Identification of counterfeit vodka using handheld Raman spectroscopy

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Introduction

Counterfeit alcohol represents a public health problem that often results in hazardous consequences. For instance, the presence of methanol in elevated concentrations causes blindness to the consumer. Handheld Raman spectroscopy offers a rapid and non-destructive technique for the identification of counterfeit alcohol.

Objective

The objective of this work was to identify counterfeit vodka using handheld Raman spectroscopy.

Experimental

Materials

Counterfeit vodkas were supplied by the United Kingdom Food Standards Agency. A total of eight authentic vodkas and 31 counterfeit vodkas were measured as received.

Method

The samples were transferred into 4 ml glass vials and measured through the glass using the Rigaku Xantus-1 handheld Raman spectrometer equipped with charge-coupled device detector (CCD) and 785 nm laser excitation wavelength.

Spectral Treatment

Data were exported to Microsoft Excel and SPSS v20. Data analysis was performed using descriptive statistics, analysis of variance (ANOVA) and principal component analysis (PCA).

Results & Discussion

Reference analysis

Reference analysis of the counterfeit vodkas was obtained from Sheffield Trading Standards. The mean alcohol content of counterfeit vodka from the analysis was 36.4% ABV (min. 28.5% ABV, max. 51.2% ABV). This was lower than the label claim for these samples (37.5 – 40% ABV).

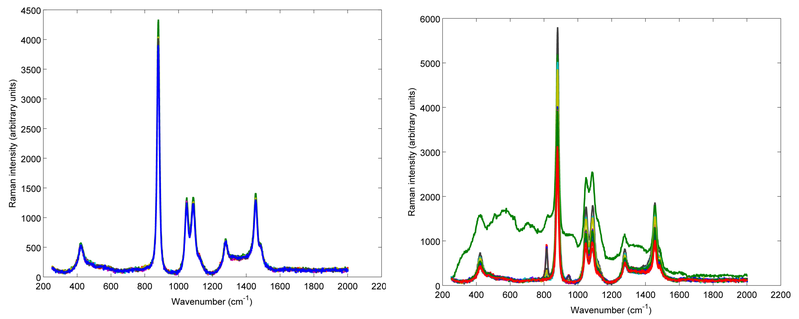

Figure 1. Raman spectra of authentic and counterfeit vodka samples.

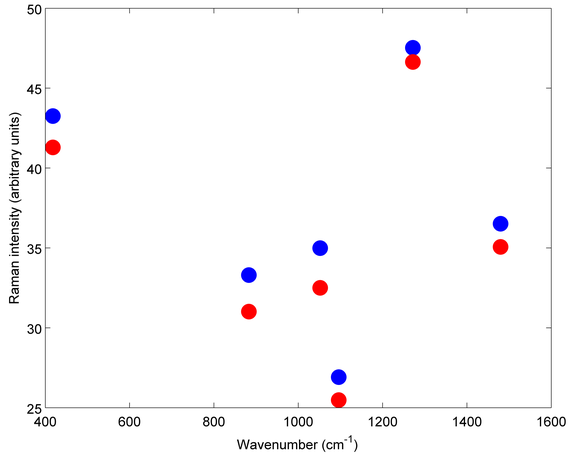

Figure 2. Average alcohol content of authentic (blue) and counterfeit (red) calculated from the six principal ethanol peaks at 418, 883, 1052, 1096, 1272 and 1450 cm^{-1} respectively.

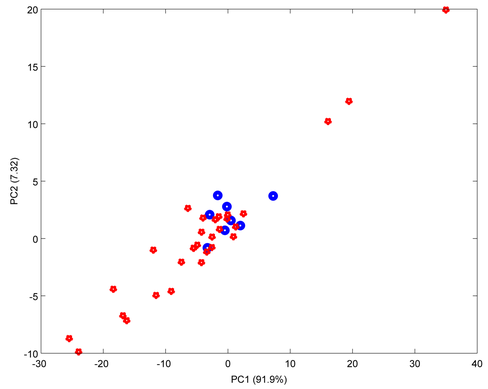

Figure 3. PCA scores plot of authentic (blue) and counterfeit (red) vodkas applied to the peak ratios with respect to ethanol.

Spectral comparison

The Raman spectra of the authentic and counterfeit vodkas (Figure 1) showed the presence of ethanol in varying concentrations. The principal ethanol peaks were selected for analysis at 418, 883, 1052, 1096, 1272 and 1450 cm^{-1}. The counterfeit vodkas displayed two additional peaks at 813 and 937 cm^{-1}.

Comparison of counterfeit and authentic vodka samples

Shapiro-Wilk normality tests illustrated that both authentic and counterfeit vodka batches followed the normal distribution. However, there was a difference in ethanol content between the authentic and counterfeit vodkas. The counterfeit vodkas showed less ethanol content than the authentic vodkas (Figure 4). When PCA was applied to the authentic and counterfeit vodka spectra, it showed that some of the counterfeit vodkas had an alcoholic content similar to the authentic vodkas (Figure 3). However, when ANOVA was applied, significant difference was observed between the counterfeit vodkas with a p value less than 0.05 ($p = 6x10^{-6}$). However, high similarity among the authentic vodkas was encountered ($p = 0.98$).

Conclusion

Handheld Raman spectroscopy offered a rapid and non-destructive technique for identification of counterfeit vodka. The counterfeit vodkas showed the presence of ethanol but with significant difference in the ethanol content of individual batches.

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