Characterization of Some Local Ghanaian Herbal Alcoholic Beverages (Bitters) Using Raman Spectroscopy

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ABSTRACT

In Ghana, local alcoholic bitters are widely consumed for their perceived medicinal properties, yet there is limited scientific research on their chemical composition, especially regarding ethanol, the primary alcohol ingredient. This study uses Raman spectroscopy, a non-destructive technique, to analyze the ethanol content in 13 popular bitters brands from Kumasi. Spectra were obtained using a portable Raman spectrometer. Principal Component Analysis (PCA) identified fluorescence and ethanol as key factors in spectral differences, revealing diversity among the samples. Partial Least Squares Regression (PLSR) confirmed consistent ethanol levels across brands, while Leave-One-Out Cross-Validation (LOOCV) achieved 100% classification accuracy. The study demonstrates the effectiveness of Raman spectroscopy in ensuring the quality, consistency, and regulatory compliance of Ghanaian herbal bitters.

INTRODUCTION

Ghanaian herbal bitters are valued for their perceived health benefits and cultural significance [1,2], yet limited research exists on their characterization, particularly regarding ethanol content and specific herbal compounds. Each brand's distinctiveness arises from unique blends of ingredients, but current analytical methods fail to capture this complexity. A more precise approach is needed to analyse and differentiate these products, essential for quality control and preserving brand identity in a competitive market. This research aims to establish a framework for accurately characterizing herbal bitters.

PROBLEM STATEMENT

Despite the perceived health benefits and cultural significance of Ghanaian bitters, limited research exists on accurately characterizing and differentiating them. This study aims to address this gap by using Raman spectroscopy combined with statistical methods, including PCA, LOOCV, and PLSR, to effectively analyze and distinguish these bitters.

OBJECTIVES

Main:

To characterize local Ghanaian bitters using Raman spectroscopy.

Specific:

- To obtain samples of commonly consumed bitters from different manufacturers.
- To perform Raman spectroscopy on the samples to obtain spectra.
- To analyse the Raman spectra to characterize the bitters, determine differences between products sold by different manufacturers, and verify the consistency of the stated alcoholic content with the actual ABV.

METHODOLOGY

Materials

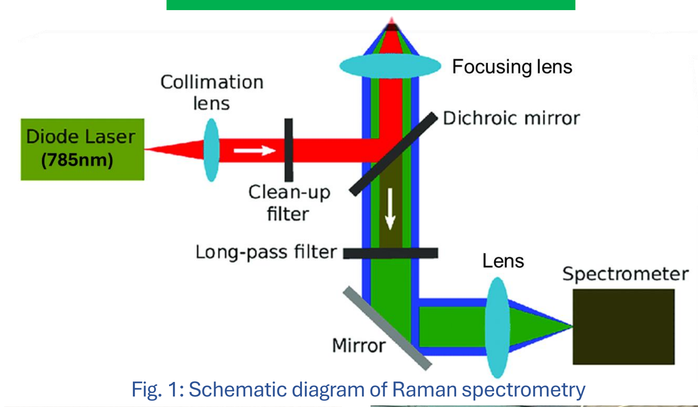


Fig. 1: Schematic diagram of Raman spectrometry

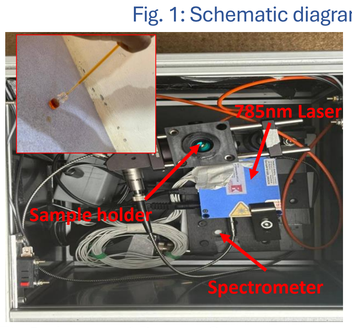


Fig 2.: Image of Raman Spectrometer setup including the laptop and the portable spectrometer.

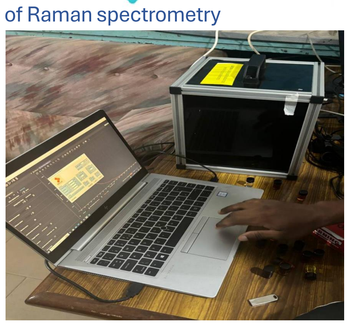


Fig. 3: Internal components of the Raman box. Inset: Image of a borosilicate glass vial being filled with alcohol sample.

Liquor Samples Used

Joy Dadi Bitters (JD); Monarch Ginseng Bitters (MG); Lawson De-Ray Bitters (LD); Obuase Gringo Bitters (OG); Origin Bitters (OB); Walata Walasa Bitters (WW); Adonko Two Fingers (2F); Adonko Bitters (AB); Monarch Ginseng Plus 1 Bitters (MGP); Mandingo Bitters (MB); Obuase Bitters (OBB); Herb Afrik (HA); Alomo Bitters (ALM); 100% Ethanol (ETH);

Fig.4: Image of acquired local alcoholic beverages

METHOD

- **Sample Collection:**

Local alcoholic bitters were collected from various pubs and drinking spots around Kumasi. The selected beverages include the 13 different samples listed under Liquor Samples used.

