Application Note AN-RS-041

Discriminating counterfeit beer with Raman spectroscopy and PCA

Protecting consumers from imitation beverages

Beer is a popular alcoholic beverage brewed from malted grain, hops, yeast, and flavorings. Thousands of international and local breweries craft high-quality beer for global enjoyment. However, in some regions criminals counterfeit beers by simply replacing the caps and labels of less expensive products with more lucrative brands, or by filling empty bottles with unregulated mixtures. In 2022 alone, national customs and police authorities in 19 EU countries seized nearly 14.8 million liters of counterfeit alcoholic beverages, including wine and beer [1].

Currently, there are no simple tests to identify counterfeit beer. This Application Note demonstrates the ability of i-Raman EX, the B&W Tek Laboratory Raman instrument with a 1064 nm laser, with principal component analysis (PCA) to distinguish between beers from different brewers and from a mixture of beers.

INTRODUCTION

In the field of food science, Raman spectroscopy is being evaluated for quality control purposes. It is used for identification and quantification of components in a mixture and for the authentication of samples.
Beer is a complex mixture of over 400 different compounds from natural product ingredients which are subjected to the fermentation process. The Raman spectrum of beer is sensitive to these unique attributes and closely reflects the recipe and brewing process. Even small spectral changes are detectable and can be used to identify counterfeit beers and trace adulteration back to the perpetrator.

EXPERIMENT

Only lagers were studied for this application. Working with different beer styles (e.g., stout vs pilsener) would show markedly increased variation in their Raman spectra.
Raman spectra were collected by immersing a probe into liquid decanted from three 12 oz. (355 mL) cans each of four popular lager brands. One «lite» lager, with a 30% lower calorie content than the other brands, was sampled. Alcohol content by volume is reported as % ABV by each manufacturer. Experimental parameters are summarized in Table 1.

Table 1. Experimental parameters and sample information.

Instrument	Acquisition
i-Raman EX System	Laser Power 330 mW
RIS100-SS Probe	Int. time 10 s
BWSpec and BWIQ Software	Average 1
Sample	kcal / % ABV
Lager-H	150 / 5.0%
Lager-B	145 / 5.0%
Lager-C	149 / 4.7%
Lager-M	96 / 4.2%

RAMAN SPECTRA OF LAGER

The Raman spectrum of beer (Figure 1) is simple compared to complex chemical products like acetaminophen, because beer generally contains around 96% water (a weak Raman scatterer). The rest is ethanol, a simple organic molecule, and trace amounts of other substances.

The Raman spectrum of lager is dominated by ethanol peaks at approximately 880, 1050, 1090, 1280, and 1450 cm^{-1}. While these spectra are visually quite similar, the regions of relatively high variance highlighted in Figure 1 reflect the different compositions of lagers.

