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Analysis of red wines using an electronic tongue and infrared spectroscopy. Correlations with phenolic content and color parameters

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Abstract

The objective of this work was to develop a methodology based on multiparametric methods (FTIR and a voltammetric e–tongue based on SPE) to evaluate simultaneously fourteen parameters related to the phenolic content of red wines. Eight types of Spanish red wines, elaborated with different grape varieties from different regions and with different aging, were analyzed with both systems. Input variables used for multivariate analysis were extracted from FTIR spectra and voltammograms using the kernel method. PCA analysis could discriminate wines according to their phenolic content with PC1, PC2 and PC3 explaining the 99.8% of the total variance between the samples for FTIR analysis and 85.8% for the e-tongue analysis. PLS calculations were used to establish regression models with phenolic content parameters measured by UV-Vis spectroscopy (TPI, Folin-Ciocalteu, CIELab and Glories) with high correlation coefficients (R^2 > 0.85), and low RMSEs (< 3.0) and number of factors (< 4). Both, PCA and PLS, were carried out using the full cross validation method. As time is a critical factor in the food industry, the main advantage of these multivariate techniques is their capability to evaluate many parameters in a single experiment and in shorter time than using independent classical techniques.

Keywords: Red wines; Electronic tongue; ATR-FTIR; Phenolic content.

Abbreviations: e-tongue (electronic tongue); D.O. (Denomination of Origin); SPE (Screen Printed Electrode); PCA (Principal Component Analysis); PLS (Partial Least Squares); TPI (Total Polyphenol Index); PC (Principal Component).

1. Introduction

Phenolic compounds (phenolic acids, flavonoids and tannins) are important components of wines as they can strongly influence their final organoleptic properties (Pinelo, Arnous, & Meyer, 2006; Setford, Jeffery, Grbin, & Muhlack, 2017; Aleixandre-Tudo & Du Toit, 2018; Blanco-Vega, Gomez-Alonso, & Hermosin-Gutierrez, 2014). In fact, the characteristic color in red wines is to a large extent ascribable to the phenolic substances present in the grape skin cells, which are transferred to the must during the maceration step. However, wine color is also influenced by the oenological practices such as, storage temperatures, length of storage and oxygen exposure (Atasanova, Fulcrand, Cheynier, & Moutounet, 2002; Obreque-Slier et al., 2013; Pinelo, Arnous, & Meyer, 2006; Ferreiro-Gonzalez et al., 2019). During conservation and aging of red wines, the concentration of anthocyanins, the main responsible for wine color, decreases progressively due to their reaction with other phenolic compounds, mainly with flavanols. This phenomenon causes the color change from red-bluish of young wines towards reddish-brown of matured wines, as well as a decrease of wine astringency

(Atasanova, Fulcrand, Cheynier, & Moutounet, 2002). Color also gives information about possible defects and changes during storage. Therefore, color is an important parameter in the quality control of wines.

Traditionally, the color of wines has been measured using Glories parameters and CIELab coordinates, a classical method established by the Commission Internationale of L'Eclairage (CIE) (Esparza, Santamaria, Calvo, & Fernandez, 2009; Rinaldi, Coppola, & Moio, 2019; Perez-Magariño & Jose, 2002; Atasanova, Fulcrand, Cheynier, & Moutounet, 2002).

In addition, the phenolic and antioxidant content in wines samples can be assessed by other recognized traditional spectrophotometric methods such as Total Polyphenol Index (TPI), FRAP, DPPH, ORAC, and Folin-Ciocalteu Index, among others. These methods are usually based on the evaluation of the capabilities of an oxidizing agent to induce an oxidative damage to a substrate. However, up to now, a single method has not been recognized as the most adequate, and the results obtained depend on the method used. When approaching the study of the phenolic and antioxidant activity of wines, it has been recommended to use more than one method (Barros, Andrade, Denadai, Nunes, & Narain, 2017; Lima et al., 2014).

The time is a critical factor in the food industry and for this reason the development of new analytical tools to determine the phenolic content and the antioxidant capacity of food is required.

