Non-Destructive Red Wine Measurement with Dispersive 1064nm Raman Spectroscopy

Superior Fluorescence Avoidance at 1064nm

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Background

Owing to technological improvements spurred on by the telecommunications boom of the last decade, Raman spectroscopy has become much more accessible to users in all fields. The combination of improved technology and the technique's molecular sensitivity have led to a surge in Raman usage in a myriad of application areas, including pharmaceutical, biomedical, agricultural, and forensic, among others. In all of these applications, however, there remains a struggle to extract useful Raman spectra from fluorescent and luminescent samples.

Fluorescence is much more likely and intense at short wavelengths where energies are more apt to cause an electronic transition. So, despite the lower Raman scattering cross-section (inversely proportional to λ^4), most users with potentially fluorescent samples long-ago switched to near-infrared wavelengths such as 785 or 830nm. These laser wavelengths push the detected signal to the spectral edge of silicon used in conventional multichannel CCD detectors, which are largely transparent above ~1050nm. Yet even at these near-IR wavelengths, many substances still fluoresce, sometimes prohibiting Raman spectral acquisition.

For those users who require longer wavelengths such as 1064nm, the only available option has been FT-Raman, which is typically noisier and slower than dispersive Raman systems. But now, BaySpec's new dispersive 1064nm Raman spectrometer family of instruments offers users a turn-key solution that combines the speed, sensitivity, and rugged design of traditional dispersive Raman instruments with the fluorescence avoidance of traditional FT-Raman instruments. In addition, this dispersive geometry permits diffraction-limited optical performance, finally allowing confocal microscopic Raman at 1064nm.

Methods

A variety of red wines were interrogated with two BaySpec benchtop Raman systems: the RamSpec™ 785 and the RamSpec™ 1064. Both systems utilized free space approach and the laser power was set at 450mW for both 785nm and 1064nm measurements. Measurement were made both through the wine bottle and on samples poured into secondary vials. Acquisition times varied for both systems due to different excitation laser wavelength and sampling methods.

Results and Discussion

Any new method for routine determination of chemical composition in beverage manufacturing processes should be non-invasive, non-destructive and rapid to ensure timely processing of the product being analyzed[1]. Raman spectroscopy offers the advantages of minimal sample preparation and fast spectral acquisition. However, the pigments in red wines are often too fluorescent to allow Raman to be measured, even at 785nm;[2] see Figure 1. But at 1064nm, a clear Raman spectrum is generated while florescence background is almost totally avoided. Additionally, because of the extended quantum efficiency of the InGaAs detector, high wavenumber features (C–H, O–H, and N–H stretching modes) are also simultaneously captured with the same acquisition.
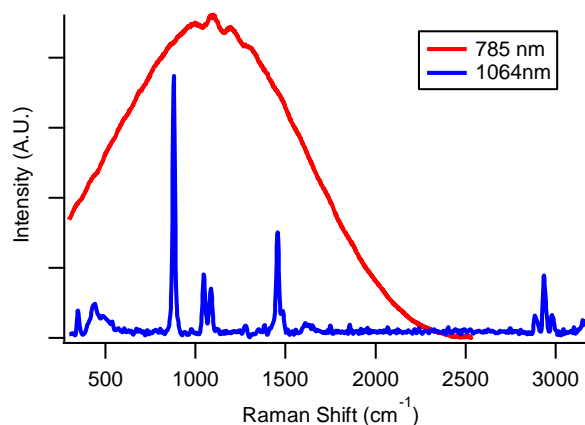
Figure 1: *Red wine is highly fluorescent at 785nm, preventing extraction of a usable Raman signal. At 1064nm, however, this fluorescence interference is largely avoided and clear Raman bands are evident.*

In addition to the fluorescence of red wine, other major obstacles to non-invasive and nondestructive Raman measurement through the bottle is the degradation of

laser and Raman signal when they travel through the glass bottle. Evaluating the optical transmission spectrum of a typical 3.0 mm empty green glass bottle, it is seen that glass is mostly transparent to NIR wavelengths (~>800nm) compared to 532nm and 785nm in Figure 2. This makes 1064nm Raman even more suitable for non-destructive measurement of red wine through the bottle.
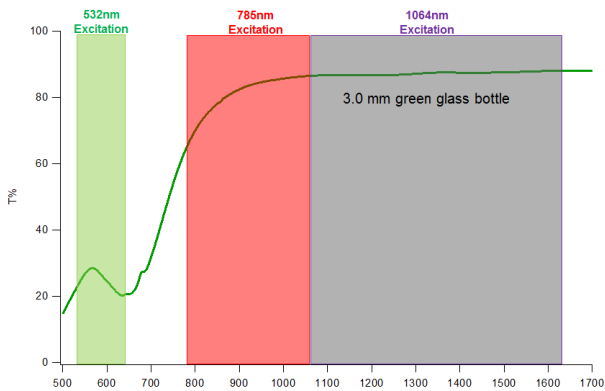
Figure 2: Transmittance of 3.0mm green glass bottle for red wine through different wavelength ranges.