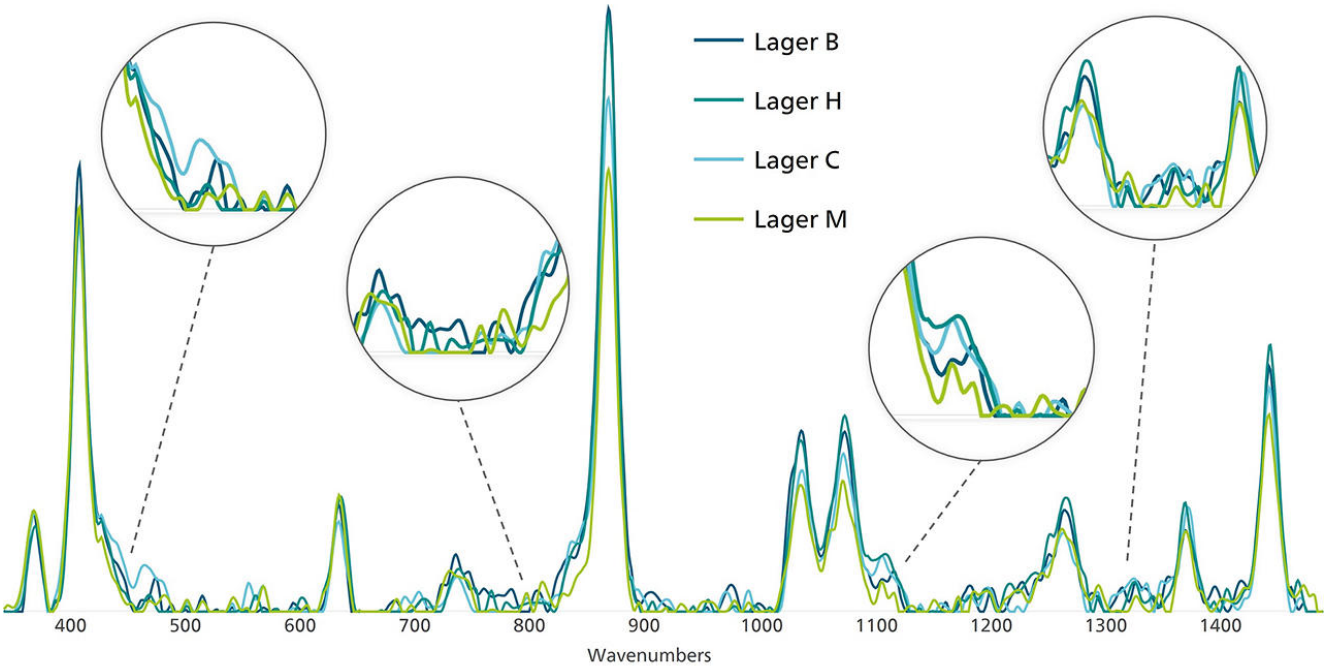

Figure 1. Raman spectra of four popular lager brands, highlighting four areas of high spectral variance.

The intensity of the ethanol C-C stretch at approximately 880 cm^{-1} represents the different % ABV of lagers well (Figure 2). This is a valuable reference point for discriminating between alcoholic beverages.

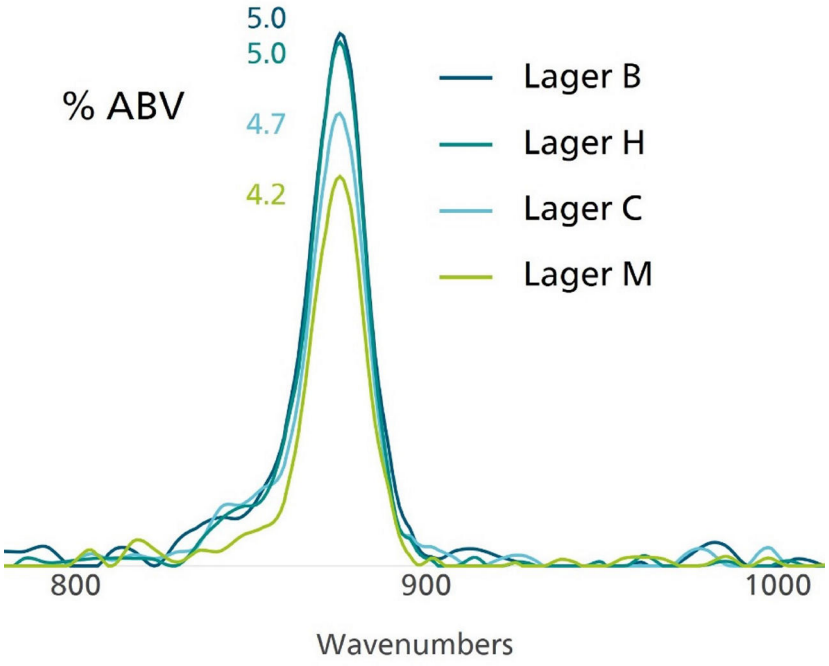

Figure 2. C-C stretching band of different lagers. % ABV corresponds to nutritional label values.

IDENTIFICATION OF LAGER BRANDS

Principal component analysis (PCA) can be used to further distinguish each sample. Figure 3 shows a PCA plot of each sample and a mixture of two different brands (H1+M1, shown in orange). Despite some slight overlap, each brand appears as a distinct group.