In recent years, multi-parametric methods have been applied in food industry (Smyth & Cozzolino, 2013). Infrared spectroscopy (FTIR, NIR) combined with chemometric methods is emerging as a useful technique to analyze red wines. It is rapid, versatile and require minimal sample preparation (Ferreiro-Gonzalez et al., 2019; Preserova, Ranc, Milde, Kubistova, & Stavek, 2015; Kadiroglu, 2018; Silva, Feliciano, Boas, & Bronze, 2014). For instance, combining Near Infrared Spectra with statistical analysis, it is possible to determine parameters such as the sugar content (Fernandez-Novales, Lopez, Sanchez, Morales, & Gonzalez-Caballero, 2009), acidity (Chauchard, Cogdill, Roussel, Roger, & Bellon-Maurel, 2004), pH value (Larrain, Guesalaga, & Agosin, 2008) or chloride and sulfate (Dos Santos, Pascoa, Porto, Cerdeira, & Lopes, 2016) in red wines. Similarly, through analysis with FTIR combined with chemometric techniques, sugar, sulfur dioxide content or pH can be measured (Bauer et al., 2008).

Additionally, electronic tongues (e-tongues) based on electrochemical sensors (potentiometric, amperometric, voltammetric or impedimetric) have been developed and used in food quality control (Rodriguez-Mendez, 2016; Jiang, Zhang, Bhandari, & Adhikari, 2018; Sanaeifar, ZakiDizaji, Jafari, & de la Guardia, 2017; Riul, Dantas, Miyazaki, & Oliveira, 2010; Peris & Escuder-Gilabert, 2016; Ghasemi-Varnamkhasti, Apetrei, Lozano, & Anyogu, 2018). In this sense, electrochemical techniques can represent an advantage thanks to higher sensitivity and relatively low cost in comparison with the spectroscopic methods.

E-tongues have been successfully applied to analyze wines (Apetrei et al., 2012; Rodriguez-Mendez et al., 2014; Lvova et al., 2018; Merkyte, Morozova, Boselli, & Scampicchio, 2018; Rudnitskaya et al., 2017; Garcia-Hernandez, Comino, Martin-Pedrosa, Rodriguez-Mendez, & Garcia-Cabezon, 2018), beers (Gutierrez et al, 2013) and strong alcoholic beverages (spirits and liqueurs) (Novakowski, Bertotti, & Paixao, 2011) as well as to evaluate the quality of non-alcoholic beverages (Pascual et al., 2018; Winquist, Olsson & Eriksson, 2011; Ghasemi-Varnamkhasti et al., 2011).

The objective of this work is to evaluate and compare the capabilities of two multiparametric methods based on different working principles (electrochemical signals and vibrational spectroscopy) to assess the phenolic content in red wines with different characteristics (aging and grape variety). On one hand, a voltammetric e-tongue using disposable and cheap sensors based on screen-printed technology has been implemented. On the other hand, wines have been analyzed using FTIR spectroscopy, were the spectral range corresponding to the fingerprint region (1500-1000 cm^{-1}) has been selected for data treatment. In both cases the input data for further statistical analysis have been extracted using kernel functions. Chemometric tools such as Principal Component Analysis (PCA) and Partial Least Squares (PLS-1) have been implemented to discriminate between wines samples and to establish correlations with classical parameters related to phenolic content of the antioxidant capacity such as CIELab coordinates, Glories parameters, TPI and Folin-Ciocalteu index. The performance of both multiparametric systems has been analyzed and compared.

2. Materials and methods

2.1. Reagents and solutions

All chemicals and solvents were of reagent grade and used without further purification. Sodium carbonate (anhydrous, powder, 99.99%), Folin–Ciocalteu reagent, and ethanol (absolute, ≥99.8%, GC) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Wine samples

Spanish red wine samples elaborated with different grape varieties from different regions (DO) (Tempranillo from Ribera de Duero origin; Tempranillo from Toro origin; Syrah from Rioja origin; and a coupage of Tempranillo, Graciano and Mazuelo from Rioja origin) and with different aging (Joven -young ine that has not been aged in oak barrel-; Crianza -aged a minimum of 24 months and at least 6 of them in oak barrel-; Reserva -minimum aging period of 36 months and at least 12 of them in oak barrel-; and Gran Reserva -wines aged for 60 months and at least 18 of them in oak barrels-) were analyzed (Table 1). Samples were provided by the Oenological Centers of Rueda (Valladolid, Spain) and Haro (La Rioja, Spain).

