

ULTRAVIOLET – VISIBLE - NEAR INFRARED SPECTROSCOPY FOR RAPID DETERMINATION OF VOLATILE COMPOUNDS IN WHITE GRAPES DURING RIPENING

ESPECTROSCOPIA ULTRAVIOLETA – VISÍVEL – INFRAVERMELHO PRÓXIMO PARA DETERMINAÇÃO RÁPIDA DE COMPOSTOS VOLÁTEIS EM UVAS BRANCAS DURANTE A MATURAÇÃO

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SUMMARY

Near Infrared (NIR) spectroscopy is increasingly used in food analysis due to its speed and ease of use. Ultraviolet-visible (UV-VIS) spectroscopy is commonly used in any laboratory worldwide. The objective of this work was to develop a rapid method based on UV-VIS-NIR spectroscopy for the determination of volatile compounds in white ‘Albariño’ grapes from DO Rias Baixas (Spain). A total of 52 samples of white ‘Albariño’ must were analysed. Gas chromatography-mass spectrometry (GC-MS) was used as reference method. Partial Least Squares regression was used to fit mathematical models to relate the UV-VIS-NIR spectra with the volatile compounds determined by GC-MS. Reliable models for predicting the following compounds were obtained: (E)-2-hexenal, 1-hexanol, (Z)-2-hexanol, benzaldehyde, phenylethanal, cis pyran linalool oxide and 2-phenylethanol. The best performance was obtained using pre-treated spectral data (1st and 2nd derived). The r² coefficients obtained were greater than 0.85 for these compounds. In conclusion, UV-VIS-NIR spectroscopy is a fast and feasible method for the determination of some volatile compounds in white ‘Albariño’ musts from DO Rías Baixas.

RESUMO

A espectroscopia de infravermelho próximo (NIR) é cada vez mais utilizada na análise de alimentos devido à sua rapidez e facilidade de uso. A espectroscopia ultravioleta - visível (UV-VIS) é comumente usada em qualquer laboratório em todo o mundo. O objetivo deste trabalho foi desenvolver um método rápido baseado na espectroscopia UV-VIS-NIR para a determinação de compostos voláteis em uvas brancas ‘Albariño’ da DO Rias Baixas (Espanha). Foram analisadas 52 amostras de mosto ‘Albariño’ branco. A cromatografia gasosa-espectrometria de massa (GC-MS) foi utilizada como método de referência. A regressão Parcial dos Mínimos Quadrados foi usada para ajustar modelos matemáticos com o intuito de relacionar os espectros UV-VIS-NIR com os compostos voláteis determinados por GC-MS. Obtiveram-se modelos fiáveis para prever os seguintes compostos: (E) -2-hexenal, 1-hexanol, (Z) -2-hexanol, benzaldeído, feniletanal, óxido de cis-pirano linalol e 2-feniletanol. O melhor desempenho foi obtido usando os dados espectrais pré-tratados (1^a e 2^a derivadas). Os coeficientes r² obtidos foram superiores a 0,85 para estes compostos. Em conclusão, a espectroscopia UV-VIS-NIR é um método rápido e viável para a determinação de alguns compostos voláteis em mostos brancos da casta ‘Albariño’ da DO Rías Baixas.

Key words: volatile compounds, UV-VIS-NIR spectroscopy, rapid method.

Palavras-chave: compostos voláteis, espectroscopia UV-VIS-NIR, método expedito.

INTRODUCTION

Grape composition at harvest is one of the most important factors determining the future quality of wine. Volatiles, important flavour components in

white wine, are formed during grape berry metabolism and they are very influenced by the ripening stage. Measurement of grape volatile composition in the last ripening stages is an important requirement for an optimum production of white

wines. Therefore a rapid method is necessary to know the aromatic ripening of grape.

Several authors have reported the use of NIR spectroscopy to measure total soluble solids (TSS) in grapes (Shenk *et al.*, 1992; Osborne *et al.*, 1993; Gishen and Damberg, 1998; Gishen *et al.*, 2000; Damberg *et al.*, 2003a; Arana *et al.*, 2005) or ethanol, tartaric acid and malic acid in wines (Martelo-Vidal and Vázquez, 2015). Some authors have studied and developed Vis-NIR or NIR non-destructive systems in order to determine technological parameters useful for classifying grapes (Gishen and Damberg, 1998; Damberg *et al.*, 2003b; Herrera *et al.*, 2003; Cabassi *et al.*, 2006; Casiraghi *et al.*, 2006; Damberg *et al.*, 2006). Vis-NIR spectroscopy has also been used to predict TSS, pH, total anthocyanins and polyphenolic compounds in red grapes by several authors (Damberg *et al.*, 2003a; Cozzolino *et al.*, 2004; Martelo-Vidal and Vázquez, 2014). NIR also was used to measure volatile aroma compounds in Riesling wine (Smith *et al.*, 2008). However, NIR spectroscopy has never been applied to know the volatile composition of grapes during ripening.

