Application Note 410000019-B

Quantification of methanol in contaminated spirits with Raman

Protecting consumers from contaminated beverages

An alarming global trend highlights the serious harm that can result from ingesting illegally brewed alcohol. Home-distilled spirits prepared with industrial solvents (i.e., wood alcohol) and presented as alcoholic beverages often contain methanol. This ingredient causes blindness and can lead to death when ingested. This has led to fatal consequences on multiple continents [1–3].

The breaking point for the Czech Republic came in September 2012. The sale of hard liquor was temporarily banned after 20 people died from the consumption of spirits with dangerous levels of methanol [2]. After an exhaustive study using different screening tools, the Czech Republic turned to Raman spectroscopy as the method of choice for identification and quantification of methanol in contaminated spirits.

This Application Note discusses the reasons why Raman spectroscopy is the ideal choice for this application and shows a real-world example of Raman analysis of methanol-laced rum.

INTRODUCTION

Raman spectroscopy is a fast and easy analytical tool for quantifying the amount of methanol contamination present in alcoholic beverages. It is an ideal method for the discrimination of very similar molecules like ethanol (CH_3CH_2OH) and methanol (CH_3OH), as shown in Figure 1.

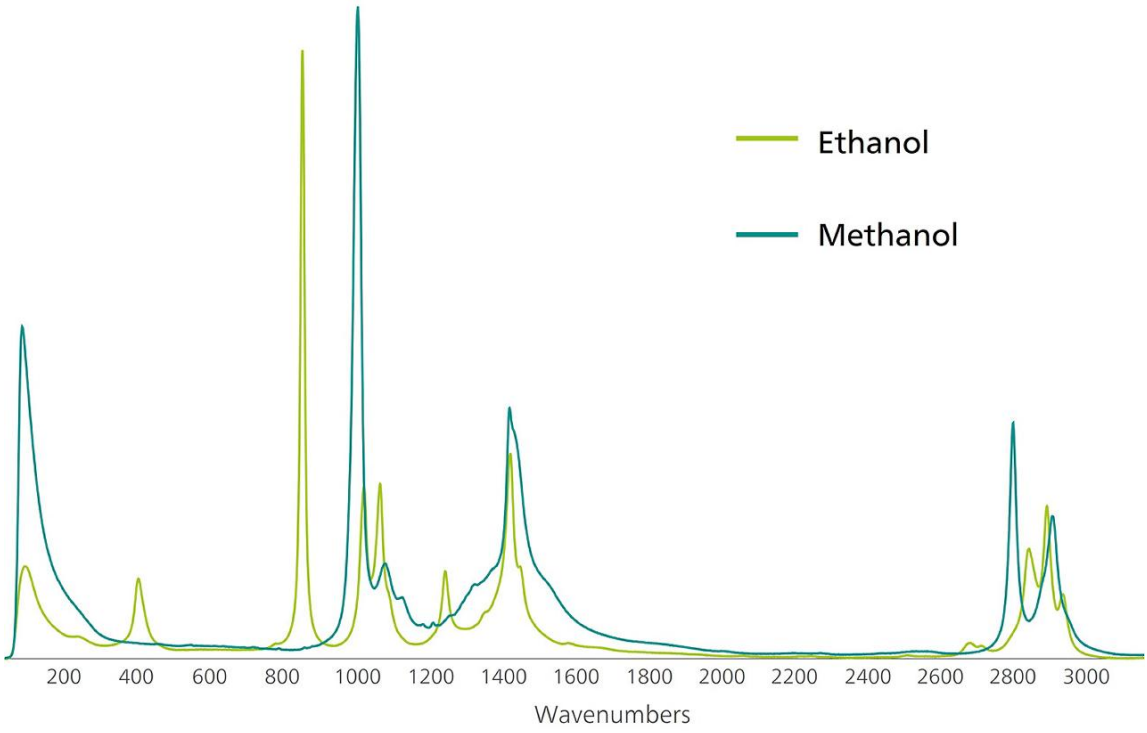
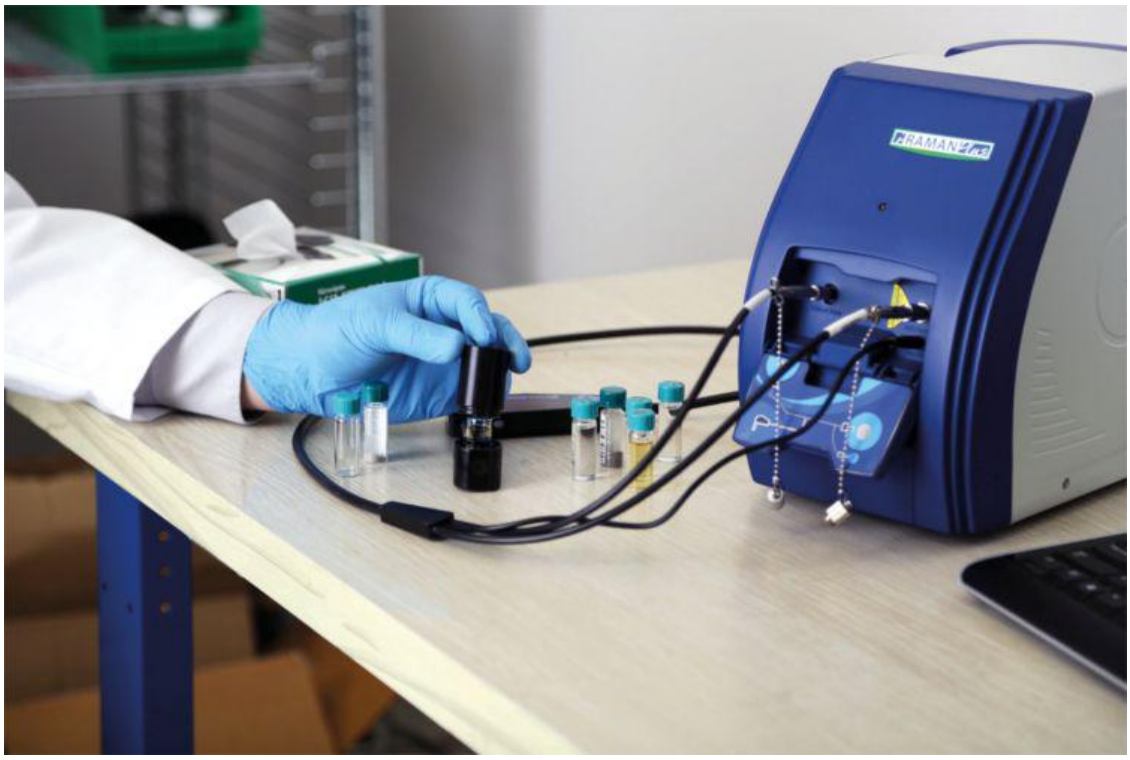


Figure 1. Raman spectra of pure ethanol (green) and pure methanol (blue).

Raman spectroscopy is superior to comparative technologies such as infrared spectroscopy (e.g., FTIR) because of its:

- ability to measure through optically transparent containers
- insensitivity to interference from water

These two key properties enable accurate detection of methanol down to approximately 1% by volume in the field with no need to open the bottles being tested.



EXPERIMENT

An in-house study measured commercially available coconut rum that was spiked with methanol in concentrations between 0.33% and 5.36%. The i-Raman® Plus, a sensitive high resolution laboratory system with a fiber-optic probe, was used to collect Raman spectra of the mixtures, shown in Figure 2. Table 1 lists the relevant equipment and instrument settings used for this application study.