<Table 1>

2.3. Phenolic content and antioxidant capacity

Polyphenol content was measured following official methods (OIV, 2013) using a spectrophotometer Shimadzu UV-1603 (Kyoto, Japan) with a 10.0 mm path length quartz cuvettes.

Determination of TPI280. Red wine was diluted with ultrapure water (1:100) and the absorbance was measured directly at 280 nm. The value of TPI280 was calculated as the absorbance x 100.

Determination of Folin-Ciocalteu Index. Red wine samples were diluted 1:5 in ultrapure water. Then, 0.1 ml volume of red wine sample, 5 ml of distilled water, 0.5 ml of Folin–Ciocalteu reagent, and 2 ml of 20% w/w sodium carbonate solution were introduced in a 10 ml calibrated flask, diluted to volume with distilled water and allowed to stand for 30 min before measuring the absorbance at 750 nm. The same procedure but replacing the 0.1 ml of wine sample with distilled water was used for determining the blank value. The value of the total polyphenol index is given by the absorbance x 100 for red wines.

Glories parameters. Absorbance values at 420, 520 and 620 nm were measured to determine Glories parameters (Perez-Magariño & Jose, 2002): color density (CD), color intensity (CI), hue (H), proportion of red color produced by flavylium cations (dA%), proportion of yellow color (Y%), proportion of red color (R%) and proportion of blue color (B%).

$$CD = A420 + A520 \quad (1)$$

$$CI = A420 + A520 + A620 \quad (2)$$

$$H = A420/A520 \quad (3)$$

$$dA\% = (A520 - ((A420 - A620)/2)/A520) * 100 \quad (4)$$

$$Y\% = A420/CI\ x\ 100 \quad (5)$$

$$R\% = A520/CI\ x\ 100 \quad (6)$$

$$B\% = A620/CI\ x\ 100 \quad (7)$$

CIELab coordinates were determined by measuring the transmittance of the wine every 10 nm over the visible spectrum (from 380 to 780 nm) using the illuminant D65 and 10° standard observer, following the CIE recommendations (Commission Internationale of L'Eclairage) (Sliwinska et al., 2016). These parameters are: a* (redness or –a*: greenness), b* (yellowness or –b*: blueness), L* (lightness), C* (chroma or saturation) and h* (hue angle).

2.4. Electronic tongue

A voltammetric electronic tongue based on screen-printed electrodes, SPEs (DropSens, Asturias, Spain), has been used to analyze the wines by means of cyclic voltammetry. For this purpose, six SPEs with different materials as working electrode were selected. Each sensor device contained a reference electrode (Ag), an auxiliary electrode (C or Pt) and a working electrode (Table 2).

<Table 2>

2.5. ATR-FTIR analysis

A Jasco Model FT/IR-6600 Spectrometer (Tokyo, Japan) with a diamond ATR crystal accessory was used. The software used for FTIR data collection was Spectra Manager II (Jasco, Tokyo, Japan). Before the analysis the instrument was purged with nitrogen for 10 min. As reference, the background spectrum of air (100 BKG) was collected before the acquisition of the sample spectrum. After each sample, the crystal was rinsed with ethanol with a cotton swab and dried. To record spectra, wine samples were dropped on the ATR crystal. Spectra were recorded at 26 ^{o}C with a resolution of 2 cm^{-1} and 300 scans were averaged for each spectrum (scan from 4000 to 400 cm^{-1}).

2.6. Data preprocessing and chemometric analysis

The multivariate data analysis was performed by using Matlab v2014b (The Mathworks Inc., Natick, MA, USA) and The Unscrambler (CAMO Software AS, Oslo, Norway). Voltammograms and ATR-FTIR spectra provided curves with a high number of variables that must be pre-treated to select a reduced number of variables without a loss of information. Data pre-processing has been done based on a compression method described by Gutierrez-Osuna & Nagle (1999). Voltammogram curves were multiplied by 10 smooth and bell-shaped windowing function (8) while infrared spectra were multiplied by 30 smooth and bell-shaped windowing function (8) (Gutierrez-Osuna & Nagle, 1999, Medina-Plaza et al., 2016; Muñoz et al., 2018).