With the advantages of superior fluorescence avoidance and minimal signal loss through the bottle, Raman spectra of the same red wine in vial and through the bottle were collected with a RamSpec™ 1064 using the same acquisition time. As shown in Figure 3, comparing the red wine spectrum in a secondary vial with that collected through the bottle, despite a small attenuation in the signal intensity, the Raman features are maintained and distinguishable for further identification and quantification.
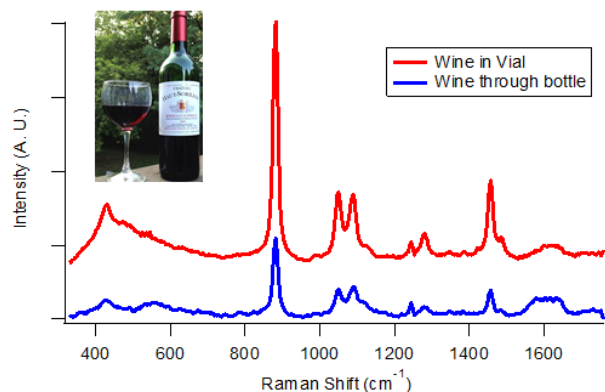

Figure 3: Raman spectra of red wine collected in vial and through its bottle, using 1064nm Raman system

Based on the results of the red wine measurement with 1064nm Raman, further component analysis was performed by adding methanol into the wine and measured as before. As seen in Figure 4, most of the Raman features from pure red wine matches ethanol and could be easily identified. For the Raman spectrum of red wine with methanol added, a Raman peak centered around 1020 cm^{-1} is apparent, and this peak can be utilized for the quantification of the methanol in different red wine samples as seen in Figure 5. Slight variances in spectral intensity and predicted methanol percentage on different measuring spots were found due the heterogeneity of the bottle glass.
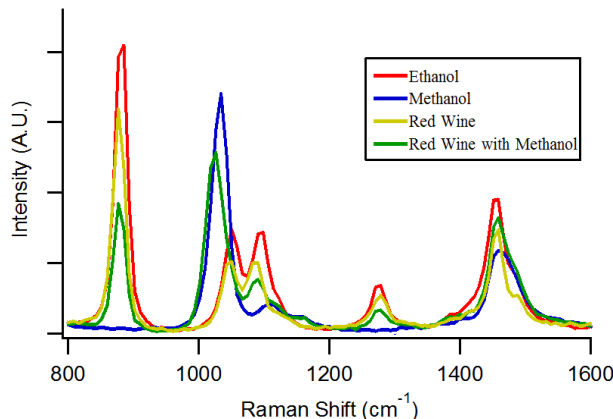
Figure 4: Identification of methanol in red wine based on its unique Raman features different from ethanol.
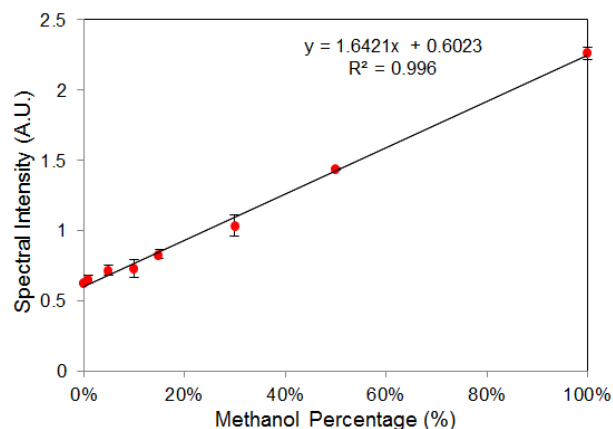
Figure 5: Quantification of methanol concentrations in red wine based on the intensity of one major Raman feature.

Based on these experiments, 1064nm dispersive Raman is demonstrated as a viable new option to determine wine composition and contamination in the bottle. Further, chemometrics tools such as principal component analysis (PCA) and partial least squares regression (PLS) can significantly increase the accuracy and precision of identification and quantification of the chemical composition of red wine with Raman spectroscopy. It can be expected that future development of such application may provide the wine industry a fast and non-destructive quality control and assurance tool for composition monitoring. This methodology can be easily applied to other beverages like distilled spirits, beer and others.

References
1) Nordon, A., et al., *Anal. Chim. Acta,* **2005**, 548, 148-158.
2) Gallego, A. L., et al., *IEEE TIM,* **2011**, 60, 507-512.