Application Note 410000019-B

携帯型ラマン分光計による汚染された蒸留酒に含まれるメタノールの定量

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**.

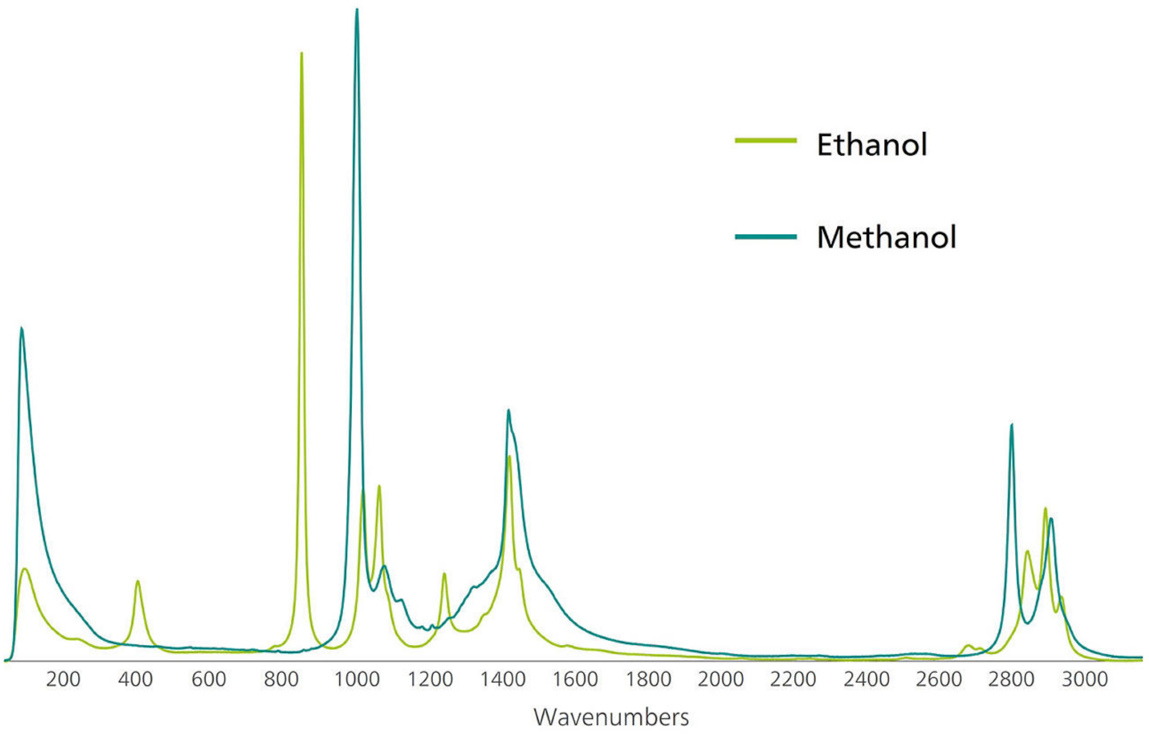

Figure 1. Raman spectra of pure ethanol (green) and pure methanol (blue).

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.

