

# Comparison of non-invasive NIR and Raman spectrometries for determination of alcohol content of spirits

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## Abstract

The suitability of non-invasive NIR and Raman spectrometries for determination of % ethanol content has been investigated. Samples of whisky, vodka and sugary alcoholic drinks were analysed in 200 mL (flat) and 700 mL (round) glass bottles. The NIR spectrometer used double transmission measurements and was limited mainly to analysis of the signal produced at about  $10,000\text{ cm}^{-1}$  by water and ethanol in the samples. The Raman measurements, produced using a 785 nm laser, were based on a sharp signal from ethanol at  $880\text{ cm}^{-1}$ . A multivariate calibration model, based on a combined PCA–PLS algorithm, was required for analysis by NIR spectrometry, whereas a univariate calibration model was suitable for Raman spectrometry. Both techniques were limited to measurements in clear glass bottles as strong absorption/fluorescence occurred with coloured glass bottles. Bottle-to-bottle variations contributed the largest uncertainty to the measurements obtained for a 20% (v/v) ethanol solution in flat bottles: 2.3% R.S.D. for NIR spectrometry and 2.2% R.S.D. for Raman spectrometry. For 700 mL round bottles, which have stricter manufacturing tolerances on glass thickness, the bottle-to-bottle variability for Raman spectrometry was 1.4% R.S.D. When spirit samples with ethanol concentrations in the range 19.9–61.7% (v/v) were analysed, the precision (average R.S.D.) was 0.4 and 0.5% for NIR (flat bottles) and Raman (round bottles) spectrometries, respectively, and the average accuracy was 2.1 and 2.9%, respectively. When a calibration model constructed from NIR data acquired on 1 day was applied to data sets collected over a 15-day period, the average error was 3.9%.

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## 1. Introduction

In the UK, Customs and Excise require the alcohol content of beverages to be determined with an accuracy of  $\pm 0.05\%$  (v/v). Most of the methods that are employed currently are based on density measurements. Although such methods are accurate, they possess a number of disadvantages. Usually, density measurements are performed off-line in a centralised analytical laboratory, and hence, there can be a considerable delay before the alcohol content of a sample is reported. For those alcoholic beverages that possess a high dissolved solids content (e.g. sugars), the sample must be distilled to

remove the alcohol prior to performing a density measurement. Off-line density measurements are also destructive in the sense that once a bottle has been opened or a sample has been removed from the process line, it cannot be resealed or returned, respectively.

Spectroscopic techniques offer a faster and simpler method for the determination of alcohol content. Off-line mid infrared (MIR) spectrometry has been used to determine the ethanol content of spirits and a range of beer samples in a micro flow transmission cell [1,2]. Off-line near infrared (NIR) spectrometry has been used to determine the alcohol content of beers [3,4], wines, whiskies, gin, rum and liqueurs [5]. The ethanol content of different types of alcoholic beverages has been determined using off-line NIR measurements, which employed a transmittance immersion probe [6] and a

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quartz cell [7]. In the latter study [7], it was demonstrated that accurate prediction of alcohol content could be obtained between 15 and 35 °C by removal of temperature induced spectral changes using orthogonal signal correction [8] or piecewise direct standardisation [9]. Alcoholic beverages have also been analysed using off-line Raman spectrometry with univariate [10,11] or multivariate [6] calibration models. A stopped-flow NIR system was used for the analysis of beers to provide a greater throughput of samples [12]. For both MIR and NIR spectrometry, the presence of sugars interferes with the ethanol signal. In cases where a separate sugar signal can be isolated, this can be used to correct for the sugar contribution to the ethanol signal [1,2,4,5,12]. Alternatively, different calibration models may be constructed for different types of alcoholic beverages. Partial least squares (PLS) calibration models have been prepared from off-line MIR spectra of wines to determine the concentration of glucose, fructose, glycerol, ethanol and organic acids [13,14]. Recently, a small portable hand-held UV–vis spectrometer was developed for authentication of whisky samples in the field [15]. One of the major advantages of MIR, NIR, UV–vis and Raman spectrometries is that no sample preparation, other than degassing for certain types of samples (e.g. beers [3]), is required. However, use of these techniques either off-line or at-line still requires the removal of a sample from the process line.

