ETHANOL IN SINGLE MALT SCOTCH BY RAMAN SPECTROSCOPY

APPLICATION NOTE RAMAN-022 (A4)

Author: A.J.R. Bauer, Ph.D.

Abstract

This application note documents the use of a TSI ChemLogix™ ProRaman-L instrument to measure ethanol in samples of single malt Scotch whisky.

Motivation

In November 2017, a Chinese millionaire paid $10,050 for a dram of Scotch, allegedly from an unopened bottle of Macallan single malt, dated 1878. It was believed to be the largest sum ever paid for a glass of whisky. It was shortly thereafter proved to be a fake.[1]

In March of that same year, Canadian authorities recalled hundreds of bottles of Georgia Bay Vodka after inspectors discovered that the alcohol content was 81%, twice the amount stated on the label.[2]

A recent report from the Centre for Indonesian Policy Studies (CIPS) states that 487 people died in the years 2013 to 2016 from illegal alcohol, in most cases locally-produced liquor with naturally fermented methanol intact. Indonesia has a high alcohol tax, and traditional liquor made from coconut palm, sugarcane or rice is sold as vodka, whisky and gin. In most distilling processes, the product is heated sufficiently for the methanol to evaporate or to be burned off. Imported alcoholic drinks are not available to many because of price, opening the door for amateurs to make the traditional "arak" and not bother with the important final step.[3]

These stories demonstrate the need for several different types of analytical support to the liquor industry: discovery of fraudulent spirits, the measurement of alcohol and the discovery of methanol contamination. In this application note, we will examine the measurement of ethanol concentration in a collection of single malt Scotch whisky. Subsequent notes will address these other issues and more.

Figure 1. Scotch is served both neat and on the rocks.
Photo credit[4].

TSI and TSI logo are registered trademarks of TSI Incorporated.
ChemLogix is a trademark of TSI Incorporated.

The Celts coined the name "uisge beatha:" water of life. Whiskies are ethanol/water mixtures that contain volatile phenolic compounds and an incredible range of congeners. Scotch may only have a handful of ingredients, but it is chemically very complex. Microorganisms create hugely diverse flavor profiles during fermentation through production of secondary metabolites. In addition to the thousands of pre-existing chemical compounds within barley, yeast, and bacteria, there are secondary metabolites generated by yeast, bacteria, and other fungus during fermentation, and chemical reactions during barley germination, drying, peating (origin of the phenolics), and fermentation. Finally, there is the interaction between all the individual compounds and their interaction with the wooden ageing cask, the source of most of the congeners.

These flavors and scents also reflect the whisky's place of origin, it's "terroir." The local geology, soil, climate and vegetation all play into the sensory profile of the whisky.

Scotch is expensive and, in some cases, rare, and is; therefore, a target for dilution, adulteration and fraud. The applications group at TSI had momentary access to a large collection of single malt Scotch whisky, the samples discussed within this note. These samples are listed, along with their alcohol content, some information about phenol content and location of origin, in Table 1.

Samples

These samples were not generally pristine when the aliquots for analysis were poured. Several of the bottles had been open some months, and a couple some years. For this reason, we expect there to be some uncontrolled variability in the alcohol concentrations given on the bottle's labels.

The samples were poured into 2 ml vials, and put into the vial/cuvette measurement accessory interfaced to a TSI ChemLogix ProRaman-L spectrometer.

Table 1. Samples of Scotch Whiskey used in this Note.

Single Malt Scotch	%EtOH	[Phenol] ppm	Location of Origin
Auchentoshan 3 Wood	43		Lowland
Highland Park Dark Origins	46.8		Orkney
Bruichladdich Islay Barley	50		Islay
Laphroaig Triple Wood	48	30-45	Islay
Octomore 8.2	58.4	167	Islay
Octomore 6.2	58.2	167	Islay
Ardbeg 10 yr	46	~50	Islay
Port Charlotte Scottish Barley	50	40	Islay
Octomore 6.1	57	167	Islay
Bunnahabhain Cruach-Mhòna	50	35	Islay
Talisker 10 yr	45.8		Isle of Skye
Dewar's White Label	40		Blend
Johnny Walker Black Label	40		Blend

Measurements and Results

The ProRaman-L contains a 785 nm excitation laser, and was used at approximately half-maximum output (130 mW). The samples were presented to the laser in vials housed in a darkened vial/cuvette holder. 15 s acquisition periods were used. Samples of 70% EtOH in water and pure MeOH were also submitted to analysis. Methanol and ethanol are easily differentiated, as seen in Figure 2.