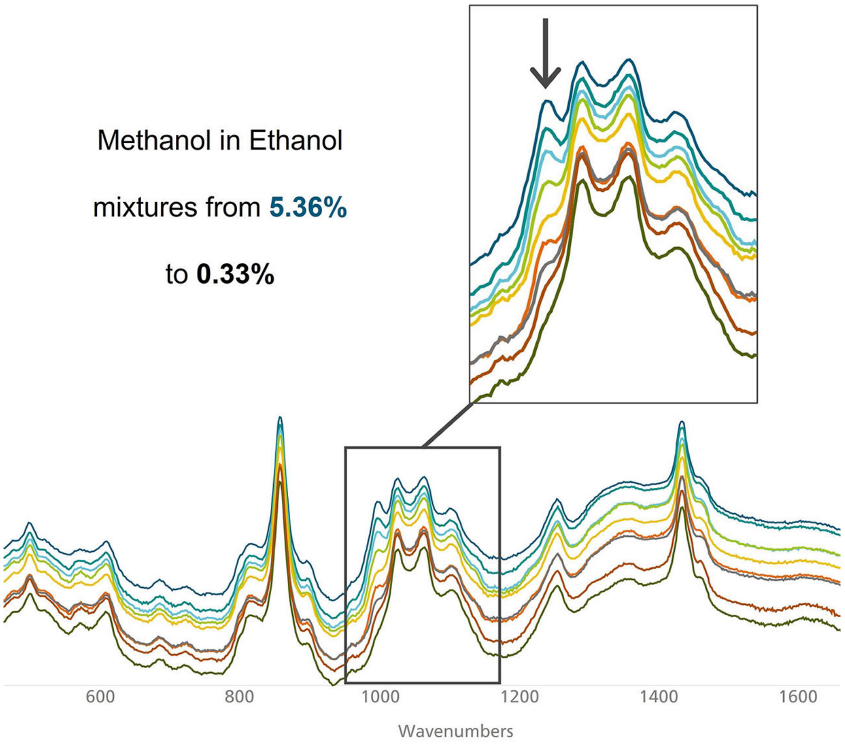

Figure 2. Raman spectra of methanol-laced rum with varying concentrations of methanol. Inlay: The peak noted with the arrow grows with increasing concentration of methanol.

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.

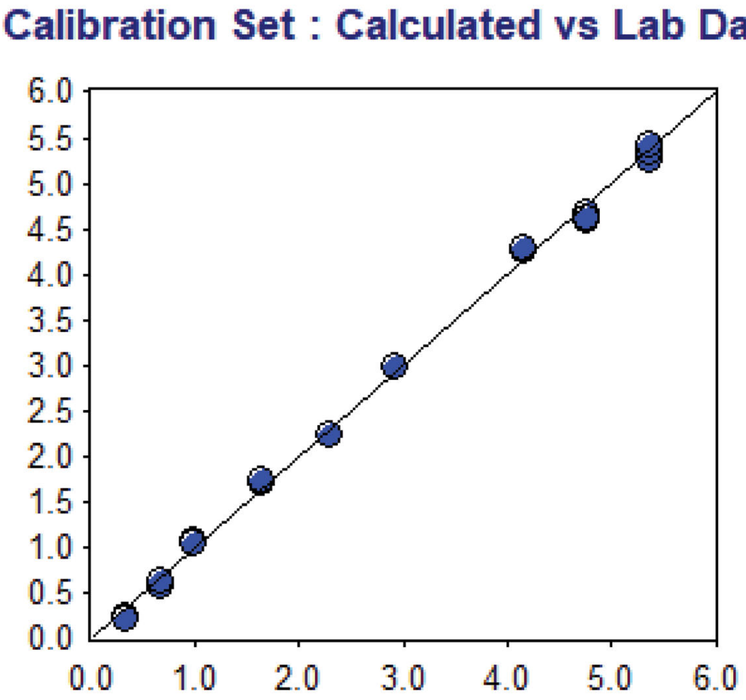

Figure 3. PLS regression model to predict the amount of methanol in rum.

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
R2	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.

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CONFIGURATION

i-Raman Plus 785S

i-Raman® Plus 785S は、弊社の革新的かつインテリシェントなスヘクトロメーターテクノロシーを備えた i-Raman ホータフル型ラマンスヘクトロメーターの受賞歴のあるシリースの構成要素てす。このホータフル型ラマンスヘクトロメーターは、高い量子効率、TE 冷却、ならひに高いタイナミックレンシを備えた CCD アレイ検出器を用い、積分時間てさえ最長30分、低ノイスの傑出した性能を提供します。こうして、弱いラマン信号も測定することかてきます。

i-Raman Plus 785S は、65 cm^{-1} から 3350 cm^{-1} までの測定を可能にするコンフィクレーションを有する幅広いスヘクトル範囲と高分解能のユニークな組み合わせを特徴としています。 システムの小さな底面、軽量構造、そして低消費電力により、とこてもラマン分析を研究レヘルて実施することかてきます。i-Raman Plus には、サンフル採取を簡単にする光ファイハーフローフか装備されており、キュヘットホルター、ヒテオマイクロスコーフ、フローフホルター付き XYZ スライトテーフル、ならひに弊社独自の多変量解析ソフトウェア BWIQ®および同定ソフトウェア BWID®と共に使用することかてきます。i-Raman Plus により、品質分析および定量分析のための高精度のラマンソリューションを常に使用することかてきます。

9.5mmBAC100/BAC10215 mm (15 mm) 6

Vision 4.1

Vision B&W TekMetrohm XDSNIRSVision