- **Sample Preparation:**

5 ml of each sample was collected using droppers into separate borosilicate glass vials as illustrated in fig.3. Each vial was labelled from one to thirteen, with the fourteenth vial labelled "Eth" for the pure ethanol sample.

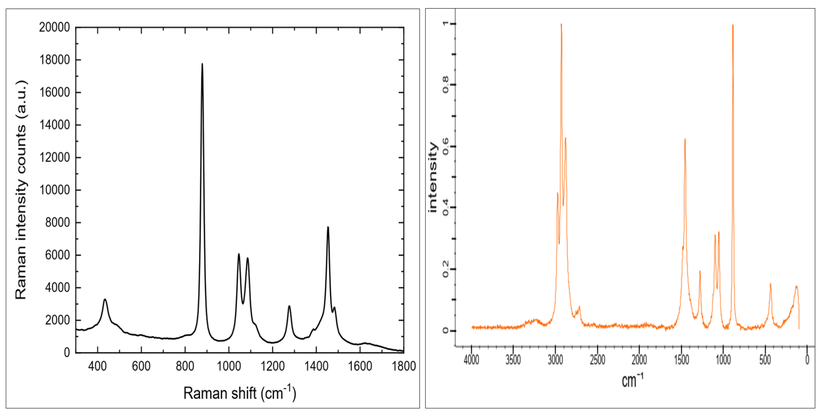
- **Data Acquisition:**

Spectral readings for each sample were obtained using OceanView software and saved in an Excel workbook. Ten different spectral readings were recorded for each alcohol sample.

- **Analysis of Spectral Data:**

Spectra were pre-processed in SpectraGryph to select wavenumber range of interest. Data analysis was performed using Partial Least Squares Regression, Leave-One-Out Cross-Validation, and Principal Component Analysis. The spectra of pure ethanol and the average spectra for each sample were plotted using Origin software and compared to public spectra libraries. Spectragryph was used for background subtraction on the average spectra with the least fluorescence, demonstrating the presence of Raman peaks for ethanol in the bitters.

RESULTS AND DISCUSSION



(a) (b)

Fig. 5: Comparison of Raman Spectra of Pure Ethanol as measured with that which is stored in SpectraBase [3]

Figure 5 (a) shows the measured Raman spectrum of 100% ethanol using a portable Raman spectrometer, highlighting significant peaks. Figure 5 (b) presents the Raman spectrum of 100% ethanol from the SpectraBase database for comparison. Both spectra display peaks at the same Raman shifts, validating the accuracy of our measurements.

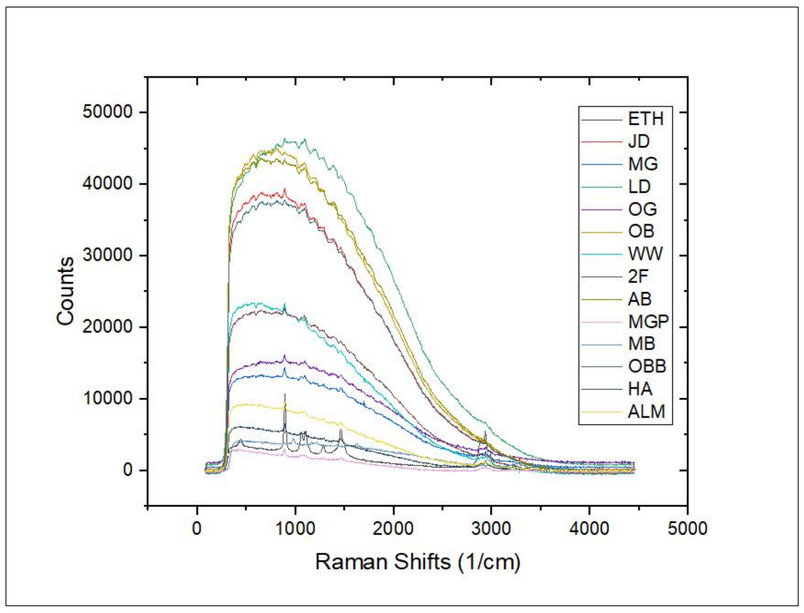


Fig. 6: Comparative Raman Spectra of the 13 Bitters samples and the measured ethanol