‘Albariño’ is one of the most important white grape varieties in Galicia (NW Spain). The aim of this work was to apply of UV-Vis-NIR spectroscopy to predict the volatile composition of grapes during ripening with the objective of optimizing the wine aroma.

MATERIAL AND METHODS

Vineyard locations and grape samples

This study was tested on ‘Albariño’ grapes grown on the Controlled Designation of Origin Rías Baixas (Galicia, Spain). A total of 52 grape samples of *Vitis vinifera* ‘Albariño’ were studied at different maturity stages, 13 from M-1 (16.3 °Brix), 19 from M-2 (17.8 °Brix) and 20 from M-3 (18.7 °Brix). The grape samples (1 kg) were collected during 2014 vintage. After harvest, °Brix was analyzed by refractometry and the samples were immediately frozen and stored at -20°C until chemical analyses. Grape samples of 500 g were used to analyze free volatile composition of ‘Albariño’ musts.

Extraction, identification and quantification of free volatile compounds

About 500 g of frozen berries were thawed at 4 °C overnight, and then manually crushed, centrifuged (9287 rpm, 20 min, 4 °C) and filtered through a glass wool bed. To 75 mL of juice 4-nonanol (Merck, ref. 818773) was added as internal standard (10 µL of 40 µg/L solution in 10 %, v/v ethanol) and passed

through a LiChrolut EN cartridge (Merck, 500 mg, 40-120 µm) according to Oliveira *et al.* (2000). The resin was previously pre-conditioned with 10 mL of dichloromethane, 5 mL of methanol and 10 mL of aqueous alcoholic solution (10 %, v/v). Free volatile compounds were eluted with 5 mL of pentane-dichloromethane. The pentane-dichloromethane elute was dried over anhydrous sodium sulphate and concentrated to 200 µL by solvent evaporation under a nitrogen stream prior to analysis.

Gas chromatographic analysis of volatile compounds was performed using a GC-MS system constituted by an Agilent Chromatograph 6890N and an ion-trap mass spectrometer 5975C. A 1 µL injection was made into a capillary column, coated with CP-Wax 52 CB (50 m × 0.25 mm i.d., 0.2 µm film thickness, Chrompack). The temperature of the injector (SPI-septum-equipped programmable temperature) was programmed from 20 °C to 250 °C, at 180 °C/min. The oven temperature was held at 40 °C for 5 min, then programmed to rise from 40 °C to 250 °C at 3 °C/min, then held 20 min at 250 °C and finally programmed to go from 250 °C to 255 °C at 1 °C/min. The carrier gas was helium N60 (Air Liquide) at 103 kPa, which corresponds to a linear speed of 180 cm/s at 150 °C. The detector was set to electronic impact mode (70 eV), with an acquisition range from 29 to 360 *m/z*, and an acquisition rate of 610 ms.

Identification was performed using the software Saturn version 5.2 (Varian), by comparing mass spectra and retention indices with those of pure standard compounds. All of the compounds were quantified as 4-nonanol equivalents.

Spectral analysis

Samples of musts (5 mL) were analysed in a spectrophotometer V-670 (Jasco Inc, Japan) using transmittance mode at 2 nm intervals in UV-VIS-NIR regions (190 nm–2500 nm). Prior spectral analysis, samples were equilibrated at 33 °C for 10 min before scanning and filtered through 0.45 µm filter (Cozzolino *et al.*, 2007). Cell quartz with 1 mm path length was used to scan samples. Data were collected using Spectra Manager™ II software (Jasco Inc, Japan). Samples were scanned in duplicate obtaining 104 spectra.

Chemometric analysis

The chemometric analysis was performed according to Martelo-Vidal and Vazquez (2014). Spectral data were exported from Spectra Manager™II software into Uncrambler software (version X 10.2; CAMO, Oslo, Norway) for pre-treatment and obtain calibration models. Two replicates of each sample (104 spectra) were analysed in Unscrambler software.

