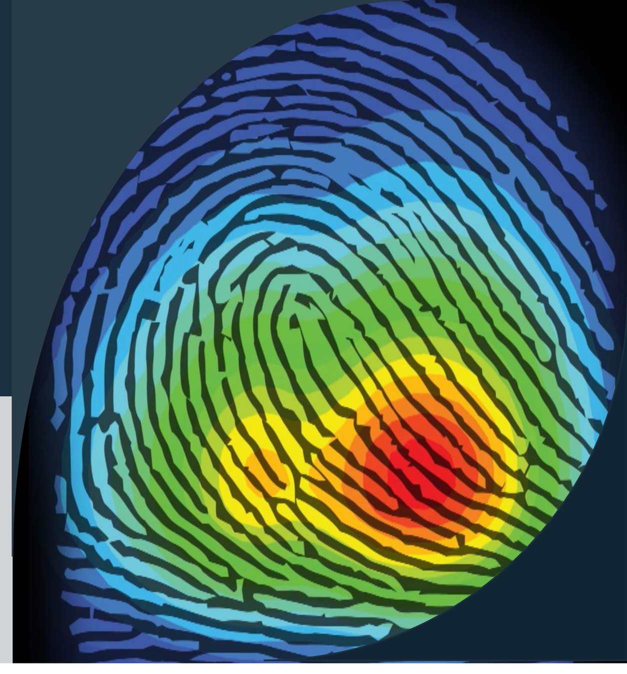
From wine additive classification to monitoring red wine maturation and ageing: Novel approaches based on spectrofluorometric fingerprints



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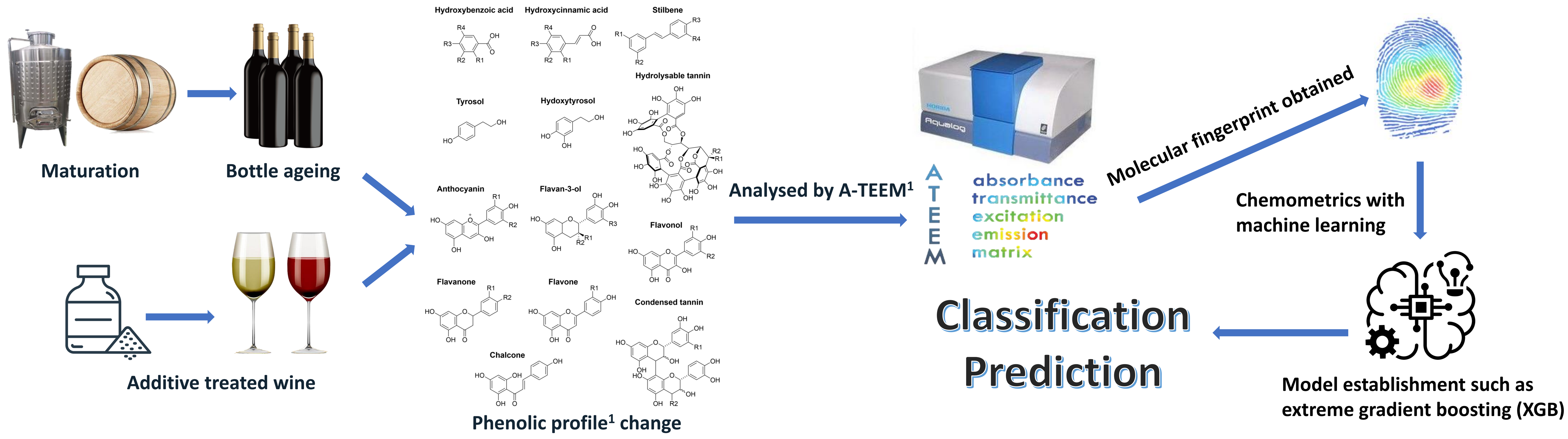
INTRODUCTION & AIMS