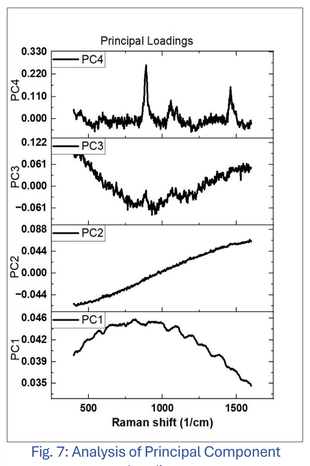


Fig. 7: Analysis of Principal Component Loadings

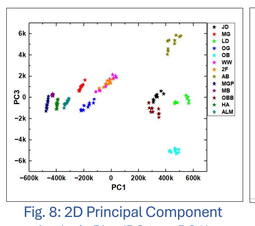


Fig. 8: 2D Principal Component Analysis Plot (PC1 vs. PC3)

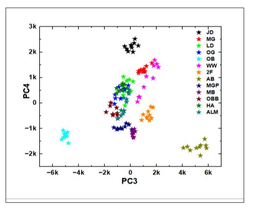


Fig. 9: 2D Principal Component Analysis Plot (PC3 vs. PC4)

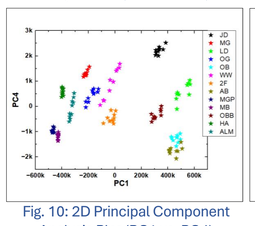


Fig. 10: 2D Principal Component Analysis Plot (PC1 vs. PC4)

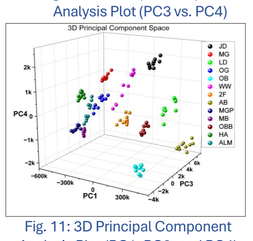


Fig. 11: 3D Principal Component Analysis Plot (PC1, PC3, and PC4)

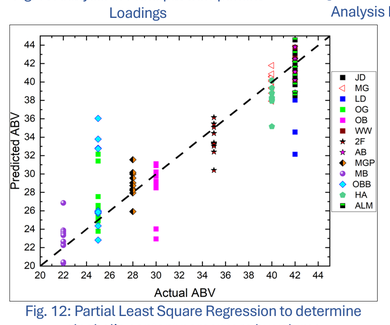


Fig. 12: Partial Least Square Regression to determine alcoholic content percentage by volume

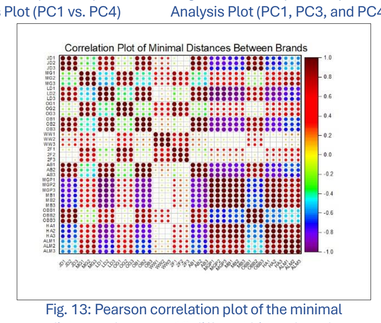


Fig. 13: Pearson correlation plot of the minimal distances between 13 different bitters brands

Table 1: Leave-One-Out Cross-Validation (LOOCV) Classification Results.

Actual/Predicted	JD	MG	LD	OG	OB	WW	2F	AB	MGP	MB	OBB	HA	ALM	Unknown
JD	10	0	0	0	0	0	0	0	0	0	0	0	0	0
MG	0	10	0	0	0	0	0	0	0	0	0	0	0	0
LD	0	0	10	0	0	0	0	0	0	0	0	0	0	0
OG	0	0	0	10	0	0	0	0	0	0	0	0	0	0
OB	0	0	0	0	10	0	0	0	0	0	0	0	0	0
WW	0	0	0	0	0	10	0	0	0	0	0	0	0	0
2F	0	0	0	0	0	0	10	0	0	0	0	0	0	0
AB	0	0	0	0	0	0	0	10	0	0	0	0	0	0
MGP	0	0	0	0	0	0	0	0	10	0	0	0	0	0
MB	0	0	0	0	0	0	0	0	0	10	0	0	0	0
OBB	0	0	0	0	0	0	0	0	0	0	10	0	0	0
HA	0	0	0	0	0	0	0	0	0	0	0	10	0	0
ALM	0	0	0	0	0	0	0	0	0	0	0	0	10	0

CONCLUSION

This study effectively characterized 13 popular Ghanaian herbal alcoholic beverages, known as bitters, using Raman spectroscopy. The analysis provided insight into the composition and quality of the samples, revealing distinct features and patterns that confirmed the variations among different manufacturers reflect the uniqueness of each product. This demonstrates that manufacturers are not simply rebranding the same product under different names but are genuinely offering diverse formulations. The assessment of alcoholic content (ABV) further confirmed that the actual ABV matched the stated values, ensuring regulatory compliance and consumer safety. While this research underscores the effectiveness of Raman spectroscopy in characterizing bitters, it also highlights the authenticity of these products.

Recommendation: Future research should

- Expand the sample size to better capture the diversity of bitters available in the market.
- Check for possible lacing of the bitters samples with methanol using Raman Spectroscopy.

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