Technospex

Determining Alcohol Content in Whisky Using Raman Spectroscopy

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Introduction

Alcoholic beverages are often adulterated with methanol to increase its alcohol content. However, methanol is a highly toxic chemical which can cause blindness, brain damage, hypothermia, seizures, and even death in severe case. In countries with under-regulated alcohol industry, it is often reported that people died from methanol poisoning after consuming adulterated alcoholic beverages.

In this app note, we demonstrate that our uRaman system can be used for *in-situ* and rapid detection of alcohol content and quantification of its alcohol (ethanol) volume percentage in non-destructive way. In particular, we directly identify and differentiate the Raman molecular fingerprint of methanol from ethanol in lab-prepared samples. In addition, we are able to precisely quantify the alcohol percentage of an unknown whisky sample obtained from a prominent whisky bar in Singapore using a Raman calibration plot of alcohol-water solution [1,2].

Method and setup

Methanol and ethanol were obtained from JT Baker and Fisher Chemical with purity more than 99.5 %. The unknown whisky sample was provided by a local whisky bar in Singapore. The uRaman-Ci-532 was used for this experiment (Figure 1). The system consists of a uRaman module mounted on the Nikon Ci-L upright research microscope. The uRaman module is configured with 532 nm frequency stabilized laser with linewidth less than 100 Mhz. All measurements were performed in liquid form with cuvette holder attached to the objective turret. The acquisition time is 1 s. The spectra presented in this app note is the average of at least 5 spectra.

Figure 1 uRaman 532nm (equipped with motorised stage and several objective lens.

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Results and Discussion

Differentiating Methanol from Ethanol

The Raman spectra of methanol (MeOH), ethanol (EtOH) and a mixture (MeOH:EtOH = 1:1) are shown in Figure 2 Methanol exhibits very sharp C-O stretching band at 1019 cm^{-1}, whereas ethanol has two smaller peaks at 1030 and 1080 cm^{-1} (Figure 2). EtOH also exhibits an exclusive C-C stretching band at 879cm^{-1}. At the higher wavenumber, MeOH has two C-H stretching bands at 2833 and 2946 cm^{-1}, while EtOH has three bands at 2885, 2929 and 2974 cm^{-1}, respectively. The (MeOH:EtOH) mixture has all these signature bands in the Raman spectroscopy. Table 1 is the summary of the Raman band assignments from the measurements.

The Raman shift at 2833 cm^{-1} is a good indicator for distinction of MeOH from EtOH. This peak can be used as the fingerprint for the presence of MeOH in alcoholic beverages.

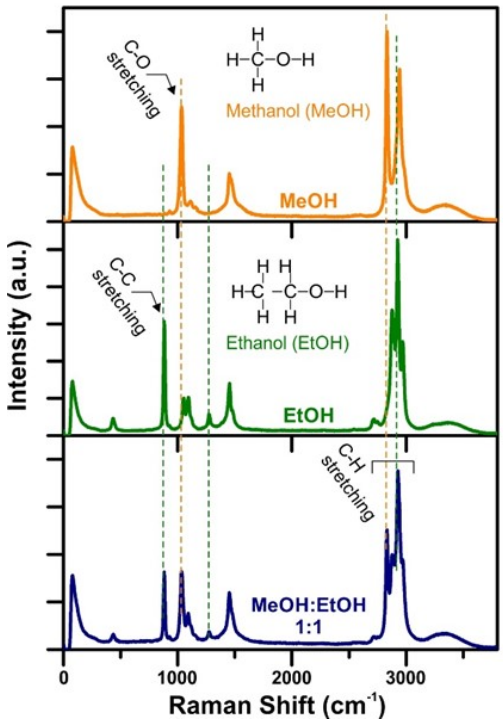

Figure 2 Raman spectrum collected from Methanol, Ethanol and 1:1 mixture of methanol and Ethanol, respectively.

Table 1 Raman peak assignment for Methanol and Ethanol.

Sample	Raman shift (cm^{-1})	Assignment
Methanol	1019	C-O stretching
	1448	CH_3-bending
	2833	CH-stretching
	2946	CH-stretching
Ethanol	879	C-C stretching
	1030	C-O stretching
	1079	CH_3-rocking
	1458	CH_3-bending
	2885	CH-stretching
	2929	CH-stretching
	2974	CH-stretching

Construction of calibration curve

We begin by measuring the Raman shifts of pure ethanol and ethanolic solution diluted with water to obtain EtOH solution of different volume concentrations. These solutions are measured and the Raman spectrums are plotted in Figure 3(A). We use the area under the C-H and O-H stretching bands (after baseline correction) to obtain a calibration curve such as that in Figure 3(B). As the EtOH concentration reduces, the C-H stretching band becomes less prominent. At the meantime, the O-H stretching band increases due to higher water content.

