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.

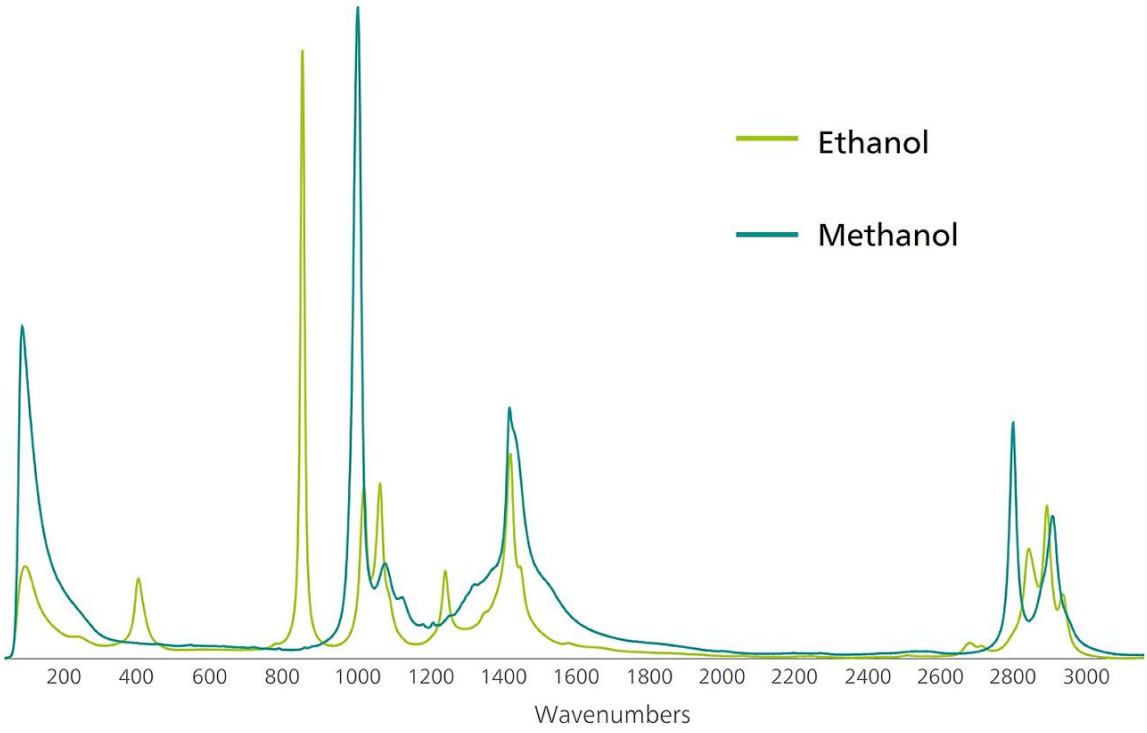
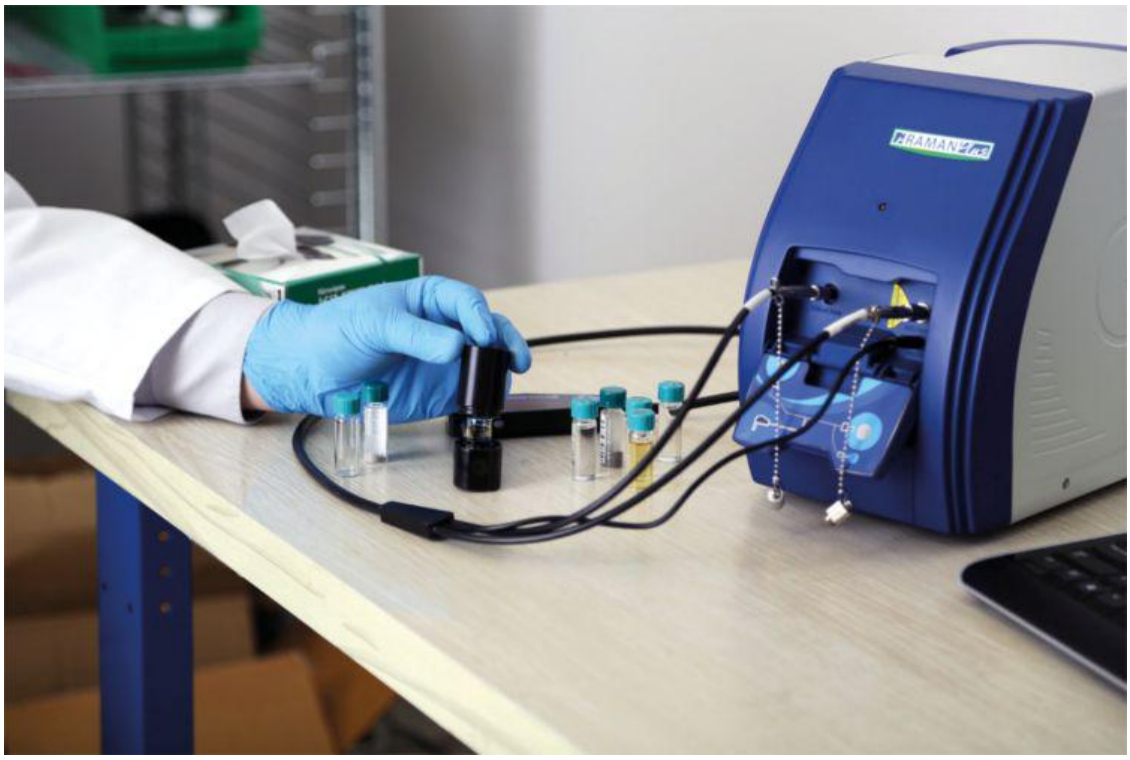