On-line determination of alcohol content could involve either insertion of a probe into the process stream (i.e. in-line analysis), analysis through a vessel or pipe wall (i.e. non-invasive analysis) or analysis of a sample in its container on a bottling line. In-line NIR spectrometry has been used to determine the concentration of ethanol in wine samples [16] and alcoholic beverages [17]. In chemical process analysis, ethanol has been determined by in-line Raman spectrometry [18] and non-invasive NIR spectrometry [19]. The non-invasive approach is only possible with optical techniques if the vessel is made of a transparent material or has a suitable window. The concentrations of ethanol, propylene glycol and water in a pharmaceutical oral liquid were determined non-invasively using NIR spectrometry [20] by direct analysis of the sample in amber plastic containers that were placed into the instrument sample compartment.

In this work, NIR and Raman spectrometries have been used non-invasively to analyse different types of spirits contained within glass bottles. The study was conducted to evaluate the techniques for possible use in non-invasive in situ quality assurance in bottling plants. However, prior to conducting any measurements with moving bottles on a bottling line, an investigation involving static bottles was carried out and is reported here. Each technique was assessed in terms of the accuracy and precision with which the alcohol content could be determined and the ease of constructing and maintaining calibration models, particularly when only a small number of samples are available. The influence of the glass bottle on the measurement has also been considered.

## 2. Experimental

### 2.1. Samples

Thirty-two samples were provided by Guinness United Distillers and Vintners (Menstrie, UK). The samples were of three different types; whiskies, vodkas and alcoholic sugary drinks. The alcohol (ethanol) concentrations for the whiskies, vodkas and sugary drinks were in the ranges 20.2–61.7, 19.9–63.3 and 11.4–35.6% (v/v), respectively. The alcohol concentrations, supplied with the samples, were obtained with at-line NIR spectrometry using either of two calibration models that comprised concentration and spectral data for 45 and 69 alcoholic samples of different types, for prediction of whisky and all other types of drinks, respectively.

All samples were supplied in 200 mL clear glass flat bottles, which had a length and width of approximately 70 and 35 mm, respectively. Additional 200 mL clear glass flat bottles and also 700 mL clear and green glass round bottles (diameter of 70 mm) were supplied. These bottles were used with a solution of 20 or 28.8% (v/v) ethanol in distilled water to assess the effects of the diameter and colour of the bottle on the signals obtained, and to investigate the variability of different types of bottles. A solution of 20% (v/v) ethanol was also used to assess the contributions of different factors to the overall analytical variance of the measurements. Samples of whisky, vodka and sugary drinks were analysed as received in the 200 and 700 mL clear glass bottles. For flat bottles, there were two possible measurement orientations; the NIR source or Raman laser could point towards the narrow (35 mm) side of the bottle (i.e. measurement across the widest part of the bottle) or towards the widest (70 mm) side of the bottle (i.e. measurement across the narrowest part of the bottle).

### 2.2. NIR spectrometry

NIR spectra were acquired with a resolution of 6 nm in the 939–1708 nm (10,650–5855 cm<sup>-1</sup>) region using a Zeiss Corona 45 NIR reflectance spectrometer (Clairet Scientific, Northampton, UK) equipped with an InGaAs diode array detector. Two spectrometers of this type (denoted spectrometer 1 and spectrometer 2), which were of identical specification, were used during the course of this work. Spectra were acquired using Aspect Plus Version 1.71 software (Zeiss, Germany), which were then exported into Excel (Microsoft Corporation, USA) as tab-delimited text files. NIR spectra were acquired for 29 samples (samples 1–23 and 27–32; 24–26 were analysed only by Raman). Samples 1–23 were analysed on the same day using spectrometer 1. Samples 27–32 were analysed on 11 different days over a 15-day period using spectrometer 2. All measurements of the whisky, vodka and sugary drinks were conducted in the 200 mL clear glass flat bottles, and across the narrowest (width of 35 mm) part of the bottle. The bottles were placed upright in front of the lens and a white tile was positioned behind the bottle to reflect the

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