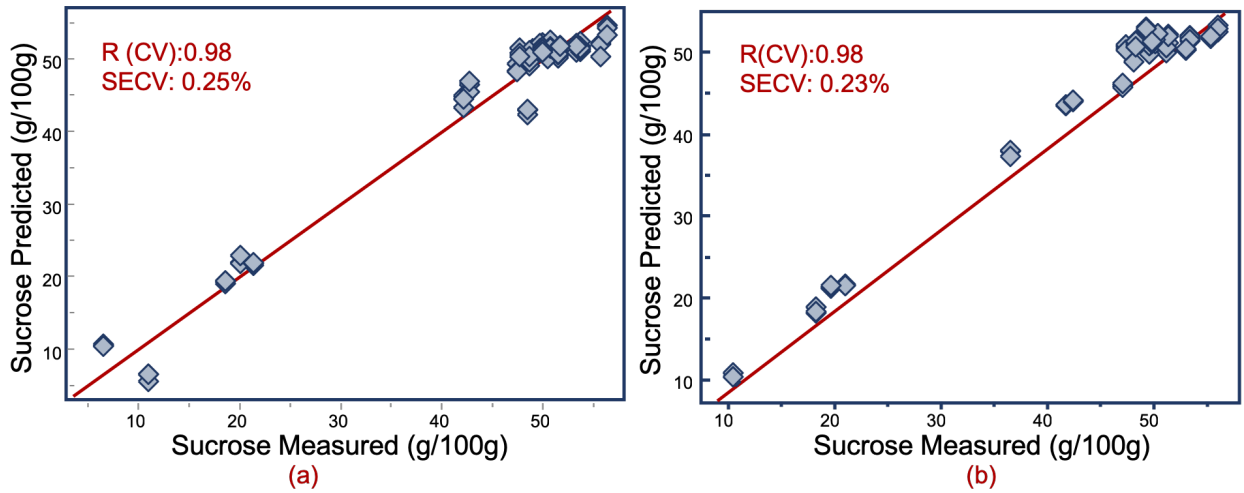


Figure 2. PLSR models of sucrose prediction by (a) FTIR and HPLC, (b)Raman and HPLC

Sucrose contents prediction by FTIR and Raman combined with PLSR was shown in Figure 2. From figure 2, both models showed great linearity with 98% correct prediction of sucrose contents and the standard error of calibration of 0.25% or 0.23%. Both spectroscopy techniques showed great capacity of authenticating and quantifying maple syrups.

## CONCLUSION

Both Raman and FT-IR fingerprints allowed to characterize different maple syrup products based on their unique chemical composition. The unique spectral features of the maple syrup samples allowed to discriminate them from potential adulterant syrups. Raman clustered maple syrup samples based on origin differences, while FT-IR grouped them based on lignin content. Maple syrups containing maltose were separated out by both FT-IR and Raman. Both techniques separated pure maple syrup from BBLs. Interestingly, Raman and FT-IR showed some BBL

samples clustering with the pure samples. Clustering of BBL maple syrups by Raman were associated with residual ethanol and amino acid compounds. FT-IR grouped BBLs based on phenolics and amino compounds. Both FT-IR and Raman combined with PLSR show very good prediction for syrup sugar contents. Both FT-IR and Raman equipment combined with SIMCA provide non-destructive and fast detection of quality traits of maple syrups, BBLs and the potential maple syrup adulterants. All units are field deployable and require minimal training making it an attractive option for the industry.

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## REFERENCE

Chamberlain AF. 1891. The maple amongst the Algonkian tribes. American Anthropologist, 4(1): 39-44.

Da-Wen S. 2018. Introduction to Food Authentication. Modern techniques for food authentication. San Diego, CA: Academic Press. p 1-21.

Ho CT, Lee CY, Huang MT. 1992. Phenolic Compounds in Food and Their Effects on Health. American Chemical Society. p 196-198.

Jerkovic I, Staver MM, Marijanovic Z, Lusic D. 2010. Volatiles from a Rare Acer spp. Honey Sample from Croatia. Molecules 15(7): 4572-4582.

Martin GG, Martin YL, Naulet N and McManus HJD. 1996. Application of $^{2}H$ SNIF-NMR and $^{13}C$ SIRA-MS analyses to maple syrup: detection of added sugars. J Agric Food Chem 44:3206–3213.

Paradkar MM, Sivakesava S, Irudayaraj J. 2002. Discrimination and classification of adulterants in maple syrup with the use of spectroscopic techniques. Journal of the Science of Food and Agriculture 82 (5):497-504.

Santos PM, Pereira-Filho ER, Rodriguez-Saona LE. 2013. Application of hand-held and portable infrared spectrometers in bovine milk analysis. Journal of Agricultural and Food Chemistry 61 (6): 1205–1211.
Stuckel JG and Low NH. 1996. The chemical composition of 80 pure maple syrup samples produced in North America. Food Res Int 29:373–379.
United State Department of Agriculture. 2018. United States Maple Syrup Production: National Agricultural Statistics Service. Washington DC. 20250