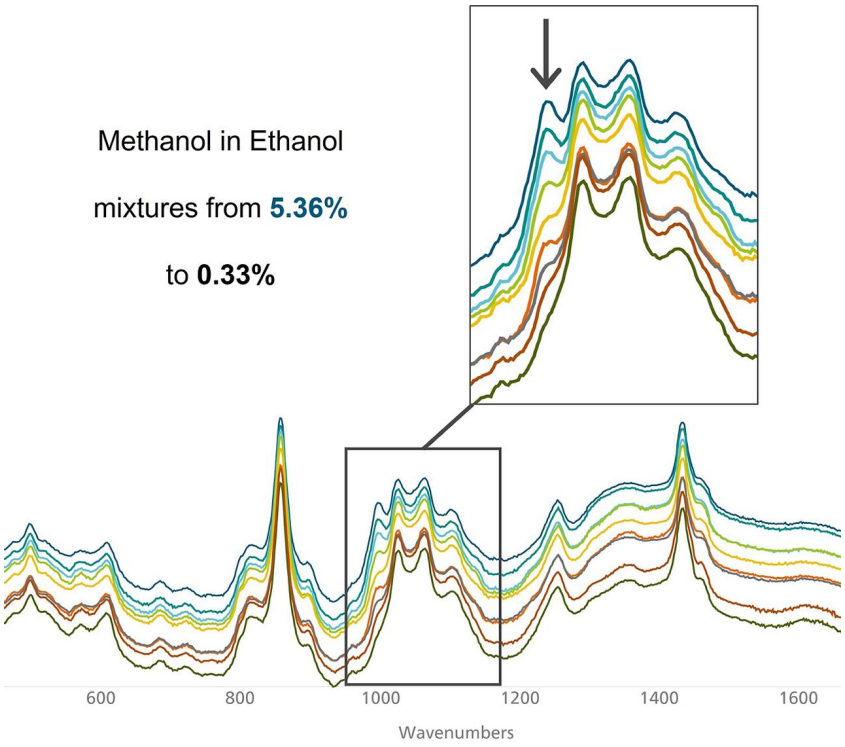


Figure 2. Raman spectra of methanol-laced rum with varying concentrations of methanol. Inlay: The peak noted with the arrow grows with increasing concentration of methanol.

The peak at around 1000 cm^{-1} visibly increases with increasing concentration of methanol, becoming significant at approximately 1%.

Table 1. Experimental parameters.

Equipment	Acquisition settings	
i-Raman Plus 785S	Laser Power	100
Vial holder (NR-LVH)	Int. time	20s
Vision Software	Average	1

This data was analyzed with Vision software, and a partial least squares (PLS) regression model was developed on normalized data. The two-factor model developed over the range from 920–1580 cm^{-1} gave the calibration curve shown in Figure 3, which has a root mean square error of cross-validation (RMSECV) of 0.1069 (Table 2). The R^2 value of 0.9977 shown in Table 2 means that the Raman method used here can be used to confidently quantify the amount of methanol in a mixed alcohol sample.

