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**.

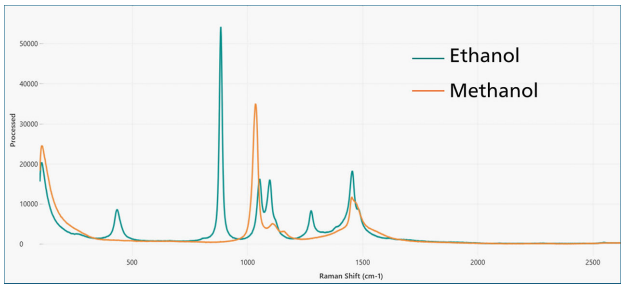

Figure 1. Raman spectra of pure ethanol (green) and pure methanol (orange).

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%.

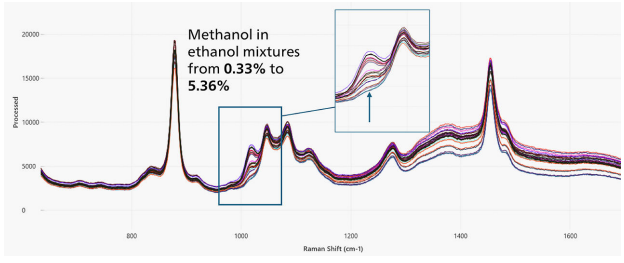

Figure 3. Raman spectra of methanol-laced rum with varying concentrations of methanol. Inlay: Peak intensities reflect changes in the methanol:ethanol ratio.

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.

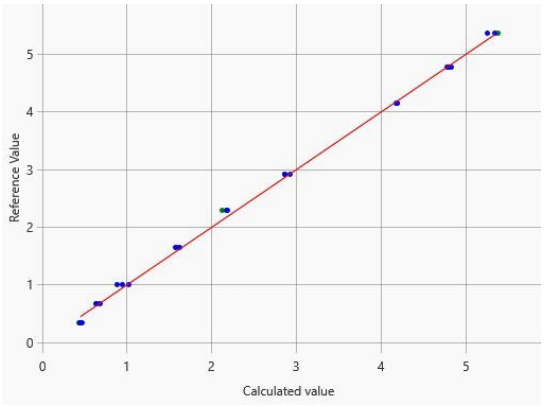

Figure 4. PLS regression model to predict the amount of methanol in rum.

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.

CONTACT

メトロームジャパン株式会社
143-0006 東京都大田区平和島6-1-1
null 東京流通センター アネックス9階
metrohm.jp@metrohm.jp

CONFIGURATION

i-Raman NxG 785H

i-Raman NxG 785Hは、特に速度、安定性、信頼性が重要な日常的な品質コントロールやプロセスのモニタリングに最適です。100~2800 cm-1のラマン散乱を測定するためのパフォーマンスと効率のバランスの取れた組み合わせを提供します。

高信号スループットに対応するように設計されたこの柔軟なシステムは、化学反応やポリマー反応のモニタリング、プロセスの最適化、医薬品錠剤の含有量均一性テストの実行に最適です。i-Raman NxG 785Hは、不透明なキャニスター越しでも簡単に透過寸法ができるため、汎用性が高まります。

i-Raman NxG 785Hは、厳しい稼働環境で信頼性の高いラマン分析を求めるチームに最適なソリューションです。

i-Raman NxGが品質コントロール寸法の制御に最適な方法である理由をご覧ください:

- 高感度スペクトロメーターは数秒で結果を提供し、最も微弱なラマン信号も検出可能です
- バイアルホルダー、キュベットホルダー、浸漬プローブ、透過アダプターなど、さまざまな付属品と互換性のある柔軟なグラスファイバープローブです
- 強力なSpecSuiteソフトウェアは、定量モデルの構築、スペクトルライブラリによる識別、日常的な分析に加えて、ラマンデータの収集を容易にします

コンパクトで積み重ね可能なので貴重なベンチスペースを節約できます。

柄の直径が 9.5 mm のラボグレードラマンプローブと使用するためのバイアルホルダー付属品です。直径 15 mm のバイアルと互換性があります。15 mm のホウケイ酸ガラスバイアル 6 個入りパックも含まれます。