K (8)

where a_i, b_i and c_i define the width, shape and center of the different windowing functions K_i, x_j is the x-variable, for voltammetric data is the voltage while for infrared spectra is the frequency in wavenumbers. The input voltammetric data matrix contained information of "8 wine samples with 5 replicas" × "10 kernels per voltammogram" × "6 sensors" extracted from the voltammogram signals acquired between -1.0 and 1.0 V. Additionally, ATR-FTIR data matrix includes information of "8 wine samples with 3 replicas" × "30 kernels per spectrum" from the spectra region ranged from 1500-1000 cm^{-1} where higher differences in the transmittance values were observed (RSD, relative standard deviation, between transmittance values were higher). The number of variables used for spectra data analysis (30 kernel functions) was higher than the number of variables selected for the voltammetric signals (10 kernel functions) due to x-axis of IR spectra contain more information than the x-axis of voltammetric curves.

These sets of variables were then used as the input for different statistical analysis: Principal Component Analysis (PCA) to discriminate wine samples, Partial Least Squares regression (PLS-1) to study the correlation between the results obtained with the electronic tongue and FTIR with the chemical parameters of phenolic content.

3. Results and discussion

3.1. Phenolic content: TPI280, Folin-Ciocalteu Index, Glories and CIELab parameters

Table 3 collects TPI280 and Folin-Ciocalteu Indexes measured in wines. As expected, whatever the variety of grape, young wines showed higher absorbance values than aged

223 wines, confirming that the phenolic content decreased due to the polymerization of
224 phenolic compounds that occurs during aging. This polymerization produces a decrease
225 in the concentration of low molecular weight polyphenolic compounds and increases the
226 concentration of polymeric polyphenols, affecting the wine color (Atasanova, Fulcrand,
227 Cheynier, & Moutounet, 2002). The TPI and Folin-Ciocalteu indexes of wines with
228 similar aging also vary from one variety to another.

229 **<Table 3>**

230 Glories parameters were used to evaluate the portion of red, yellow and blue color in
231 wines (Table 4). Due to the polymerization reactions and co-pigmentation of
232 anthocyanins occurring during the aging, wines change their color from intense red to
233 brown red. In good accordance with this idea, Glories parameters showed that red portion
234 (R%) was higher in Joven wines as well as the color intensity values did. On the other
235 hand, yellow portion (Y%), which contributes to brown color appearance, and
236 hue/tonality (H), increased during aging reaching higher values in older wines. As
237 expected, Blue portion (B%), the main responsible for red-bluish color, showed higher
238 values in young wines. However, this difference was not so clear in wines of the D.O.
239 Toro, which presented similar values of B%. Again, R%, Y% and B% were different is
240 wines elaborated from different grapes in spite of having the same time-aging.

241 **<Table 4>**

242 Results obtained for CIELab color parameters (Table 5) were consistent with those
243 obtained with Glories parameters. As a general trend, a* (the parameter, responsible for

244 red color) decreased during the aging while the parameter b* responsible for yellow
245 color, hue angle responsible for tonality (h*) and lightness (L*) increased. Again,
246 Reserva wines form Rioja prepared with the variety Syrah and the Coupage, showed
247 values relatively different to the wines prepared with the Tempranillo variety in spite of
248 having the same time-aging.

249 **<Table 5>**

250 *3.2. E- tongue: Discrimination capability*

251 The array of electrochemical sensors was immersed in the red wines. In all cases,
252 voltammograms showed a variety of peaks produced by components with redox activity
253 (i.e. polyphenols in the 0.4-0.8V regions) and by the electrode modifiers.

254 In general, it was observed that in aged wines, the anodic peak at +0.8 V showed higher
255 intensities than in voltammograms registered in younger wines (Figure 1). The increase is
256 due to the redox reactions of polyphenolic compounds formed during aging. Thus, this
257 increase is well correlated to the decrease of the phenolic content observed in TPI and
258 Folin-Cioacalteu, (as well as in the "red parameters" of Glories and CIELab analysis) that
259 occurs during the aging process in oak barrels where micro-oxygenation reduces the total
260 content of low molecular weight phenolic compounds as a result of condensation
261 reactions and increases the polymeric polyphenols which stabilize wine color (Behrends
262 & Weber, 2017). This effect has already been observed in e-tongues used to analyze
263 grape skins (Muñoz et al., 2018).

264 **<Figure 1>**

Each sensor showed different features depending on the modifier: carbonaceous electrodes (modified with carbon, CNT and MWCNT) showed anodic peaks at +0.5 and +0.8 V due to the oxidation of polyphenolic compounds of wines as well as a broad reduction peak at around 0.0 V. Sensor modified with PANI showed broad peaks, NiO showed the most intense responses while platinum could detect phenols and the decomposition of water followed by the oxidation of hydrogen at negative potentials (ca. -0.45 V).

