NIR SPECTROSCOPY AS A CONTACLESS RAPID TOOL TO ESTIMATE THE AMINO ACIDS PROFILE IN INTACT GRAPE BERRIES

Authors:Juan FERNÁNDEZ-NOVALES[1], Teresa GARDE-CERDÁN[1], Javier TARDÁGUILA[1], Sandra MARÍN-SAN ROMÁN[1], Eva P. PÉREZ-ÁLVAREZ[1], Eugenio MOREDA[1], Maria-Paz DIAGO[1*]

[1]*Instituto de Ciencias de la Vid y del Vino (Universidad de La Rioja, CSIC, Gobierno de La Rioja) Finca La Grajera, Ctra. de Burgos Km 6. 26007 Logroño, La Rioja, Spain.*

*Corresponding author:*maria-paz.diago@unirioja.es*

Abstract:

Context and purpose of the study - Nitrogen composition of grape berries plays a key role in determining wine quality, affecting the development of alcoholic fermentation and the formation of volatile compounds. Grape nitrogen composition is influenced by several factors such as viticultural practices, soil management, timing or rate of fertilization and use of rootstock, among others.In this study a proximal, non-destructive tool based on NIR spectroscopy is presented to track the accumulation of a wide range of amino acids in intact grape berries during the ripening process.

Material and methods - Clusters of grapevines of *Vitis vinifera* L. cv. Tempranillo were collected in a commercial vineyard located in Tudelilla, La Rioja, Spain (Lat. 42°18' 18.26", Long. -2°7' 14.15", Alt. 515 m) on five different dates from veraison to harvest in 2016 season. Contactless (at 25 cm from berries) spectral measurements from intact grape berries were acquired using a NIR spectrometer working in the 1100 - 2100 nm spectral range under laboratory conditions.A total of 19 individual amino acids in 120 grape clusters were quantified by HPLC, which was used as the reference method for the validation of the spectral tool. Principal component analysis (PCA) and Modified partial least squares (MPLS) regressions were used to explore the data structure and for the prediction of the amino acids profile in grape berries, by building calibration and validation models.

Results - A wide variability of all studied parameters was found during the ripening process with amino acid content ranging from 0.07 mg N/l (Glycine) to 534 mg N/l (Arginine). On average, Arginine was the most abundant amino acid (46.64 %), followed by Glutamine (14.70 %) and Proline (6.76 %). The best calibration and cross-validation models were built for Arginine, Cysteine and Proline with correlation coefficients values of 0.80, 0.77 and 0.75, while the standard errors of cross validation (SECV) were 43.04 mg N/l, 0.40 mg N/l and 5.87 mg N/l, respectively. In terms of the Free Amino Nitrogen content (FAN) the values of 0.71 and 104.85 mg N/l were gathered for the correlation coefficient of cross validation and SECV, respectively. The potential of NIR technology to fingerprinting the amino acid content in intact berries has been investigated. This technology could be used to select or classify grape berries during ripening in the vineyard, or at harvest time at the reception of the grapes in the production line (winery). This could be very useful to adapt the enological fate or grape berries to different wine qualities or styles, as well as to adopt different viticultural (thinning, selective harvesting) or enological decisions. Nevertheless, further examination of the influence of more varieties, seasons, and origins should be conducted with the aim of developing more robust, global, and predictive models.

Keywords: Grape ripening, non-destructive evaluation of berries, nitrogen composition, spectral techniques.

1. Introduction.

21st GiESCO International Meeting
Thessaloniki, Greece - June 23-28, 2019

NIR SPECTROSCOPY AS A CONTACTLESS RAPID TOOL TO ESTIMATE THE AMINO ACIDS PROFILE IN INTACT GRAPE BERRIES

Juan FERNÁNDEZ-NOVALES[1], Teresa GARDE-CERDÁN[1], Javier TARDÁGUILA[1], Sandra MARÍN-SAN ROMÁN[1], Eva P. PÉREZ-ÁLVAREZ[2], Eugenio MOREDA[1], Maria-Paz DIAGO[1]*

[1]Instituto de Ciencias de la Vid y del Vino (Universidad de La Rioja, CSIC, Gobierno de La Rioja). Finca La Grajera. Ctra. Burgos Km 6 (26007) Logroño, La Rioja (Spain). maria-paz.diago@unirioja.es
[2]Centro de Edafología y Biología Aplicada del Segura (CEBAS), Campus Universitario Espinardo Ed. 25, (30100) Murcia, Spain

Introduction & Objective

Nitrogen and amino acid composition of grape berries plays a key role in determining wine quality, affecting the development of alcoholic fermentation and the formation of volatile compounds. In this study a proximal, non-destructive tool based on NIR spectroscopy is presented and validated against HPLC, to track the accumulation of a wide range of amino acids in intact grape berries during the ripening process.

