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# Front-face fluorescence spectroscopy in combination with parallel factor analysis for profiling of clonal and vineyard site differences in commercially produced Pinot Noir grape juices and wines

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ABSTRACT

The applicability of using front-face fluorescence spectroscopy to compare profiles of commercially produced New Zealand Pinot Noir grape juice and wine samples from closely related vineyard sites and different grapevine clones was assessed by monitoring eleven batches of grape juices (different sites and clones) during the commercial winemaking process (pre-fermentation, pre-barrelling, barrelled wines). Deconvolution of the recorded fluorescence excitation-emission matrices was carried out using parallel factor analysis (PARAFAC) and the scores plots thereof showed sample groupings on the basis of clone and indicated chemical differences based on vineyard site, winemaking and barrel properties. The four components revealed by the PARAFAC models had their excitation/emission maxima at 278/360 nm, 260/390 nm, 278/315 nm and 320/415 nm, respectively and were tentatively assigned to multiple fluorophore contributions of tryptophan and hydroxyl benzoic acid derivatives (vineyard site discrimination), caffeic acid (clone discrimination), catechin and tyrosol related fluorophores (winemaking based discrimination). The applied methods after further validation have potential to be used as a rapid way to screen grape juices and wines and to provide winemakers with information on the potential quality of their wine.

## 1. Introduction

Fluorescence spectroscopy is a non-destructive, sensitive (ppb range) and rapid methodology for the analysis of fluorescent compounds in liquid or solid samples (Luykx and van Ruth, 2008). It is relevant to food analysis as numerous intrinsic fluorophores occur in food, including aromatic amino acids and proteins, phenolic compounds and vitamins (e.g. vitamin A and E) (Christensen et al., 2006; Luykx and van Ruth, 2008; Sádecká and Tóthová, 2007). Fluorescence spectroscopy has been reported to be useful in the classification of products such as honey, olive oil, sparkling wines and cheese based on their geographical origin and quality (Dupuy et al., 2005; Elcoroaristizabal et al., 2016; Karoui et al., 2007, 2004). The main fluorescent compounds in wine are polyphenols and aromatic amino acids, which contribute significantly to flavour (in particular bitterness and astringency) and appearance (in particular colour). Fluorescence spectroscopy has been reported to be a useful technique for the characterisation of wines according to sulphur dioxide addition, vintage, variety, quality and typicity (guez et al., 2011, 2009; ; Azcarate et al., 2015; Dufour et al., 2006; Elcoroaristizabal et al., 2016) and for the quantification of polyphenols (Cabrera-Bañegil et al., 2017).

When using a common fluorescence spectrophotometer with a right-angle sample holder, as in the work reported by Yin et al. (2009), wine samples need to be diluted, owing to their high density and/or turbidity, which can cause inner filter effects that distort the spectra and decrease the fluorescence intensities (Lakowicz, 2013; Yin et al., 2009). An alternative to the dilution of samples is the use of a front-face illumination set-up, in which the incident angle of the excitation beam is set to 30°, so that absorption from the sample can be reduced, and spectral distortions avoided. The use of such a sample holder enables a high sample-throughput as un-treated samples can be used and fingerprints of the samples can be obtained rapidly by recording three-dimensional excitation and emission matrices (EEM) over multiple excitation and emission wavelengths. Front-face fluorescence

*Abbreviations:* GJ, grape juice; PB, pre-barrelled wine; BW, barrelled wine; IN, Inlet (vineyard site name); BR, Black Rabbit (vineyard site name); LG, Long Gully (vineyard site name); PT, Pipeclay Terrace (vineyard site name); TG, Target Gully (vineyard site name); F, Ferris (vineyard site name)

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spectroscopy in combination with multi-way data analysis of the three-dimensional excitation-emission matrices (EEM), using parallel factor analysis (PARAFAC), has previously been used to discriminate between un-diluted wines based on their geographical origin, variety and ageing conditions (guez et al., 2009, 2011;) and to quantify the levels of various phenolic compounds in red wine (Cabrera-Bañegil et al., 2017).

The aim of the current study was to determine if front-face fluorescence EEMs could discriminate commercially produced grape juices and wines from a single winery in New Zealand on the basis of vineyard site and/or grapevine clone using an explorative approach. The multi-way data analysis methodology PARAFAC was applied in order to de-convolute the spectra and visualise differences between the de-convoluted components of the samples.

## 2. Materials and methods

### 2.1. Samples

#### 2.1.1. Vineyard sites

The vineyard sites sampled were owned and managed by *Mt. Difficulty Wines Ltd.* located in Bannockburn, Central Otago, NZ (all within 13 $km^2$) and were under similar viticultural management. Based on historical knowledge of the winery, 6 vineyard sites were chosen (see Appendix A, Fig. A1 in Supplementary file). These vineyard sites included Target Gully, TG; Pipeclay Terrace, PT; Long Gully, LG; Inlet, IN; Ferris, F; and Black Rabbit, BR. Information on the longitude, latitude and altitude of each vineyard site is tabulated in Appendix A (Table A1 in Supplementary file).

The EEM profiles of samples originating from these six sites were obtained from the 2012 vintage. To include the winemaking process as a variable impacting on the composition of these wines, grape juices were analysed as well as wines after fermentation (immediately before barrelling) and after six months of barrel ageing (before malolactic fermentation) (see Appendix A, Fig. A2 in Supplementary file).