Various fluorescent substances occur in grape and wine, including phenolics, vitamins, and amino acids. The decisive role of phenolics in grape and wine quality, in combination with their fluorescent properties highlight the natural fit of fluorescence spectroscopy in grape and wine science. Thus, as a rapid, sensitive, easily-implemented, environmentally friendly, and cost-effective instrumental approach, fluorescence spectroscopy combined with chemometrics based on machine learning (ML) has shown advantages for quantification and prediction of phenolic substances, identification and classification of varieties, vintages and geographical regions, and detection of adulterants. In addition to discerning relatively static features of wines, the short-term developmental change of wine features can also be measured and tracked by spectrofluorometric fingerprint.[1] Concerning other potential applications of the analytical approach, a wide range of exogenous additives can be used during the winemaking process for various purposes, such as wine stabilisation and modification of sensory attributes. Types of additives include enzymes, antioxidants, clarifying or fining agents, tannins, polysaccharides, oak wood products, and so on. The use and dosage of wine additives is generally governed by regulations in different countries and regions.[2] However, the excessive use of legal additives, abuse of illegal additives, and adulteration of wine (and wine-derived spirits such as brandy) still occurs. The exploration of the detection, classification, and tracing of various additives in wine is lacking. Furthermore, methods could be improved for monitoring of long-term red wine evolution, especially, during maturation and ageing, which are crucial value-adding stages for red wine quality and sensory attributes modification. Fluorescence spectroscopy can be a potential novel approach to address these research gaps.

The study aims to explore the capacity of fluorescence spectroscopy combined with machine learning for

1. Discrimination of wines treated with different additives;
2. Monitoring of red wine evolution during maturation and ageing to predict optimum duration;
3. Establishing relationships between spectrofluorometric fingerprints and phenolics profiles of red wine during maturation and ageing.



MATERIALS & METHODOLOGY

Sauvignon Blanc — 27 bentonite treatments at 3 levels

2 Cabernet Sauvignon (C 1-2)
4 Grenache (G 1-4)
2 Shiraz (S 1-2) — 3 maturation sampling time points (1-,2-,3-)

A-TEEM data acquisition — Solo software — Data analysis, fusion and modelling for classification and prediction

Phenolics profile measurement:
- Monomeric pigments (MP)
- Large polymeric pigments (LPP)
- Small polymeric pigments (SPP)
- CIELab colour parameters
- Somers colour parameters
- BSA tannins & MCP tannins