Figure 1. Raman spectra of pure ethanol (green) and pure methanol (blue).

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.

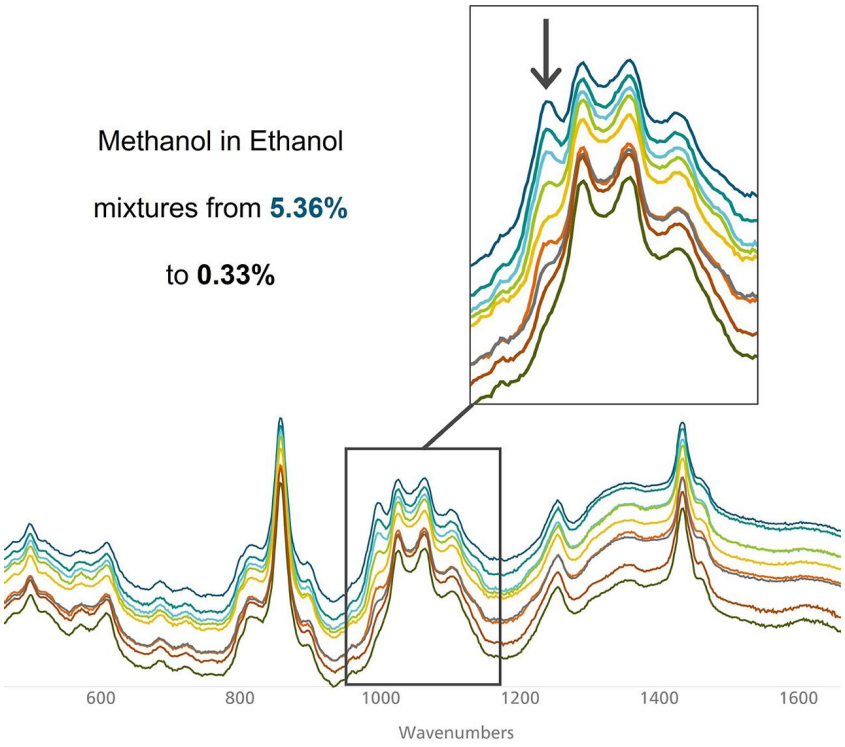


Figure 2. Raman spectra of methanol-laced rum with varying concentrations of methanol. Inlay: The peak noted with the arrow grows with increasing concentration of methanol.

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.