The repeatability of the measurements was tested by calculating the coefficients of variation in the intensity for 10 consecutive cycles. The coefficients of variation were lower than 10%.

The differences observed from one wine to another are due to their different phenolic composition. That is, as each wine has a different phenolic composition, the oxidation and reduction peaks appear at different potentials and show different intensities. The precedent results demonstrated that the sensors included in the array produced a unique response for each wine. In consequence, the response of the array can be considered a fingerprint of each sample and can be used to discriminate wines.

Figure 2 shows the 2D scores plot obtained using the variables obtained using the kernel method. PC1 and PC2 explained the 56.9% and 20.9% of the covariance respectively (PC1+PC2+PC3 = 85.8%). The diagram shows that all wines analyzed could be clearly discriminated. In addition, wines with higher polyphenol index (Young and Crianza) were located in the upper part of the diagram, in the region of positive PC2, confirming

that the polyphenolic level plays an important role in the discrimination capabilities of the electronic tongue.

With the purpose of identifying outliers in the sampling, Hotelling T2 was performed at α=0.05 and after three PCA components. Hotelling T2-values for each sample were plotted under the critical test value and, therefore, no outliers were tagged.

<Figure 2>

3.3. ATR-FTIR: Discrimination capability

ATR-FTIR average spectra of red wines are presented in Figure 3. All wine samples gave rise to similar spectra patterns. The intense band detected in the 3700–2971 cm^{-1} region originated from compounds with –OH groups such as water and ethanol, which are major compounds in wine samples, was not useful in this work. The region 1500-1000 cm^{-1}, usually referred to as the "fingerprint" region, was selected for working range since the RSD (relative standard deviation) between absorption values for the samples were high in this region. Signals from phenols can be found in this region: the antisymmetric in-plane bending of $–CH_3$ at 1448-1444 cm^{-1}, the symmetric in-plane bending of $–CH_3$ at 1376-1373 cm^{-1}, the absorption at 1340-1339 cm^{-1} assigned to CH bending and CH_2 wagging, the peak at 1281-1278 cm^{-1} corresponding to in-plane bending of O-H, and the bands at 1207 cm^{-1}, 1110-1107 cm^{-1}, 1068-1062 cm^{-1} originated from the stretching vibration of C-O. The 1382 cm^{-1} absorption band attributes to the O-H in plane deformation in polyphenols. The deformation vibration of the C-C bonds in the phenolic

307 groups adsorb in the region of 1500-1400 cm^{-1}. These assignments are based on previous
308 work on phenolic compounds in wines (Silva, Feliciano, Boas, & Bronze, 2014;
309 Cozzolino, Cynkar, Shah, & Smith, 2011). ATR-FTIR spectra showed that the intensity
310 of these peaks in young wines (Joven Ribera and Joven Toro) was clearly higher than
311 long time-aged wines (Crianza, Reserva and Gran Reserva) because the polyphenolic
312 content in young wines is higher. Moreover, for the same D.O. Ribera wines absorbance
313 follows the sequence Joven, Crianza and Gran Reserva.
314 The repeatability of the measurements was tested by calculating the coefficients of
315 variation in the transmittance for 5 FTIR spectra. The coefficients of variation were lower
316 than 4%.
317 **<Figure 3>**
318 PCA scores plot for FTIR data is shown in Figure 4. In this case, the first PC, explained
319 98.8% of the variance (PC1+PC2+PC3 = 99.8%). FTIR signals were also able to
320 discriminate the wines analyzed. However, even if Young and Crianza wines were
321 mainly located on the left part of the diagram, this trend was not followed by the Crianza
322 Toro sample that appeared on the right part of the figure. This means that ATR-FTIR is
323 not so efficient to discriminate wines according to the polyphenolic content.
324 As in the case of e-tongue, Hotelling T2 was performed at α=0.05 and after three PCA
325 components. Also in this case the Hotelling T2-values for each sample were plotted under
326 the critical test value.
327

328 **<Figure 4>**

329

330 *3.4. Regression models to correlate e-tongue or FTIR with chemical parameters*