RESULTS

Classification

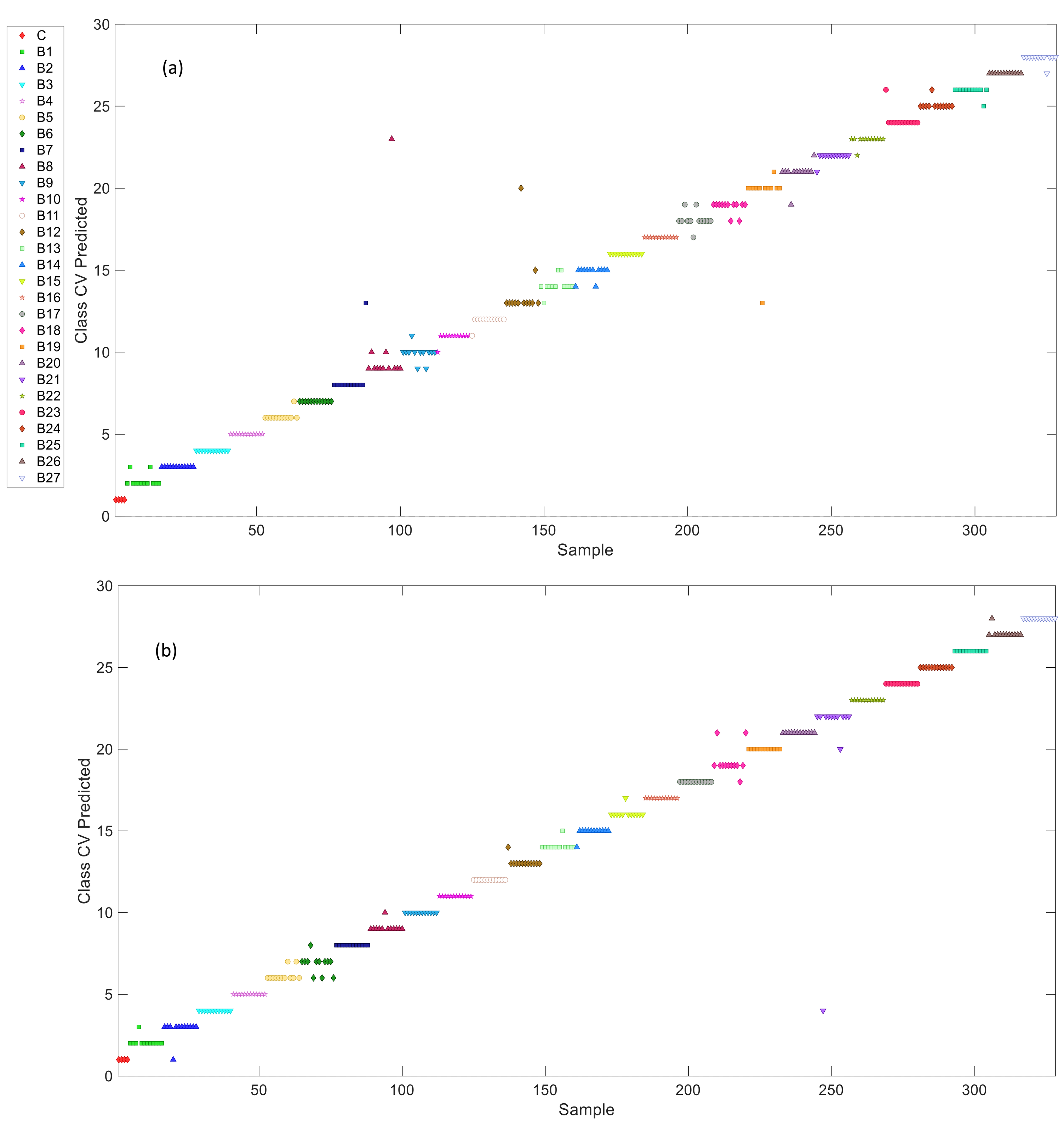


Figure 1. Class CV predicted from XGB discriminant analysis (DA) classification using (a) EEM data alone and (b) fused A-TEEM data for the untreated Sauvignon Blanc (C) and wine treated with 27 different bentonites (B1-B27)

Figure 1 shows a prediction accuracy of 90% for bentonite type from an ML model based on the EEM data. Out of a total of 328 samples, 34 samples were incorrectly predicted. The prediction accuracy from an ML model based on the fused absorbance and EEM data improved to 94%. Out of a total of 328 samples, only 19 were incorrectly predicted as a different bentonite. This illustrates the high sensitivity of A-TEEM to subtle compositional changes of wines caused by the treatments, even though the additives in this case had very similar properties.