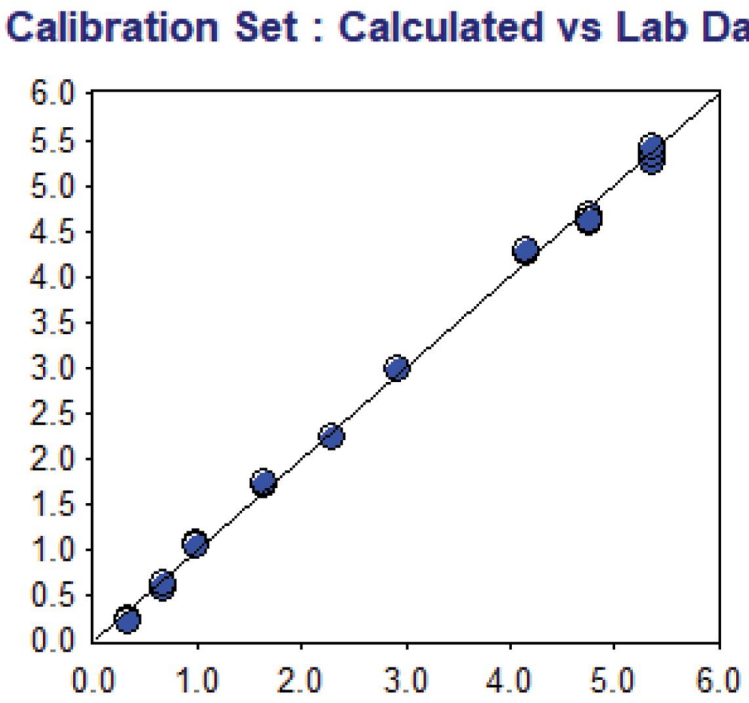


Figure 3. PLS regression model to predict the amount of methanol in rum.

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 France
13, avenue du Québec - CS 90038
91978 VILLEBON COURTABOEUF CEDEX
info@metrohm.fr

CONFIGURATION

Spectromètre Raman portable i-Raman Plus 785S

L'i-Raman® Plus - 785S appartient à notre série primée de spectromètres Raman portables « i-Raman », équipée de notre technologie de spectrométrie intelligente et innovante. Faisant appel à un détecteur à barrette CCD à haute efficacité quantique, avec refroidissement thermoélectrique et une gamme dynamique élevée, ce spectromètre Raman portable fournit des performances exceptionnelles avec un bruit réduit, même avec un temps d'intégration atteignant 30 minutes. Ainsi, les signaux Raman faibles peuvent aussi être mesurés.

Le i-Raman Plus 785S offre la combinaison exclusive d'une large gamme spectrale et d'une haute résolution avec des configurations autorisant des mesures de 65 cm^{-1} à 3350 cm^{-1}. Le faible encombrement et la légèreté de structure de ce système peu énergivore lui permettent d'effectuer partout des analyses Raman de qualité recherche. Équipé d'une sonde à fibre optique pour faciliter l'échantillonnage, l'i-Raman Plus peut être utilisé avec un support de cuvette, un microscope vidéo, une table de translation XYZ avec support de sonde ainsi qu'avec notre logiciel d'analyse à variantes multiples BWIQ® et le logiciel d'identification BWID®. Avec le i-Raman Plus, vous avez une solution Raman pérenne de haute fidelité pour l'analyse qualitative et quantitative.

Adaptateur de support de flacon

Adaptateur de support de flacon pour une utilisation avec la sonde Raman BAC100/BAC102 de qualité laboratoire, d'un diamètre de tige de 9,5 mm. Compatible avec des flacons d'un diamètre de 15 mm. Lot de 6 flacons en verre de borosilicate (15 mm).

Vision 4.1

Vision est une solution logicielle d'acquisition de données et de développement de méthodes pour l'analyse spectroscopique et la commande des appareils Raman portables de B&W Tek, des appareils de laboratoire Metrohm XDS et de procédures NIRS. Une interface d'analyse graphique conviviale permet une application simple d'algorithmes chimiométriques pour créer des méthodes d'identification, de qualification et de quantification et les exécuter en temps réel. Avec Vision, vous pouvez stocker, gérer, retraiter et échanger des données.