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.

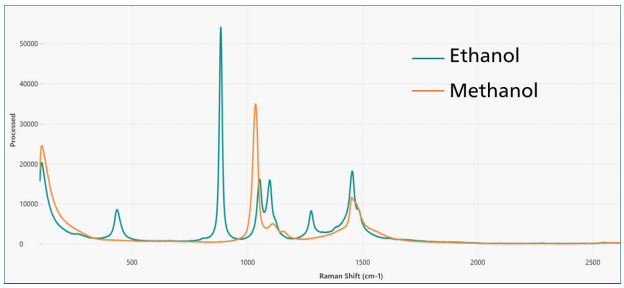

Figure 1. Raman spectra of pure ethanol (green) and pure methanol (orange).

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%.

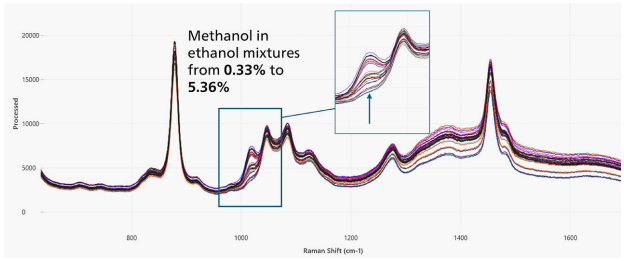

Figure 3. Raman spectra of methanol-laced rum with varying concentrations of methanol. Inlay: Peak intensities reflect changes in the methanol:ethanol ratio.

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.

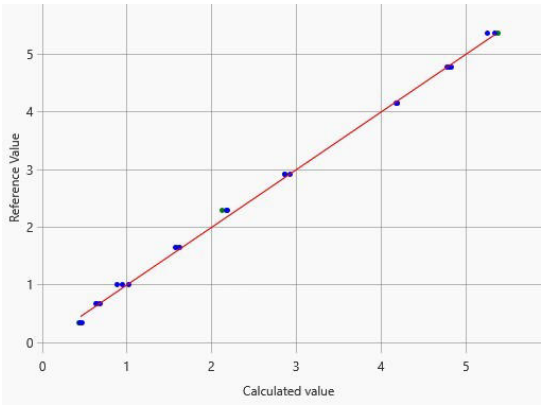

Figure 4. PLS regression model to predict the amount of methanol in rum.

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.
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 Deutschland
In den Birken 3
70794 Filderstadt

info@metrohm.de

CONFIGURATION

i-Raman NxG 785H

Das i-Raman NxG 785H ist ideal für die routinemässige Qualitätskontrolle und Prozessüberwachung, insbesondere dort, wo Geschwindigkeit, Stabilität und Zuverlässigkeit von entscheidender Bedeutung sind. Es bietet eine ausgewogene Kombination aus Leistung und Effizienz zur Messung der Raman-Streuung von 100 - 2800 cm-1.

Dieses flexible System ist auf einen hohen Signaldurchsatz ausgelegt und eignet sich ideal für die Überwachung von chemischen und Polymerreaktionen, die Prozessoptimierung und die Prüfung der Gleichförmigkeit des Wirkstoffgehalts pharmazeutischer Tabletten. Das i-Raman NxG 785H kann mit Leichtigkeit für Messungen durch (selbst undurchsichtige) Verpackungen angepasst werden, was es umso vielseitiger macht.

Das i-Raman NxG 785H ist die erste Wahl für Teams, die zuverlässige Raman-Analysen in anspruchsvollen Arbeitsumgebungen benötigen.

Erfahren Sie, warum das i-Raman NxG perfekt geeignet ist, um die Kontrolle über Ihre Qualitätskontrollmessungen zu übernehmen:

- Hochempfindliche Spektrometer liefern Resultate in Sekundenschnelle und können selbst die schwächsten Raman-Signale erfassen.
- Flexible Lichtleitersonde, die mit einer breiten Palette an Zubehör kompatibel ist, einschliesslich Vialhalter, Küvettenhalter, Transflexionssonde und See-Through-Adapter.
- Leistungsstarke SpecSuite Software für die einfache Erfassung von Raman-Daten sowie die quantitative Modellentwicklung, die Identifizierung mit Spektrenbibliotheken und die Routineanalytik.

Kompakt und stapelbar für Platzersparnis auf der Arbeitsfläche.

Vialhalterzubehör

Vialhalterzubehör zur Verwendung mit Raman-Sonden in Laborqualität mit einem Schaftdurchmesser von 9.5 mm. Kompatibel mit Vials mit einem Durchmesser von 15 mm. 6er Pack mit 15-mm-Vials aus Borosilikatglas ist im Lieferumfang enthalten.