Monitoring & Prediction

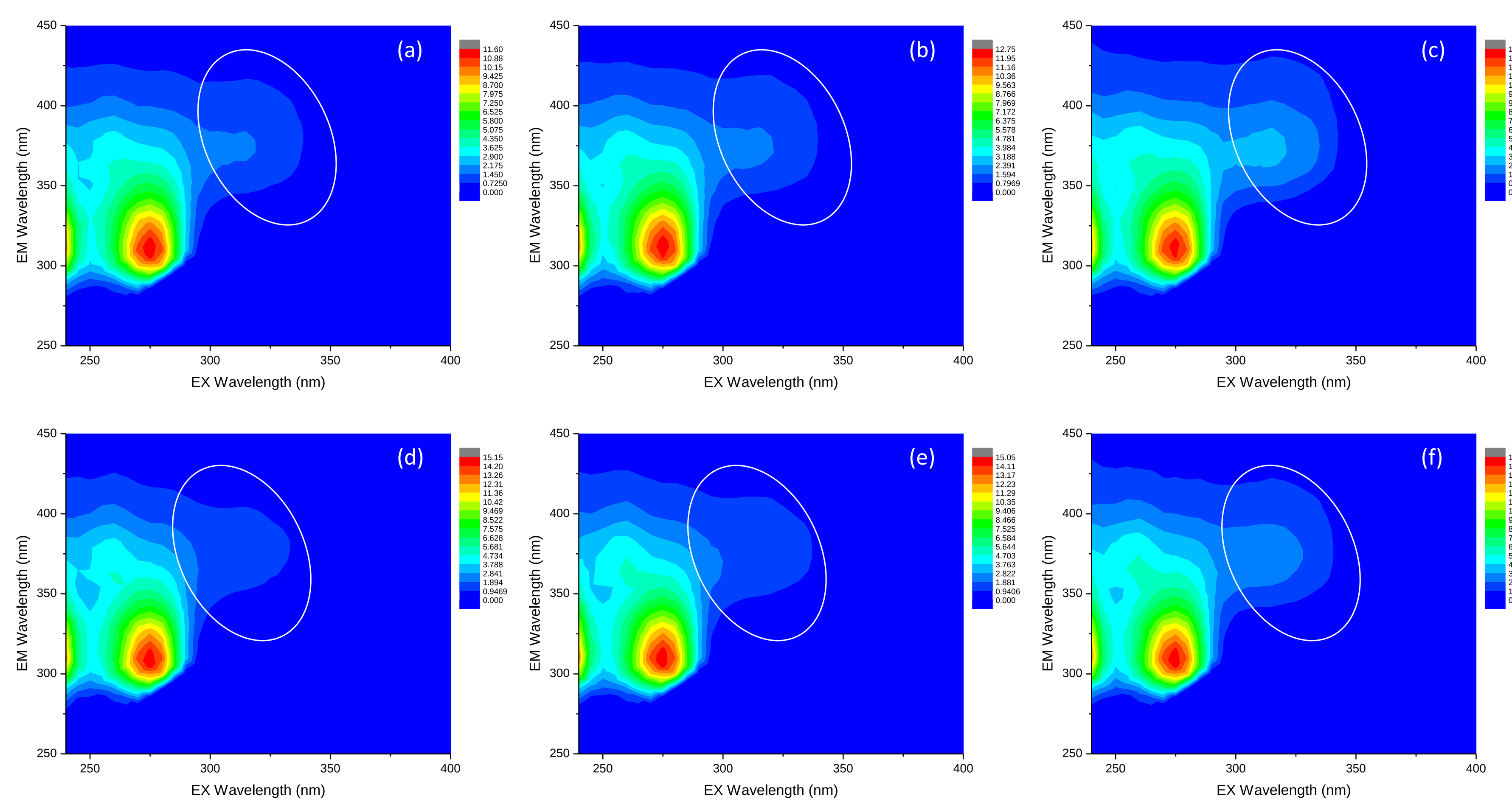


Figure 2. EEM contour maps of separate Shiraz wines collected from Yalumba during maturation showing (a) 1st, (b) 2nd and (c) 3rd sampling time points in stainless tank and (d) 1st, (e) 2nd and (f) 3rd time points in oak barrel.