Principal Component Analysis (PCA) was performed to detect patterns and outliers (Cozzolino *et al.*, 2011; Cetó *et al.*, 2013; Keckes *et al.*, 2013).

Calibration models for measurement of volatile compounds were performed using partial least square regression (PLS). Calibration models were developed using full-cross validations. Spectral data were pre-treated before PLS modeling. The pre-treatments tested were standard normal variate (SNV), first derived Savitzky–Golay (1st derived), second derived Savitzky–Golay (2nd derived). The statistical parameters Correlation Coefficient-squared (r^2), Root Mean Square of Calibration (RMSEC), Root Mean Square Error of Cross Validation (RMSECV) and Residual Predictive Deviation (RPD) was used to evaluate how well the calibration model of spectra could predict volatile compounds (Cozzolino *et al.*, 2004, 2011; Lorenzo *et al.*, 2009; Garde-Cerdan *et al.*, 2012).

RESULTS AND DISCUSSION

Chemical analysis

‘Albariño’ cultivar from controlled designation of origin Rías Baixas was sampled at different ripening dates, which influences in the volatile composition.

Table I and Figure 1 shows the variation of concentration volatile compounds identified and quantified in 52 samples of ‘Albariño’ musts during 3 stages of ripening (16.3, 17.8 and 18.7 °Brix). Data in Table I have been arranged into the nine chemical families where were identified and quantified 26 free volatile compounds: 6 alcohols, 7 C₆ compounds, 3 volatile acids, 2 terpenes, 2 ethyl esters and acetates, 2 aldehydes, 1 lactone, 2 volatile phenols and 1 carbonyl compound.

Table I

Free volatile composition (µg/L) of ‘Albariño’ musts (mean + SD) by ripening stage (expressed in °Brix)

Composição volátil livre (µg/L) de mostos ‘Albariño’ (média + SD) na maturação (°Brix)

Compound	M-1 (16.3 °Brix)	M-2 (17.8 °Brix)	M-3 (18.7 ° Brix)
1-butanol	7.38±4.96	18.51±16.19	13.57±7.95
2+3-methyl-1-butanol	7.93±4.55	75.10±118.77	92.75±95.79
3 methyl -3- buten-1-ol	4.12±1.59	10.03±5.44	16.86±12.59
2,3-butanodiol	0.00	8.98±7.05	5.39±4.02
Benzylic alcohol	33.17±13.11	76.58±37.61	44.99±18.37
2-Phenylethanol	81.59±48.76	991.23±1754.85	1020.38±1508.73
Hexanal	164.61±82.32	181.17±107.80	192.39±134.59
(E)-2-hexenal	255.35±79.43	550.85±250.45	455.26±313.88
1-hexanol	455.68±231.25	1546.29±676.89	824.47±213.42
(E)-3-hexenol	6.37±3.30	18.83±6.82	16.90±18.51
(Z)-3-hexanol	34.91±12.29	79.85±83.79	55.57±111.21
(Z)-2-hexanol	757.21±401.92	1802.23±741.22	707.35±428.31
(E)-2-hexanol	10.62±5.68	30.88±14.81	22.75±13.53
Hexanoic acid	44.48±51.28	61.89±40.34	38.39±18.68
(E)-2-hexanoic acid	17.94±19.72	20.85±22.97	13.38±5.87
Hexadecanoic acid	38.23±18.33	128.00±122.51	137.09±82.81
2-ethyl-hexanol	3.12±2.38	10.50±12.99	11.04±6.66
2-Phenylethylacetate	6.37±5.62	17.47±17.25	18.47±17.28
Benzaldehyde	3.56±1.24	26.19±35.90	18.40±22.00
Phenylethanal	65.44±66.71	325.70±574.91	335.04±305.02
cis piran linalol	8.28±3.31	20.39±22.63	14.96±8.31
Diendiol I	3.68±3.92	22.28±24.56	17.01±12.07
Butyrolactone	37.71±27.50	31.56±19.71	31.12±21.80
4-ethylphenol	10.04±5.06	19.04±14.75	25.32±0.00
Vanillin	19.18±6.93	18.91±7.27	38.63±42.87
Acetoin	20.37±14.63	20.30±14.21	34.42±37.38

