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The use of derivatives and chemometrics to interrogate the UV–Visible spectra of gin samples to monitor changes related to storage

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ABSTRACT

Extensive research has been carried out to study and characterise different properties of alcoholic beverages using spectroscopy methods. Although UV-VIS spectroscopy is being used for the routine analysis of several beverages and foods, it has not been extensively used as a high throughput method. The objective of this study was to evaluate the application of derivatives to interrogate the UV-VIS spectra of gin samples to monitor changes related with storage conditions. Samples were analysed using an UV-VIS (200–800 nm) spectrophotometer with 1 cm path length. The raw spectra, second, third and fourth derivatives were used to analyse and interpret the UV-VIS spectra related to storage conditions. The results of this study indicated that the use of derivatives (third and fourth) as pre-process method to the UV-VIS spectra of gin samples allowed for a better identification of wavelengths as well as interpretation of the spectra associated with the different storage conditions.

1. Introduction

Gin is a flavoured alcoholic beverage that generally contains between 40 and 50% alcohol [1–5]. Originated from Holland, gin was initially used by doctors as a formulation for disorders relating to the stomach [1–5]. It was believed that the properties of the juniper berries which were infused in the gin were responsible for this medicinal and health benefits [1–5]. The fashion for gin in the eighteenth century led to a dramatic increase in the production and consumption of gin (approximately 53 L/person/year are consumed in England) and this beverage is among the most widely consumed spirits around the globe after scotch whisky and vodka [6].

The taste of gin is characterized by the botanicals added to it where essential oils and aroma are infused into the gin during this distillation procedure with other ingredients such as Juniper berries (*Juniperus communis*), angelica roots (*Archangelica officinalis*), coriander seeds (*Coriandrum sativum*), orange and lemon peels give gin its characteristic flavour [1–6]. In addition, the use of this flavouring ingredients contributes with other compounds such as phenolic and flavonoids [1–6].

In the past, extensive research has been carried out to study and characterise different properties of alcoholic beverages using methods based in vibrational spectroscopy [7–10]. The routine use of UV-VIS spectroscopy provides with an easy, rapid and economical method allowing for the analysis of different compounds in beverages as reported by other authors [11–23]. However, most of these methods are only based in the identification of single wavelengths related with specific chromophores in the sample, even if the whole scan is collected during the analysis [10]. Therefore, this rich data UV-VIS spectrum is not fully utilised and important information about the chemical composition of the sample is not analysed or even lost. Nowadays, the incorporation of multivariate data analysis and processing methods (e.g. derivatives, smoothing) provide with new means to mine and better interrogate spectroscopic data in the beverage and food industries [9,11,22,23].

The objective of this study was to evaluate the application of derivatives to interrogate the UV-VIS spectra of gin samples and to monitor changes related with storage conditions.

2. Materials and methods

2.1. Gin samples

Samples (n = 12) were sourced from a commercial distillery in the Mornington Peninsula (Victoria, Australia). Commercial bottles (approx. 500 mL) were stored at room temperature (approx. 25–28 °C) and in the presence of oxygen, while another set of

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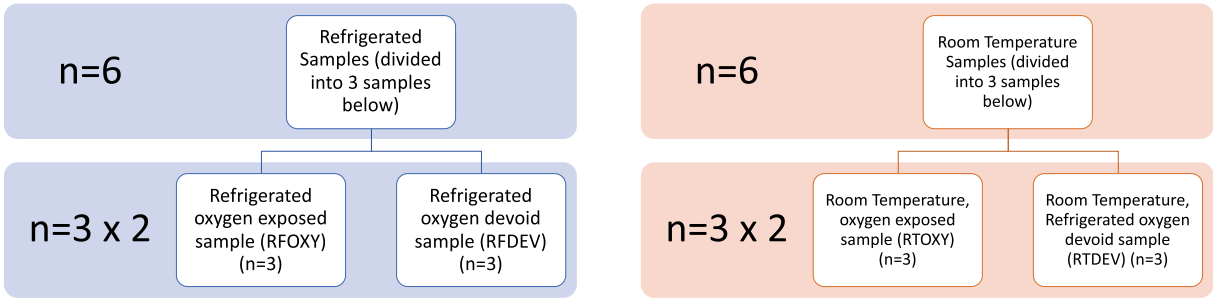
Table 1
Experimental protocol indicating sampling, samples and treatments.



samples were kept devoid of oxygen and stored at lower temperature (4 °C). In addition, one set of samples were bottled in the presence of atmospheric oxygen while the other samples were bottled under vacuum. Therefore, the sample set was comprised of refrigerated oxygen present samples (n = 3; RFOXY) and refrigerated oxygen devoid samples (n = 3; RFDEV), room temperature oxygen exposed sample (n = 3; RTOXY) and room temperature oxygen devoid samples (n = 3; RTDEV) plus control samples (see Table 1).