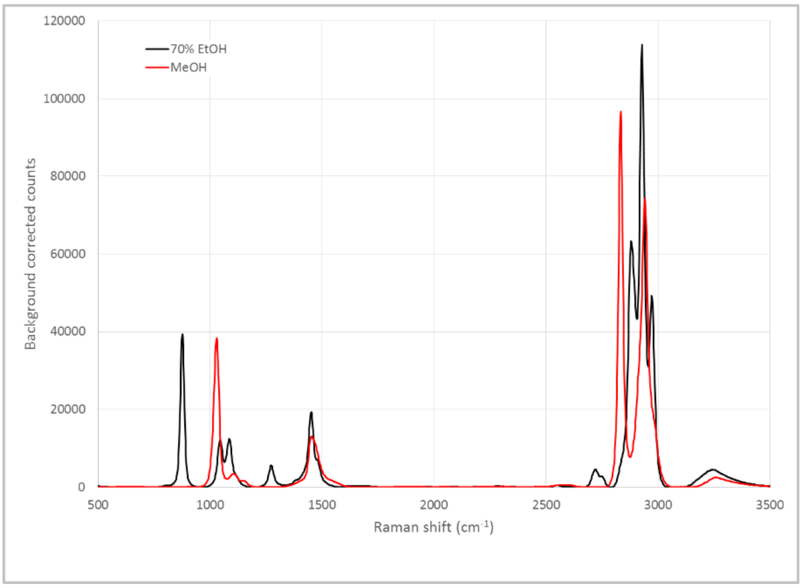

Figure 2. Raman spectra of pure methanol and 70% ethanol in water.

The chief methanol features that could be used to monitor contamination are present at 1032 and 2832 cm^{-1}. In order to establish the approximate impact of methanol on the Scotch spectra, the pure methanol spectrum was used to calculate the spectrum of methanol at 1 and 2% in the Dewar's sample. The net impact of the calculated contamination is shown in Figure 3. U.S. and Scotch whiskies tend to have methanol levels about 0.2-0.3%, and levels much above that would be considered contaminated.[5]

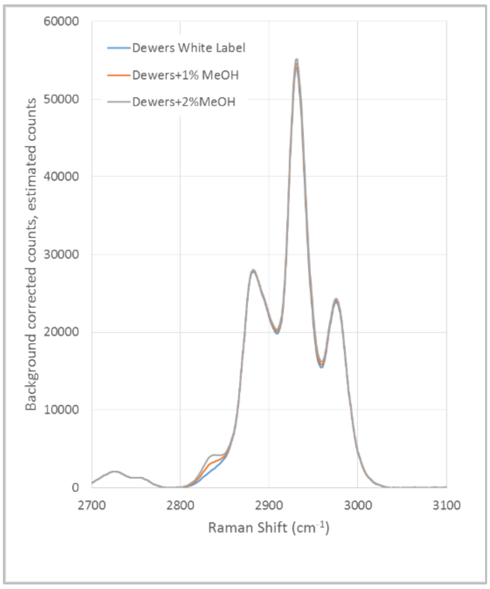

Figure 3. Acquired Dewar's spectrum with calculated methanol impact at 1 and 2%.

Without constructing a formal calibration curve for the methanol in the whisky samples, the limit of detection of methanol in these materials is likely to be close to this value. Certainly, this approach is clearly able to determine dangerous levels of methanol in aqueous solutions of ethanol. The minimum lethal dose of methanol in the absence of medical treatment is between 0.3 and 1 g/kg.[6] This issue will be formally pursued in an upcoming Application Note.