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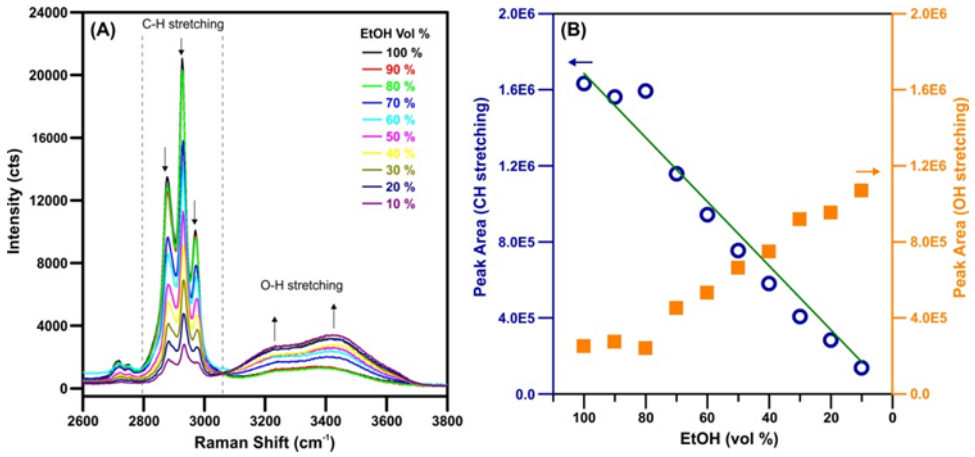

Figure 3 (A) Raman spectra collected from ethanolic solutions of different ethanol vol%. (B) Measured Raman peak area (area under the peaks) of CH- (2800-3000cm^{-1}) and OH- (3000-3650 cm^{-1}) stretchings with respect to different ethanolic solutions of different ethanol volume concentrations (vol %).

From the calibration curve in Figure 3B, we achieve the linear relationship between the Raman peak area and ethanol volume concentration as followed:

Peak Area (CH-stretching) = 16854 x EtOH (vol%).

Determination of alcohol level in unknown whisky samples

The spectrum of an unknown whisky sample received has strong fluorescent background in the measured range (Figure 4A). After the background removal, we find the peak area (CH-stretching at high wavenumber 2800-3050 cm^{-1}) is about 951088 (Figure 4B). Hence, the ethanol (vol %) is determined as:

EtOH vol(%) = 951088/16854 = 56.4 vol%.

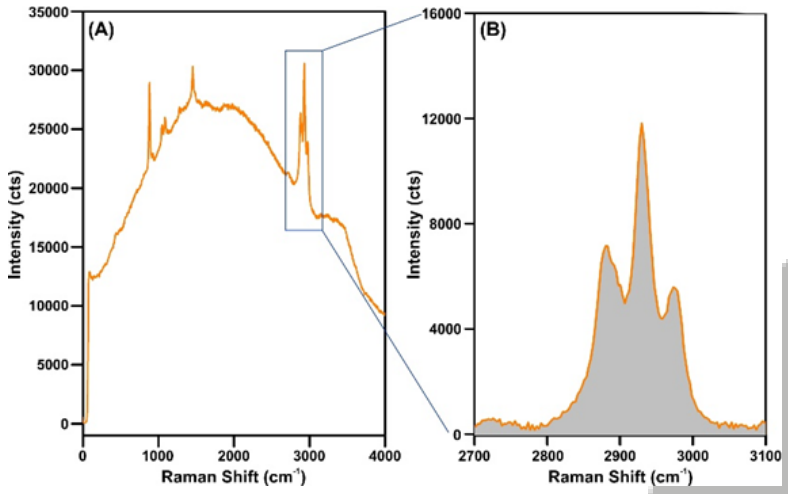

Figure 4 (A) Raman spectrum collected from unknown whisky sample and (B) peak area (shade) measured after the fluorescent background removal.

Upon checking with the customer, the beverage alcohol content provided by the brewery is ***56.9%*** (Bowmore 12 Years Old – Small Batch Islay single malt Scotch whisky). The small variation can be due to sample preparation or during linear fitting of calibration plot. Nevertheless, it showcases Raman measurement as a simple to use and non-destructive technique to determine the alcohol quantify.

Conclusion

Raman spectroscopy is a non-destructive way to detect the presence of methanol in alcohol spirit and also able to quantify the alcohol level in the beverages.

Reference

[1] J. Quant. Spectr. Rad. Transfer 2011,112, 1043. [2] J Raman Spectr. 2012,43,1171.

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