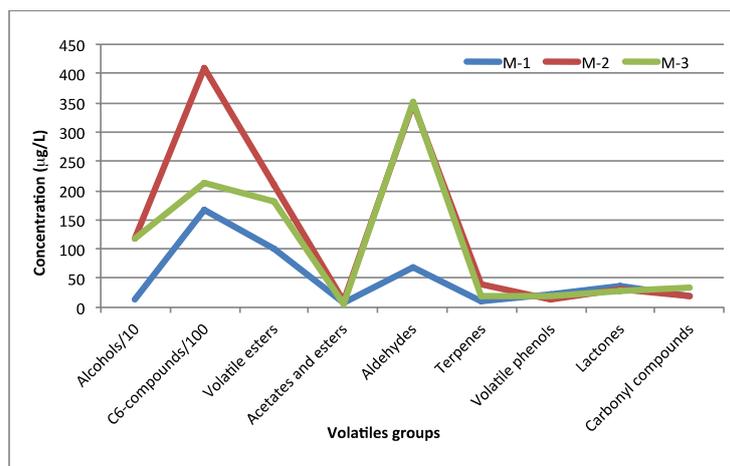


Figure 1. Evolution of volatile compounds families in ‘Albariño’ cultivar during ripening:

M-1 (16.3 °Brix), M-2 (17.8 °Brix) and M-3 (18.7 °Brix).

Evolução das famílias de compostos voláteis no ‘Albariño’ durante a maturação

M-1 (16,3 ° Brix), H-2 (17,8 ° Brix) e M-3 (18,7 ° Brix).

Analytical results showed differences in the ripening of ‘Albariño’ cultivar where C₆-compounds (represented by six compounds) were quantitatively the largest group of free volatile compounds quantified in ‘Albariño’ grape cultivar. C₆-compounds are related to varietal origin because they can be formed, via C₆-aldehydes, through lipoxygenase activity, from linoleic and linolenic acids present in grapes and supply vegetal and herbaceous nuances to the wine (Oliveira *et al.*, 2006; Kalua and Boss, 2009). ‘Albariño’ was described as a terpenic wine by several authors because the bound terpenic content of the must (Oliveira *et al.*, 2000; Vilanova *et al.*, 2007). However in our work only volatiles (free fraction) were analysed where only cis pyran linalool oxide and diendiol I was identified.

Among ripening data, the highest total value of volatile composition was showed in M-2 (17.8 °Brix) with 5.939 µg/L. Different behaviour was shown among compounds (Figure 2). Ripening data M-2 showed the highest values of C₆-compounds, volatile esters and acetates and terpenes. All volatile families have shown a decreased in the last ripening data (M-3) with exception of aldehydes and carbonyl compounds. Volatile phenols and lactones concentration decreased during ripening. The evolution of volatiles during ripening of grape juice was not proportional to the changes in sugar content, which shows that the technological and aromatic maturities did not occur at the same time (Vilanova *et al.*, 2009).

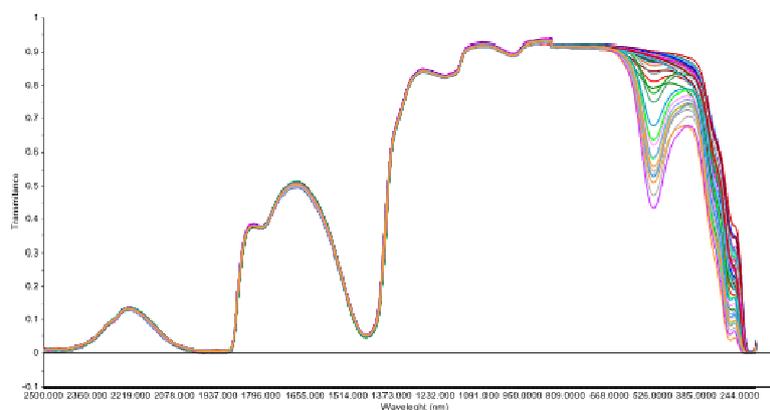


Figure 2. Raw UV-VIS-NIR spectra of ‘Albariño’ white must (DO Rías Baixas).

Espectros UV-VIS-NIR de mostos de ‘Albariño’ (DO Rías Baixas).

