Application Note AN-RS-056

Quantification of methanol in contaminated spirits

Protecting consumers from contaminated beverages

An alarming global trend highlights the serious harm that can result from ingesting illegal, improperly distilled alcohol. Home-distilled spirits prepared using industrial solvents (i.e., wood alcohol) and presented as legitimate alcoholic beverages often contain methanol. Methanol causes blindness and can lead to death when ingested. This has led to fatal consequences around the world [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 various screening tools, the Czech Republic adopted Raman spectroscopy as the method of choice for identifying and quantifying methanol in contaminated spirits.

This Application Note demonstrates how Raman spectroscopy can be employed as an efficient and rapid screening method for samples of rum contaminated with methanol.

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.

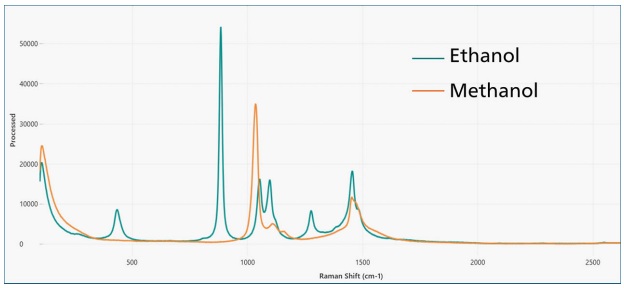

Figure 1. Raman spectra of pure ethanol (green) and pure methanol (orange).

The ability of Raman spectrometers to measure through containers and the lack of sensitivity to water make them better suited to measure methanol in beverage samples. 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 for testing. In the lab, the i-Raman NxG and SpecSuite software elevate the detection capabilities of Raman spectroscopy by adding the ability to quantify adulterants. (Figure 2)

Figure 2. The i-Raman NxG combined with SpecSuite software is ideally suited for rapid detection and quantitative screening of dangerous adulterants in alcoholic beverages.

EXPERIMENT

This example study measures commercially available coconut rum that is spiked with methanol in concentrations between 0.33% and 5.36%. The i-Raman NxG 785H with a fiber-optic probe is used to collect Raman spectra of the mixtures (Figure 3). Table 1 lists the relevant equipment and instrument settings used for this application study.

The peak at around 1000 cm^{-1} (highlighted by the inlay of Figure 3) visibly increases with increasing concentration of methanol, becoming significant at approximately 1%.

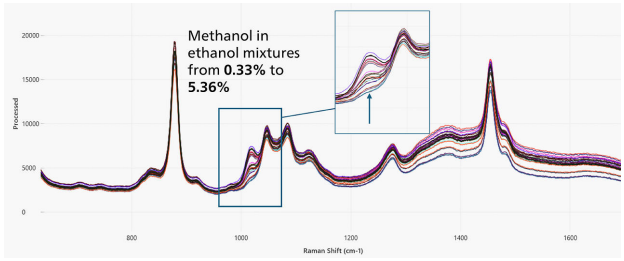

Figure 3. Raman spectra of methanol-laced rum with varying concentrations of methanol. Inlay: Peak intensities reflect changes in the methanol:ethanol ratio.

Table 1. Experimental parameters.

Equipment	Acquisition settings	
i-Raman NxG 785H	Laser Power	100
Vial holder	Int. time	1 s
SpecSuite Software	Average	1

This data is analyzed with SpecSuite software, and a partial least squares (PLS) regression model is developed on normalized data. The two-factor model developed over the range from 980–1040 cm^{-1} gives the calibration curve shown in Figure 4, which has an error of cross-validation (SECV) of 0.0794 (Table 2). The R^2 value of 0.9980 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.

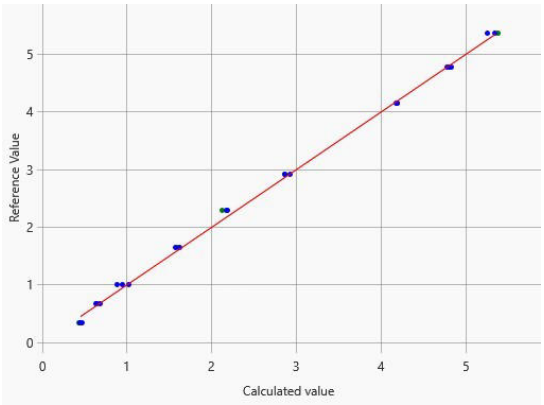

Figure 4. PLS regression model to predict the amount of methanol in rum.

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

Parameter	Value
Spectral processing	Mean centering Savitzky-Golay derivative
R^2	0.9980
SEC	0.0681
SECV	0.0794

CONCLUSION

These results validate that Raman spectroscopy can be used for rapid, quantitative screening of dangerous adulterants in alcoholic beverages. 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.
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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 NxG 785H

i-Raman NxG 785H est idéal pour le contrôle de la qualité de routine et le contrôle des processus, notamment lorsque la vitesse, la stabilité et la fiabilité sont essentielles. Il offre une combinaison équilibrée de performance et d'efficacité pour mesurer la dispersion Raman de 100 à 2 800 cm-1.

Concu pour prendre en charge un débit de signal élevé, ce système flexible est idéal pour contrôler les réactions chimiques et polymères, optimiser les processus et réaliser des tests d'uniformité de teneur des comprimés pharmaceutiques. L'i-Raman NxG 785H s'adapte facilement aux mesures transparentes, même à travers des bidons opaques, ce qui renforce sa polyvalence.

i-Raman NxG 785H est la solution de référence pour les équipes à la recherche d'une analyse Raman fiable dans des environnements opérationnels difficiles.

Découvrez pourquoi l'i-Raman NxG est la solution idéale pour maitriser vos mesures de contrôle de la qualité :

- Les spectromètres à haute sensibilité fournissent des résultats en quelques secondes et peuvent détecter les signaux Raman les plus faibles.
- La sonde à fibres optiques flexible est compatible avec une large gamme d'accessoires, y compris un support de flacon, un support de cuve, une sonde de transflexion et un adaptateur transparent.
- Le logiciel puissant SpecSuite facilite la collecte des données Raman, en plus de la création de modèles quantitatifs, de l'identification à l'aide de bibliothèques spectrales et de l'analyse de routine.
- Compact et empilable pour un gain d'espace conséquent sur le banc.

Accessoire support de flacon

Accessoire support de flacon utilisé avec des sondes Raman de qualité laboratoire dont le diamètre de la tige est de 9,5 mm. Compatible avec des flacons de 15 mm de diamètre. Pack de 6 flacons en verre borosilicaté de 15 mm inclus.