331 Regression models were built to correlate the e-tongue or the ATR-FTIR results with
332 TPI280, Folin-Ciocalteu, Glories or CIElab parameters using PLS-1. The validation
333 method used for PLS analysis was full cross validation (n=40 samples). Calibration fits
334 the model to the available data, while validation checks the model for new data. Results
335 of PLS-1 models are shown in Table 6. Both techniques showed good correlations with
336 the 14 parameters analyzed. Particularly good correlations were found with the TPI280
337 with the lowest number of latent variables (2 for e-tongue and 3 for ATR-FTIR). This is
338 illustrated in Figure 5 where the explained variance vs. the number of factors for the
339 PLS-1 models are represented. The models performed for each technique were
340 representative due to residual variance curves (calibration and validation) for each
341 technique are close together. As observed in the Figure the model correlating e-tongue
342 and TPI280 requires 2 factors (or latent variables) to explain 90% of the variance. The
343 similarity between calibration and validation curves corroborated the high quality of the
344 model. On the other hand, the PLS-1 model correlating the FTIR and the TPI280 requires
345 3 latent variables to explain the 90% of the variance.
346 In conclusion, according to PLS analysis results, it can be concluded that e-tongue
347 analysis has a certain advantage over FTIR because it shows better correlations (higher

coefficients of correlations and lower residual errors) with a lower number of latent variables (factors).

<Table 6>

<Figure 5>

An interesting advantage of the proposed multivariate techniques is that they reduce the time required to obtain information about 14 parameters.

The time required to analyze a wine sample with the e-tongue was about 6.5 minutes (including 10 cycles to obtain a reliable response) and 10 minutes in the case of the FTIR (300 scans). When systems are trained appropriately, the statistical data treatment takes only few seconds.

In contrast, the assessment of the fourteen parameters studied here, requires four different sets of experiments (TPI, Folin-Ciocalteu, CIELab and Glories parameters). The time required in each technique is different, but time ranges from 5 to 20 minutes (for instance, Folin requires 30 minutes before measuring the absorbance at 750 nm). Other techniques such as HPLC require larger times (typically 80 minutes/sample). Therefore, one can conclude that the use of multivariate techniques like e-tongue and FTIR means a clear advantage for reducing the time of the analysis.

4. Conclusions

Two multiparametric techniques, e-tongue and ATR-FTIR combined with an appropriate pre-processing method could be successfully used to discriminate red wines according to

their phenolic content. Using PLS-1, both techniques showed good correlations with 14 parameters related to the polyphenolic content and can be used to predict simultaneously TPI, Folin-Ciocalteu, CIELab and Glories parameters in a single experiment. This is an important advantage for the wine industry where time is a critical factor. E-tongue showed better correlations (higher coefficients of correlations and lower residual errors) with a lower number of latent variables (factors) than ATR-FTIR. In summary, these systems provide information about the phenolic content in a fast and reliable manner assessing more than one parameter at once.

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Conflicts of Interest

The authors declare that they have no conflict of interest.

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List of Tables

Table 1. Spanish red wines under study

Ageing	D.O.	*Vitis vinifera L.* Grape Variety
Joven	Ribera	Tempranillo (Tinta del País)
Crianza	Ribera	Tempranillo (Tinta del País)
Gran Reserva	Ribera	Tempranillo (Tinta del País)
Joven	Toro	Tempranillo (Tinta de Toro)
Crianza	Toro	Tempranillo (Tinta de Toro)
Reserva	Toro	Tempranillo (Tinta de Toro)
Reserva	Rioja	Syrah
Reserva	Rioja	Tempranillo, Graciano, Mazuelo (denoted as “coupage”)

Table 2. List of the SPE sensors forming the array

DropSens Ref.	SPE working electrode
DRP-110	Carbon
DRP-110NI	Nickel (II) Oxide / Carbon
DRP-110PANI	Polyaniline / Carbon
DRP-110CNT	Carboxyl functionalized Multi-Walled Carbon Nanotubes / Carbon
DRP-110SWCNT	Carboxyl functionalized Single-Walled Carbon Nanotubes / Carbon
DRP-550	Platinum

Table 3. TPI280 and Folin-Ciocalteu Indexes measured in wines.