Spectral analysis

Figure 2 shows raw UV-VIS-NIR spectral data of 'Albariño' musts samples. UV-VIS zones (234 a 850 nm) showed big differences among samples meanwhile NIR zone (850 a 2500 nm) showed more homogeneity. The variability observed in UV-VIS-NIR could be useful to obtain mathematical models that relate the volatile compounds with the spectra. PLS was performed on raw or pre-treated spectral data with the aim to correlate the volatile compounds and the spectral data. Results showed significant

correlations between spectral data and some volatile compounds.

With the aim of showing the variability in volatile composition and spectral data, a score plot of the PCA of UV-VIS-NIR spectra from must samples is shown in Figure 3. This PCA explains 81 % of total variance with the first two PC. Separation among ripening samples was observed in the score plots. Some of the most ripening samples (18.7 °Brix, samples 1-19) were located in the positive side of PC1 and negative side of PC2.

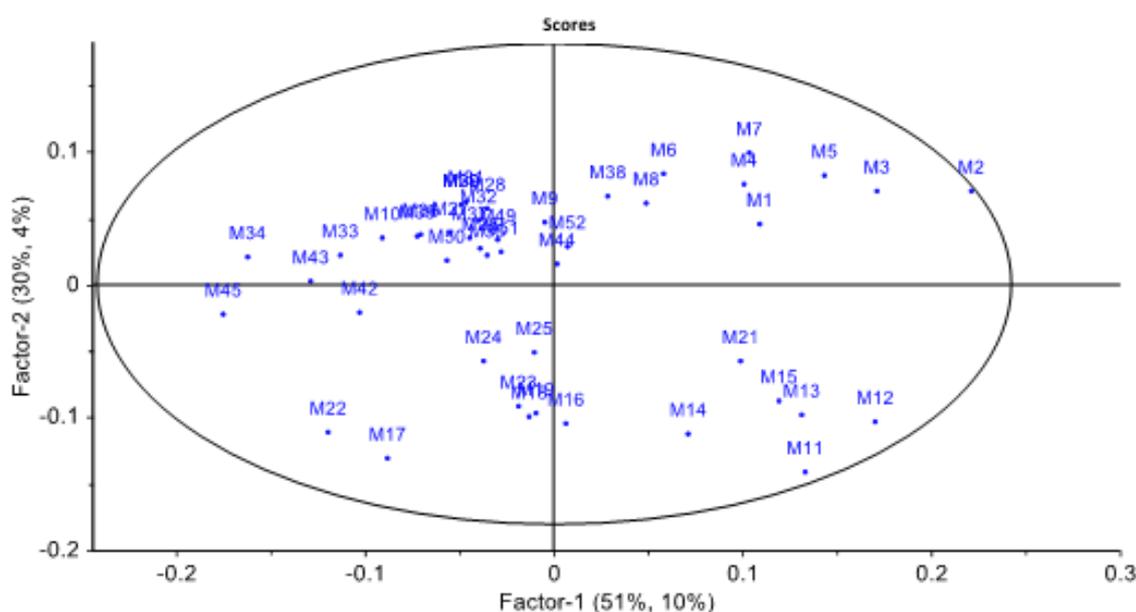


Figure 3. Score plots of two principal components from raw UV-VIS-NIR data of 'Albariño' white musts (M1-M52) from DO Rías Baixas.

Análise em componentes principais de dados brutos UV-VIS-NIR de mostos de 'Albariño' (M1-M52) da DO Rías Baixas.

The PLS analysis showed that UV-VIS-NIR spectra allowed to obtain accurate mathematic models to predict some volatile compounds concentrations from spectral data. Statistical results of the models for volatile compounds and UV-VIS-NIR spectral data (raw and pre-treatments) are shown in Table II. Only statistical results for the model of the best pre-treatment are showed.

Results showed variations based on the treatments (raw, 1st derived, 2nd derived or SNV). For many

volatile compounds, the best models were obtained with the pre-treatments 1st derived and 2nd derived. For only one compound the best pre-treatment was SNV (vanillin) and for only one no treatment was the best (2-phenylethylacetate). Models for one alcohol and three C₆-compounds showed a $r^2 > 0.9$ using the 2nd derived pre-treatment while two aldehydes and one terpenes showed values of $r^2 > 0.8$ using the 1st derived. Other studies performed in 'Tannat' grapes showed lower values of r^2 in glycosylated aroma compounds (Boido *et al.*, 2013).