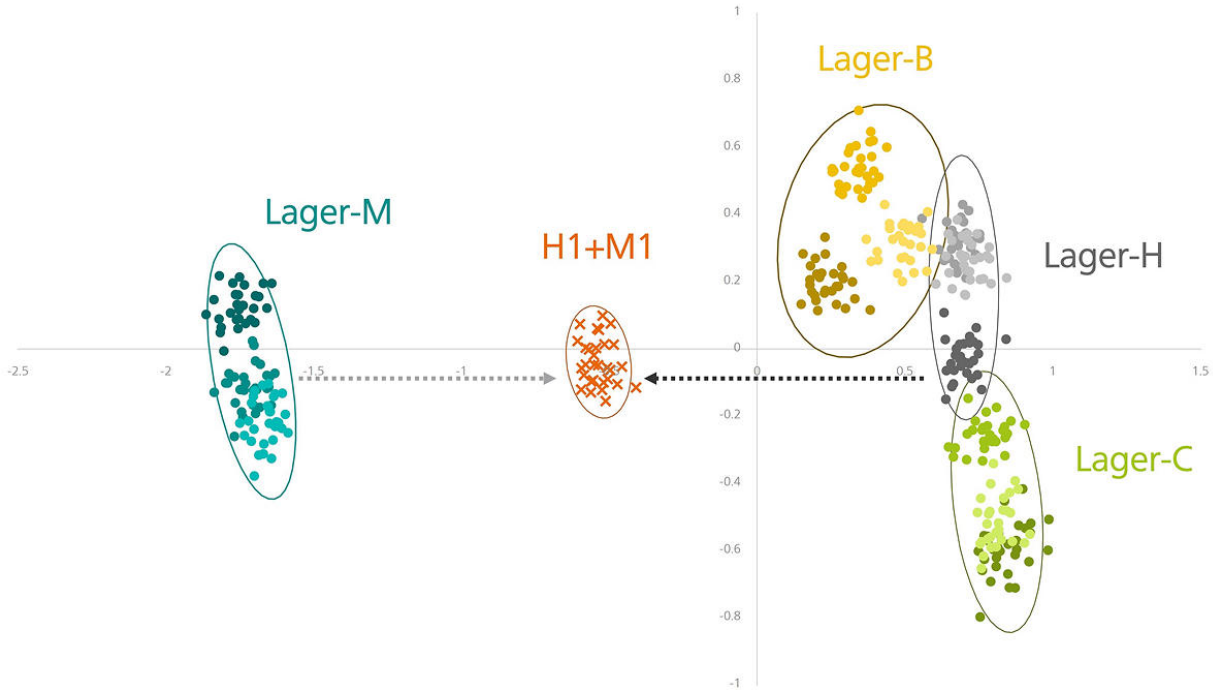

Figure 3. PCA plot of different lagers and mixture of lagers (confidence ellipse 0.95).

Note that Lager-M is easily distinguished from other brands. Lager-M was the only «American-Light Lager» with lower calories and alcohol content (96 kcal, 4.2% ABV) compared to the other brands (145–150 kcal, 4.6–5.0%).

H1+M1, which is a 1:1 mixture of Lager-H and Lager-M, appears as a separate cluster between the two, and demonstrates the ability of Raman and PCA to easily discern adulterated products.

FIELD TEST NOTE

- 1064 nm excitation generates reliable data despite strong fluorescence from natural products found in beer.
- Constant sampling conditions generate the most reliable data. For example, temperature differences could artificially increase spectral variation.
- The sapphire ball probe used here provides fewer nucleation sites for fewer CO_2 bubbles, which could interfere with measurements.
- Integration times of 10 seconds and longer provide the most reliable data.

CONCLUSION

A B&W Tek i-Raman EX system configured with an immersion probe easily distinguished lagers from different breweries and a mixture of lagers, demonstrating its ability to authenticate samples and detect counterfeit products. Even a small amount of adulteration can be identified with detailed PCA analysis of the Raman spectrum of beer.

REFERENCE

1. *14.8 million litres alcoholic drinks seized across Europe*. https://anti-fraud.ec.europa.eu/media-corner/news/148-million-litres-alcoholic-drinks-seized-across-europe-2022-11-17_en (accessed 2023-03-21).

CONTACT

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CONFIGURATION

i-Raman EX Portable Raman Spectrometer

The i-Raman® EX is part of our award-winning series of i-Raman portable Raman spectrometers with our patented CleanLaze® laser with 1,064 nm laser excitation. Using a high-sensitivity InGaAs array detector with deep TE cooling, high dynamic range, and a high throughput spectrograph design, this portable Raman spectrometer delivers a high signal-to-noise ratio without inducing autofluorescence, making it possible to measure a wide range of natural products, biological samples (such as cell cultures), and colored samples.

The i-Raman EX provides a spectral coverage range from 100 cm-1 to 2,500 cm-1, enabling you to measure across the entire fingerprint region. The system's small footprint, lightweight design, and low power consumption ensure research-grade Raman analysis capabilities at any location. The i-Raman EX comes equipped with a high throughput fiber probe and an XYZ-positioning-stage with probe holder. It can be used with a range of sampling accessories to facilitate measurements on a wide range of different samples. For expanded analysis capabilities, it can be used with our proprietary Vision software as well as BWIQ® multivariate analysis software and BWID® identification software. With the i-Raman EX, you always have a high precision Raman solution for qualitative and quantitative analysis without fluorescence.

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