#### 2.1.2. Commercial winemaking process

The six vineyard sites were under similar viticulture practice and climatic conditions and the winemaking processes were similar between the wines from those sites. Grape bunches were hand-picked (at around 25°Brix) and delivered to the winery to be processed immediately. The bunches of grapes were destemmed and added to stainless steel tanks ranging in volume from 2050 to 4950 L (some batches contained a portion of whole bunch as can be seen from Table 1). Approximately 50 mg $L^{-1}$ of $SO_2$ was added (as potassium metabisulphite) to avoid the premature onset of fermentation. Maceration (cold-soak) for approximately 9 days at around 9°C was followed by heating to 18–20°C to facilitate the onset of fermentation by indigenous yeast (no inoculation). After fermentation, at approximately 26°C (5–14 days), a period of post-fermentation maceration (6–16 days) was allowed for the additional extraction of phenolic compounds. The length of this maceration process depended on the availability of tanks in the winery. The wines were subsequently racked off, the grape remnants pressed and the resulting wines filled into 12–24 French oak barrels (225 L) of various characters (brand, age, wood type and toast level).

**Table 1**
Sample batches and their according vineyard site and clone origin and the proportion of added grapes as whole bunch. PT, Pipeclay Terrace; BR, Black Rabbit; LG, Long Gully; TG, Target Gully; IN, Inlet; F, Ferris.

| Batch | Vineyard site | Clone ratio (%)[a] | Whole bunch ratio (%)[b] |
|---|---|---|---|
| **1** | PT | 115 (100) | 0 |
| **2** | | 5 + 6 + 13 (33:33:33) | 0 |
| **3** | BR | 5 (100) | 0 |
| **4** | | 115 (100) | 0 |
| **5** | LG | 6 (100) | 0 |
| **6** | TG | 5 + 6 (50:50) | 35 |
| **7** | | 777 (100) | 0 |
| **8** | IN | 6 (100) | 40 |
| **9** | | 777 + 6 (56:44) | 0 |
| **10** | F | 6 (100) | 0 |
| **11** | | 115 + 5 (80:20) | 0 |

[a] Definition of clone: a genetically uniform group of plants derived from a single individual by asexual/ vegetative propagation (e.g. reproduction by cuttings and grafting) (Nicholas, 2006).

[b] Whole bunch ratio: addition of grapes as cluster/bunch (including stems, not destemmed).

### 2.2. Sampling

As the winery is not a research-based institution, the authors had no control over the winemaking procedures (harvest time, fermentation, temperatures, blending etc.) and it is to be noted that tank replicates could not be obtained. The composition of the ferment tanks (batches) sampled during the winemaking process is shown in Table 1. The grapevine clones in this study were imported to New Zealand from either the University of California, Davis (UCD) in the case of clones 5, 6 and 13 or from the Côte d'Or (ENTAV-INRA®), the so called Dijon clones 115 and 777 (Riversun Nursery Limited, Gisborne, NZ). The different clones were a genetically uniform group of plants derived from a single individual by asexual/vegetative propagation, e.g. reproduction by cuttings and grafting (Nicholas, 2006). According to the Riversun Nursery Ltd staff the clones give typical bunch size and density, canopy density and fertility with variation within these attributes, resulting in different flavour characters in the wines. However, scientific data on this observation is not available.

As shown in Table 1, some sample batches contained a mix of whole bunches and de-stemmed grapes. For the vineyard site PT, two batches were obtained, both containing only de-stemmed grapes with the first batch consisting of 100% of clone 115 and the second containing equal amounts of clone 5, 6 and 13 (33:33:33%). Two sample batches from BR were obtained containing 100% clone 115 and 100% clone 6 respectively and both contained only de-stemmed grapes. For LG, one batch was obtained with 100% clone 6 and only de-stemmed fruit. Grapes from TG consisted of 35% whole bunch of clones 5 and 6 in a ratio of 50:50 and the second batch containing only de-stemmed fruit and 100% of clone 777. Two sample batches were obtained from IN, containing only clone 6, with 40% of the grapes present as whole bunch and the second batch containing only de-stemmed grapes of clone 777 and 6 in the ratio of 56:44. The final two batches from F were both 100% de-stemmed grapes and consisted of 100% clone 6 and the other of clone 115 and 5 (54:46) respectively. The Brix at harvest varied between 23.1° and 26.8° and the pH between 3.07 and 3.22 (see Appendix A, Table A2 in Supplementary file). Samples from the batches in Table 1 were subsequently obtained at three stages throughout the winemaking process (see Appendix A, Fig. A2 in Supplementary file). Sample IN777_6 was only taken after pressing and after 4 months in barrel.

The first sample was taken after seven days of cold extraction (at around 9 °C). The second sample was taken after completion of fermentation, immediately before the wines were barrelled. The third sample was taken after four months of maturation in oak barrels, just before malolactic fermentation commenced. Samples were taken from barrels that had been used for at least two prior vintages in order to reduce/minimise the impact of the oak wood on the wine composition.

All samples were taken from the tank (stage 1 and 2) or barrel (stage 3) and filled into their storage containers. Green glass bottles (750 mL, BVS Burgundy wine bottle AG056, VinPro, Cromwell, NZ) were used for samples from stages 2 and 3. The grape juices were stored in 750 mL Hexagonal PET jars (Stowers, Christchurch, NZ). All wine samples were immediately purged with oxygen free nitrogen (BOC, Auckland, New Zealand) and sealed with Novatwist press-on screw caps (Kauri, Wellington, New Zealand). Samples were stored at −18 °C until