Table II

Full cross-validation statistics obtained with PLS models for volatile compounds measured in 'Albariño' musts by UV-VIS-NIR spectroscopy ($\mu\text{g/L}$)

Estatísticas completas de validação cruzada obtidas com modelos PLS para compostos voláteis determinados em mostos 'Albariño' por espectroscopia UV-VIS-NIR ($\mu\text{g/L}$)

Volatile compound	Best pre-treatment data	r^2	RMSEC	RMSECV	RPD
1-butanol	1 st derived	0.53	7.98	12.71	0.99
2+3-methyl-1-butanol	2 nd derived	0.59	64.18	109.27	0.93
3 methyl -3- buten-1-ol	2 nd derived	0.54	6.62	10.41	0.93
2,3-butanediol	2 nd derived	0.82	1.44	3.55	1.69
Benzylic alcohol	2 nd derived	0.82	14.07	34.55	0.94
2-Phenylethanol	2 nd derived	0.999	45.93	1550	0.97
Hexanal	2 nd derived	0.78	52.47	115.48	0.99
(E)-2-hexenal	2 nd derived	0.919	77.92	294.2	0.94
1-hexanol	2 nd derived	0.9898	66.28	730.81	0.88
(E)-3-hexenol	1 st derived	0.47	9.54	13.31	0.99
(Z)-3-hexanol	2 nd derived	0.67	51.21	95.26	0.94
(Z)-2-hexanol	2 nd derived	0.98	123.25	738.52	1.05
(E)-2-hexanol	2 nd derived	0.51	10.69	15.66	0.93
Hexanoic acid	1 st derived	0.52	25.55	36.42	1.01
(E)-2-hexanoic acid	2 nd derived	0.48	12.79	16.95	1.07
Hexadecanoic acid	2 nd derived	0.67	57.22	99.78	1.01
2-ethyl-hexanol	1 st derived	0.24	4.64	5.61	1.41
2-Phenylethylacetate	raw	0.63	6.82	14.25	1.01
Benzaldehyde	1 st derived	0.889	8.79	28.12	0.98
Phenylethanal	1 st derived	0.986	48.89	456.19	0.94
cis piran linalol	1 st derived	0.85	6.31	15.87	1.03
Diendiol I	1 st derived	0.587	11.72	17.62	1.13
Butyrolactone	1 st derived	0.49	15.55	22.8	0.95
4-ethylphenol	2 nd derived	0.53	4.84	7.81	1.34
Vanillin	SNV	0.131	21.78	25.64	1.04
Acetoin	2 nd derived	0.58	17.27	28.59	0.94

Statistical parameters: Correlation Coefficient-squared (r^2), Root Mean Square of Calibration (RMSEC), Root Mean Square Error of Cross Validation (RMSECV) and Residual Predictive Deviation (RPD)

Figure 4 shows the predicted *vs* real values of the three best models for the volatile compounds 2-phenylethanol, 1-hexanol and phenylethanal by UV-VIS-NIR spectroscopy. A good correlation can be observed.

Considering that C_6 compounds in grape are a ripening marker, which could be a good indicator of optimal timing of harvest, the application of UV-VIS-NIR spectroscopy for the rapid analysis of these compounds can be new tools for winemakers to define the harvest time. High concentrations of these compounds indicate lower ripening of the grapes,

providing an herbaceous aroma in future wines.

Residual predictive deviation (RPD) was used to evaluate the prediction capacity of models. RPD is the most commonly used statistical index to account for model reliability. In our study a good capacity of prediction for PLS calibrations was achieved for any volatile compounds quantified. Values around 1 were considered good for the prediction models. A total of 25 free volatile compounds from 26 showed RPD values > 0.9 . Similar results were shown by Boido *et al.* (2013) when they analyzed bound glycosidically compounds in 'Tannat' juice.