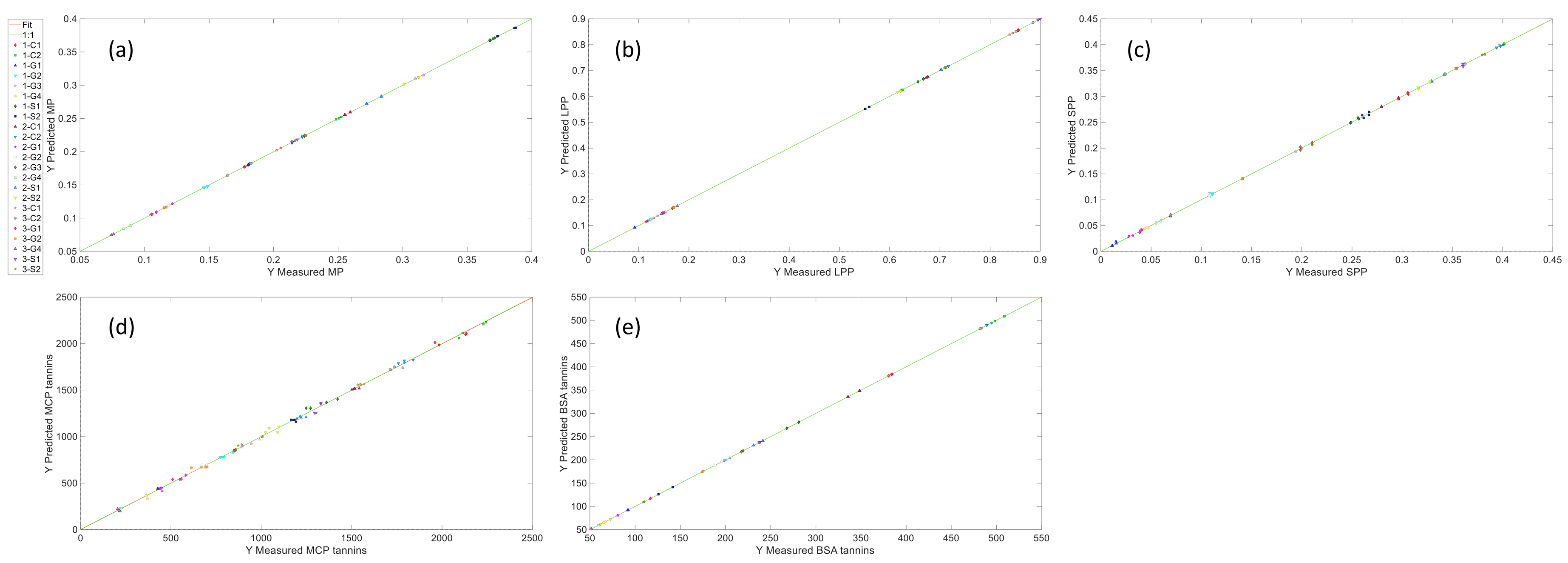


Figure 3. XGB regression of measured vs. CV predicted for (a) MP, (b) LPP, and (c) SPP, and tannins by (c) MCP and (e) BSA assays for 8 red wines collected from 3 sampling time points during maturation at Yalumba

In Figure 2, the evolution of EEM contour maps of two Shiraz wines matured in tank and barrel are reasonably apparent. This revealed that fluorescence spectroscopy can discern and track subtle chemical changes of red wines during a dynamic process. In Figure 3, XGB regression was applied to the phenolics data to build regression models. Table 1 shows high values for coefficient of determination of cross-validation (R^2 CV) and low root mean square error of cross-validation (RMSECV). These results highlight that fluorescence spectroscopy can be a powerful tool for prediction of phenolics parameters in red wine.

Table 1 Evaluation of established models by XGBR based on EEM data and phenolics parameters

Model	R^2 CV	RMSECV
MP	0.922	0.024
LPP	0.974	0.049
SPP	0.938	0.034
MCP tannins	0.974	90.729
BSA tannins	0.995	10.026

CONCLUSION & PERSPECTIVE

1. Data fusion can enhance the classification accuracy of the model established by the XGBDA.
2. The phenolics profile change of wines induced by maturation and additive treatments can be discerned by the spectrofluorometric fingerprints.
3. Further data analysis and model optimisation will be implemented to enhance the capacity of A-TEEM data to classify and predict wine features and phenolic profiles.

REFERENCE:

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