Materials & Methods

A total of 120 clusters of *Vitis vinifera* L. cv. Tempranillo were collected in a commercial vineyard located in Tudelilla (La Rioja, Spain) on five different dates from veraison to harvest in season 2016. Contactless (at 25 cm from the sample) spectral measurements (Fig. 1A) from intact grape berries were then acquired using a NIR spectrometer working in the 1100 - 2100 nm spectral range under laboratory conditions (Fig. 1B).

Prior to HPLC analysis of amino acids, the berry samples were subjected to a process of sample preparation. Each sample of 35 berries was homogenized using an Ultra Turrax. Then, a total of 19 individual amino acids were quantified by HPLC, which was used as the reference method for the validation of the spectral tool. Modified partial least squares (MPLS) regressions were developed for the prediction of the amino acids profile in grape berries, by building calibration and cross-validation models (Table 1 and Figure 2).

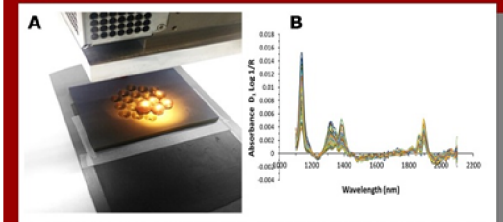

Figure 1: (A) Contactless spectral acquisition set up and (B) First derivative of the NIR spectrum acquired on the grape berry sample in the NIR range.

Results

Table 1: Calibration and Cross-validation results for the NIRS models of amino acids content (mg N/l) in grape berries.

Compound	Spectral Treatment	N	Range	PLS Factor	SEC	r_c	SECV	r_{cv}
FAN	1.4.4.1	113	107.81 - 789.75	3	83.94	0.83	104.85	0.71
Proline	Snv-DT 1.4.4.1	115	7.27 - 46.32	2	4.94	0.83	5.87	0.75
NFA	Snv-DT 1.4.4.1	117	91.00 - 485.00	2	56.01	0.72	65.90	0.58
Aspartic acid	1.4.4.1	116	1.69 - 6.12	3	0.56	0.82	0.67	0.72
Glutamic acid	1.4.4.1	112	1.68 - 9.71	3	0.95	0.82	1.19	0.70
Serine	1.4.4.1	112	3.07 - 11.83	3	1.11	0.81	1.37	0.69
Glutamine	1.4.4.1	114	7.11 - 169.35	3	22.20	0.75	27.37	0.59
Histidine	1.4.4.1	112	5.35 - 46.39	3	5.13	0.82	6.50	0.69
Glycine	1.4.4.1	116	0.70 - 2.79	2	0.35	0.68	0.40	0.54
Threonine	Snv-DT 1.4.4.1	115	0.69 - 12.93	2	1.67	0.74	2.00	0.60
Citrulline	1.4.4.1	93	0.81 - 9.42	3	1.10	0.80	1.43	0.63
Arginine	1.4.4.1	108	39.59 - 362.31	3	34.39	0.88	43.04	0.80
GABA	2.4.4.1	111	11.28 - 32.84	2	2.65	0.78	3.26	0.64
Tyrosine	1.4.4.1	102	0.35 -1.19	4	0.08	0.87	0.11	0.72
Cystine	1.4.4.1	111	0.77 - 3.90	3	0.32	0.87	0.40	0.77
Methionine	Snv-DT 1.4.4.1	89	0.13 - 2.24	2	0.33	0.74	0.40	0.59
Tryptophan	1.4.4.1	112	2.72 - 11.44	3	0.97	0.85	1.19	0.75
Phenylanine	1.4.4.1	103	0.52 - 2.09	3	0.19	0.82	0.24	0.70
Isoleucine	Snv-DT 2.4.4.1	104	0.26 - 4.07	4	0.49	0.87	0.81	0.62
Leucine	Snv-DT 1.4.4.1	105	0.60 - 7.42	2	1.09	0.75	1.29	0.63
Lysine	Snv-DT 1.4.4.1	111	0.23 - 3.92	4	0.30	0.91	0.47	0.76

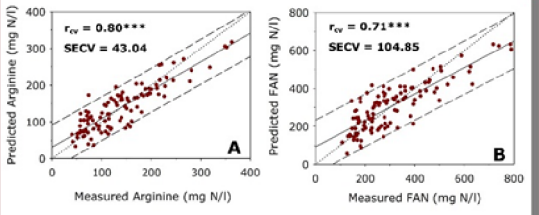

Figure 2: Regression plots for amino acids correlation using the best MPLS prediction models in the NIR range: (A) Arginine and (B) FAN. * indicate significance at $p \leq 0.001$**

Conclusion

Contactless, non-destructive spectroscopy could be an alternative to destructive methods, such as HPLC to provide information about grape amino acid composition. This technology could be used to select or classify grape berries during ripening in the vineyard, or at harvest time at the reception of the grapes in the production line (winery).

Acknowledgments: Maria P. Diago (RYC-2015-18429), Teresa Garde-Cerdán (RYC-2014-14967) and Eva P. Pérez (FJCI-2016-30931) are funded by the Spanish Ministry of Science, Innovation and Universities. Sandra Marín-San Román is funded by the Gobierno de La Rioja.