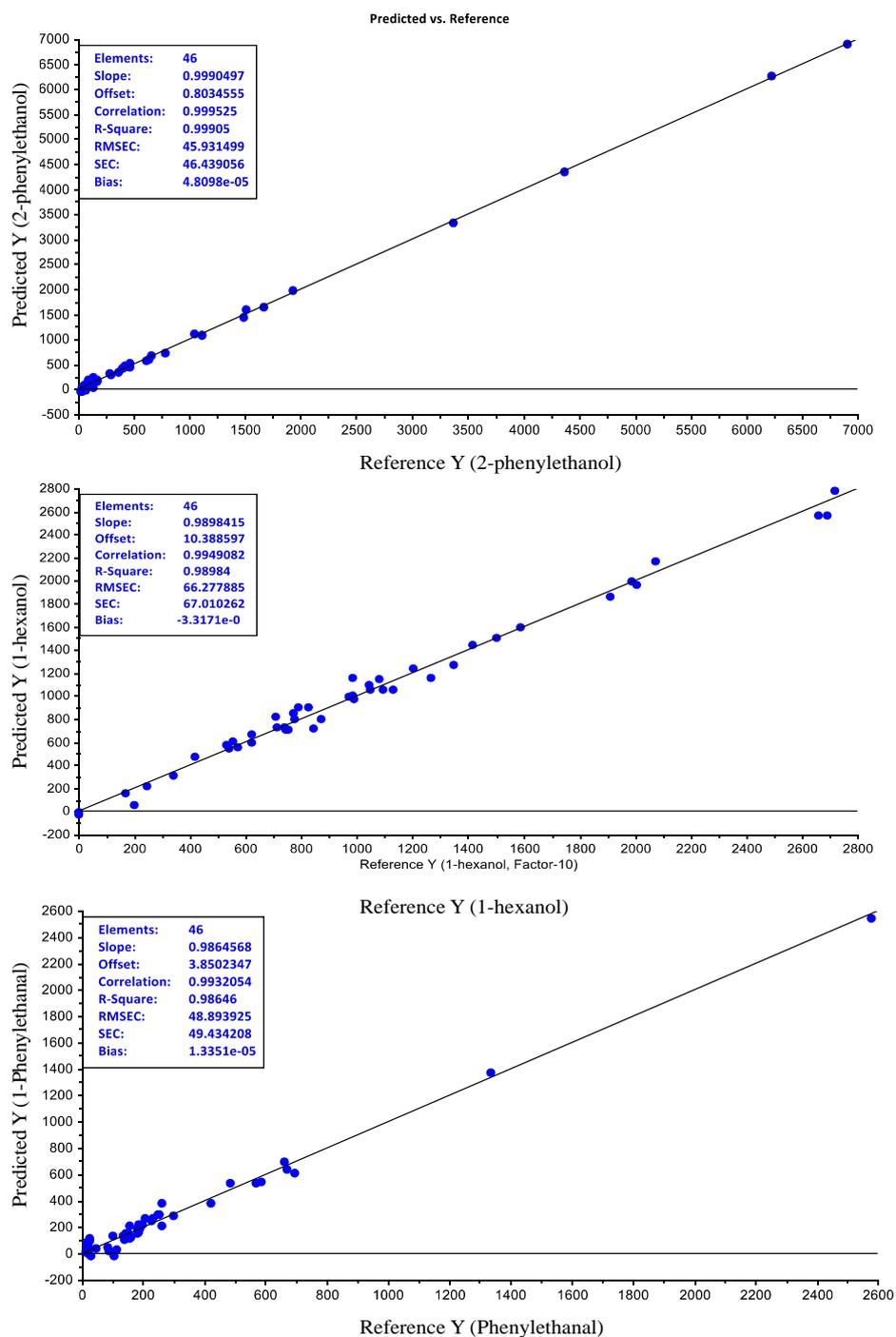


Figure 4. Prediction and real values of some volatile compounds ($\mu\text{g/L}$) studied in all ‘Albariño’ musts. 2-phenylethanol and 1-hexanol were adjusted with the 2nd derived models and phenylethanol with the 1st derived model. RMSEC: Root mean square of calibration; SEC: Standard error of calibration.

Valores reais e previstos de alguns compostos voláteis ($\mu\text{g/L}$) estudados em todos os mostos ‘Albariño’. 2-fenil-etanol e 1-hexanol foram ajustados com a 2^a derivado do modelo e o feniletanol com a 1^a derivada do modelo. RMSEC: Raiz quadrada média de calibração; SEC: Erro do padrão de calibração.

CONCLUSIONS

PLS regression models showed good results for some compounds related with grape ripening. UV-VIS-NIR spectroscopy could be a rapid and non-destructive method for evaluating grape aroma during ripening and establish the harvest data. UV-

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VIS-NIR spectroscopy could be a good tool for viticulture decisions in the vineyard. In conclusion, UV-VIS-NIR spectroscopy is a fast and feasible method for the determination of some volatile compounds in white 'Albariño' musts from DO Rías Baixas.

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