More interesting with respect to these particular samples is the development of a relationship between the ethanol content claimed on the labels of the Scotch bottles and the collected Raman spectra.

The first observation made is that the only lowland sample on the list (Auchentoshan 3 Wood) had much more native fluorescence than the other samples (highland, blend and Islay). In the corrected spectrum, this manifested as a nonspecific raised background between Raman shifts of 500-800 cm^{-1}.

The calibration curve developed by integrating the Raman signal from 2800–3026 cm^{-1} was the most linear of those investigated. The abscissa has been assigned with the percent ethanol listed on the labels of the whisky samples. As was previous described, most of the bottles had been open for some time, it is not expected that these x-values are extremely accurate. Nonetheless, a reasonable relationship between ethanol content and spectral features has been documented. Figure 4 shows the best of these relationships. This approach was used at the 875 cm^{-1} feature with similar results, indicating that methanol, present 2832 cm^{-1}, inside the region integrated for the ethanol signal, is present only in minute quantities.

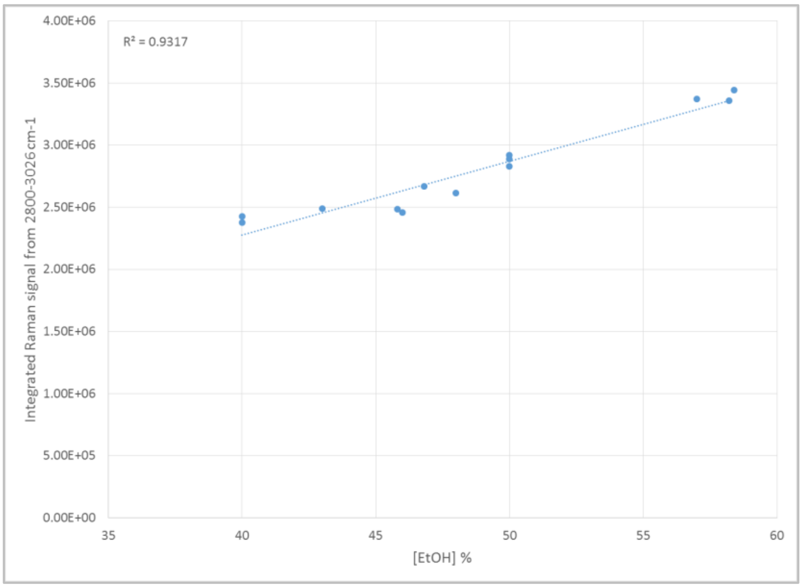

Figure 4. Calibration curve relating reported ethanol content and integrated Raman signal.

Summary

Raman spectroscopy has been used to determine a calibration curve relating reported (but possibly not precise) ethanol content with integrated signal. Also, an estimate of methanol limit of detection has been given. This measurement will be more fully examined in a future Application Note.

References

1. https://www.bbc.com/news/uk-scotland-scotland-business-41695774
2. https://medicalxpress.com/news/2017-03-canada-recalls-strong-alcohol-vodka.html#nRlv
3. https://asiancorrespondent.com/2017/10/contaminated-alcohol-indonesia-killing-hundreds-people-year/
4. https://www.huffingtonpost.com/michelle-pruett/whiskey-bourbon-scotch-ry_b_9548538.html
5. https://homedistiller.org/intro
6. https://toxnet.nlm.nih.gov/cgi-bin/sis/search2/r?dbs+hsdb:@term+@rn+@rel+67-56-1

UNDERSTANDING, ACCELERATED

TSI Incorporated – Visit our website **www.tsi.com** for more information.

USA	**Tel:** +1 800 680 1220	**India**	**Tel:** +91 80 67877200
UK	**Tel:** +44 149 4 459200	**China**	**Tel:** +86 10 8219 7688
France	**Tel:** +33 1 41 19 21 99	**Singapore**	**Tel:** +65 6595 6388
Germany	**Tel:** +49 241 523030		

 ©2018 TSI Incorporated Printed in U.S.A.