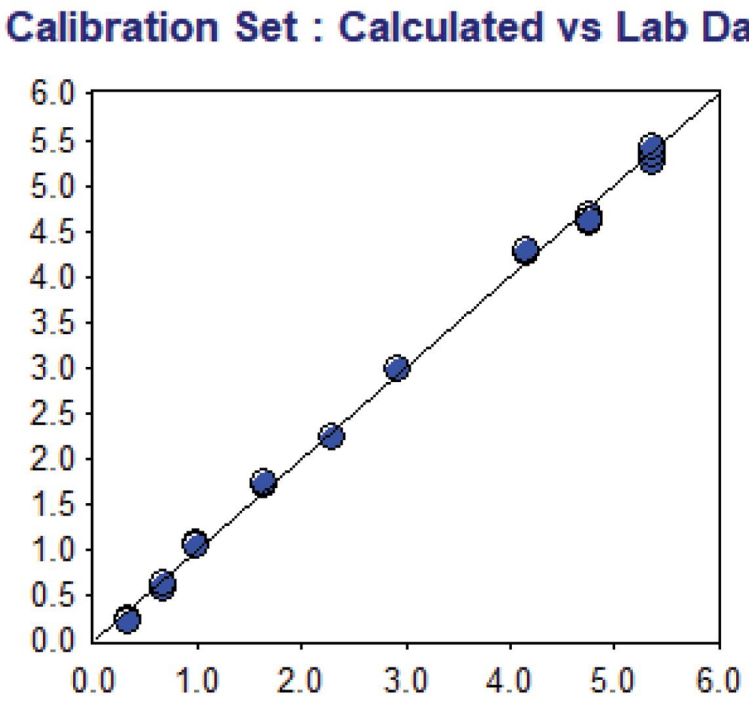


Figure 3. PLS regression model to predict the amount of methanol in rum.

Table 2. Regression parameters used for the development of the PLS model to determine methanol in rum with the i-Raman Plus 785S.

Parameter	Value
Spectral processing	Standard Normal Variate Savitzky-Golay derivative
R^2	0.9977
RMSEC	0.0976
RMSECV	0.1069

CONCLUSION

These results verify that Raman can be used for rapid, quantitative screening of dangerous adulterants in alcoholic beverages that pose a public safety risk. This technique can be expanded to investigate adulteration in other media such as food, petroleum, and pharmaceutical drugs [4].

REFERENCES

1. Lachenmeier, D. W.; Schoeberl, K.; Kanteres, F.; Is Contaminated Unrecorded Alcohol a Health Problem in the European Union? A Review of Existing and Methodological Outline for Future Studies. *Addiction* **2011**, *106* (s1), 20–30. https://doi.org/10.1111/j.1360-0443.2010.03322.x.
2. Spritzer, D.; Bilefsky, D. Czechs See Peril in a Bootleg Bottle. *The New York Times*. USA September 17, 2012.
3. Collins, B. Methanol Poisoning: The Dangers of Distilling Spirits at Home. *ABC*. Australia June 13, 2013.
4. Gryniewicz-Ruzicka, C. M.; Arzhantsev, S.; Pelster, L. N.; et al. Multivariate Calibration and Instrument Standardization for the Rapid Detection of Diethylene Glycol in Glycerin by Raman Spectroscopy. *Appl Spectrosc* **2011**, *65* (3), 334–341. https://doi.org/10.1366/10-05976.

CONTACT

Metrohm Brasil
Rua Minerva, 161
05007-030 São Paulo
metrohm@metrohm.com.br

CONFIGURATION

i-Raman Plus 785S Portable Raman Spectrometer

The i-Raman® Plus 785S is part of our award-winning series of i-Raman portable Raman spectrometers powered by our innovative intelligent spectrometer technology. Using a high-quantum-efficiency CCD array detector with TE cooling and high dynamic range, this portable Raman spectrometer delivers excellent performance with low noise, even at integration times of up to 30 minutes, making it possible to measure weak Raman signals.

The i-Raman Plus 785S features the unique combination of wide spectral range and high resolution with configurations which allow measurements from 65 cm^{-1} to 3,350 cm^{-1}. The system's small footprint, lightweight design, and low power consumption ensure research-grade Raman analysis capabilities at any location. The i-Raman Plus is equipped with a fiber probe for easy sampling, and can be used with a cuvette holder, a video microscope, an XYZ positioning stage with a probe holder, as well as our proprietary BWIQ® multivariate analysis software and BWID® identification software. With the i-Raman Plus, you always have a high precision Raman solution for qualitative and quantitative analysis.

Vial Holder Adapter

Vial holder adapter for use with the BAC100/BAC102 lab-grade Raman Probe with 9.5 mm shaft diameter. Compatible with vials with a diameter of 15 mm. Shipped with 6 vials made from borosilicate glass (15 mm).

Vision 4.1

Vision is data acquisition and method development software solution for spectroscopic analysis and control of B&W Tek portable Raman instruments, Metrohm XDS laboratory and process NIRS instruments. A user-friendly graphical analysis interface enables a simple application of chemometric algorithms for creating identification, qualification, and quantification methods and running them in real-time. With Vision you can store, manage, reprocess and exchange data.