2.2. UV-VIS spectroscopy

Samples were diluted in 1:10 (v/v) gin:water where triplicate samples were taken for each sample of gin which gave 12 samples. An Agilent Cary 3500 UV–Visible (VIS) spectrophotometer was used to obtain spectra of the gin samples where samples were scanned in a quartz cell with 1 cm path length (Agilent Technologies, 2019). The spectrophotometer used a xenon flash lamp and Littrow monochromator which enable rapid collection of data and a wide absorbance range (Agilent Technologies, 2019). The scans were taken between 200 and 800 nm, in progressive steps of 1 nm and at 25 °C (Agilent Technologies, 2019).

2.3. Data analysis

Spectra were exported from the Agilent software in csv format to The Unscrambler software (Version X, CAMO ASA, Oslo, Norway) for chemometric analysis and spectra pre-processing. Second, third and fourth derivatives were calculated using the Savitzky-Golay transformation (10-point smoothing, second, third and fourth polynomial order) [9,11,24]. Principal component analysis (PCA) was carried out using the spectra from the refrigerated oxygen present, refrigerated oxygen devoid, room temperature oxygen present and room temperature oxygen devoid. Cross validation (leave one out) was used to test and minimise the effect of overfitting of the models developed [9,24]. Cross validation is a method used to evaluate and compare the models by dividing the data set into two segments one used to train a model and the other used to validate the model. During cross validation the training and validation sets must cross-over in successive rounds such that each data point has a chance of being validated against (leave one out) [9,24].

3. Results and discussion

3.1. Spectra interpretation

Figs. 1–3 shows the raw UV-VIS spectra of gin samples sourced from different storage conditions and after pre-processing using the second, third and fourth derivative, respectively. The raw UV-VIS spectra of the gin samples showed only a single absorbance at 27 nm (Fig. 1) while the second and third derivatives showed slight changes in wavelengths around 368 nm, 320 nm, 300 nm, 275 nm and 230 nm (Fig. 2 panel A and B). In addition, the third derivative shows troughs around 286 nm and 235 nm, highlighting a clear separation between samples according to storage conditions around 276 nm. The pre-processing of the UV-VIS spectra using fourth derivative (Fig. 3) showed changes as well as shifts in the spectra of the gin samples around 267 nm and 269 nm corresponding with the effect of storage (e.g. oxygen vs devoid) in the gin samples analysed. A through around 295 nm (Fig. 3) was also observed. It has been reported by other authors that the A and B benzene rings might be responsible for the UV spectrum of flavonoids compounds between 200 and 300 nm [25–27]. Information related to the flavonoid aglycones structure was reported by these authors for various subclasses of flavonoids using UV-VIS spectroscopy where two absorptions at 240 nm and 290 nm were also reported (band II) [26]. These bands are associated with the conjugation and substitutions pattern of ring A where absorptions around 300–550 nm have been reported to be associated with the band I (conjugation of B and C rings) [25–27].

Flavanols can be differentiated from flavones in band I as flavonols are generally at a longer wavelength than flavones (e.g. chalcones at 345–390 nm, aurones at 390–430 nm) where dihydrochalcones, flavan-3-ols and proanthocyanins are reported to absorb at wavelengths around 270–290 nm. In addition, dihydroflavonols, hydroxycinnamic acids and flavanones have been seen to have a small peak around 320 nm [28–30]. The glycosylation

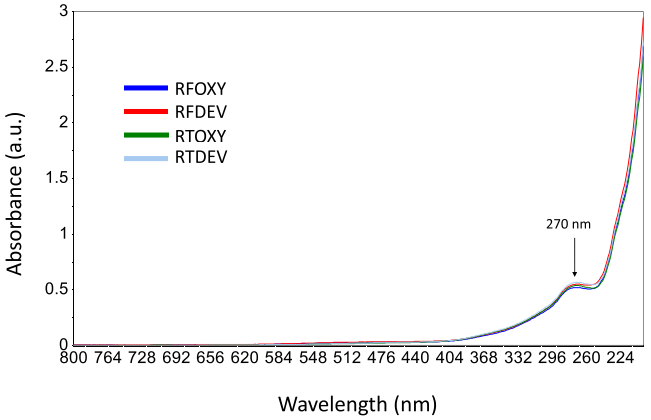


Fig. 1. Raw spectra of gin samples analysed using UV–Visible spectroscopy for (RFOXY, RFDEV, RTOXY, RTDEV), scanned at 200–800 nm.

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