Red wine	Absorbance (280 nm)	TPI280	Absorbance (750 nm)	Folin-Ciocalteu Index
Joven (D.O. Ribera)	0.67±0.05	67±5	0.73±0.08	73±8
Crianza (D.O. Ribera)	0.64±0.08	64±8	0.69±0.04	69±4
Gran Reserva (D.O. Ribera)	0.56±0.06	56±6	0.61±0.05	61±5
Joven (D.O. Toro)	0.82±0.02	82±2	0.81±0.07	81±7
Crianza (D.O. Toro)	0.64±0.07	64±7	0.70±0.09	70±9
Reserva (D.O. Toro)	0.58±0.03	58±3	0.65±0.03	65±3
Reserva (D.O. Rioja) "Syrah"	0.57±0.04	57±4	0.57±0.06	57±6
Reserva (D.O. Rioja) "Coupage"	0.59±0.04	59±4	0.64±0.08	64±8

Data: mean±SD (n=3).

9 **Table 4.** Glories color parameters of red wines under study.

Red wine	CD	CI	H	dA%	Y%	R%	B%
Joven (D.O. Ribera)	1.26±0.35	1.47±0.25	0.64±0.09	81.56±2.19	33.42±3.07	52.52±3.85	14.05±1.81
Crianza (D.O. Ribera)	1.09±0.17	1.27±0.19	0.78±0.06	75.08±3.15	37.88±3.21	48.30±3.12	13.81±1.53
Gran Reserva (D.O. Ribera)	0.94±0.23	1.08±0.17	0.81±0.07	72.17±3.33	39.26±2.37	48.47±2.89	12.28±1.52
Joven (D.O. Toro)	1.64±0.31	1.87±0.23	0.54±0.05	83.65±4.52	30.89±2.72	56.80±2.78	12.31±1.79
Crianza (D.O. Toro)	1.03±0.12	1.17±0.14	0.76±0.05	74.36±3.62	37.84±3.91	49.91±3.78	12.24±1.67
Reserva (D.O. Toro)	0.99±0.19	1.13±0.21	0.89±0.07	68.80±2.70	41.26±2.37	46.50±2.56	12.24±1.89
Reserva (D.O. Rioja) "Syrah"	1.29±0.15	1.49±0.24	0.76±0.08	75.61±3.26	37.36±3.62	49.36±3.56	13.28±2.31
Reserva (D.O. Rioja) "Coupage"	0.94±0.10	1.07±0.21	0.87±0.09	69.48±2.57	40.82±2.8	47.10±3.41	12.08±1.57

10 Data: mean±SD (n=3).

11 CD, color density; CI, color intensity; H, hue/tonality; dA%, proportion of red color produced by
12 flavylium cations; Y%, proportion of yellow color; R%, proportion of red color; B%, portion of blue
13 color.

14

15 **Table 5.** CIELab color coordinates of the red wines under study.

Red wine	**a***	**b***	**L***	**C***	**h***
Joven (D.O. Ribera)	39.74±2.37	1.13±0.13	61.48±2.50	39.76±3.12	1.63±0.16
Crianza (D.O. Ribera)	31.18±1.86	7.42±0.52	67.16±2.21	32.05±2.75	13.39±1.22
Gran Reserva (D.O. Ribera)	28.17±1.92	9.00±0.45	71.95±1.81	29.57±2.44	17.72±1.63
Joven (D.O. Toro)	51.07±3.20	0.85±0.03	54.63±2.34	51.08±3.23	0.95±0.06
Crianza (D.O. Toro)	32.27±2.94	6.47±1.12	68.50±2.11	32.91±1.77	11.34±1.01
Reserva (D.O. Toro)	25.91±2.02	12.79±1.33	71.89±1.89	28.89±1.82	26.27±1.31
Reserva (D.O. Rioja) "Syrah"	36.35±1.34	8.16±0.84	63.01±2.10	37.25±1.64	12.65±0.82
Reserva (D.O. Rioja) "Coupage"	26.68±1.97	10.96±1.35	72.51±2.87	28.84±1.82	22.33±1.12

16 Data: mean±SD (n=3).

17 a*, redness; b*, yellowness; L*, lightness; C*, saturation; h*, hue angle.

18

Table 6. Results of Partial Least Squares regressions models (PLS-1).

	Electronic Tongue data					
	Parameter	**R^2_C (a)**	**$RMSE_C$ (b)**	**R^2_P (c)**	**$RMSE_P$ (d)**	**Factors**
	TPI280	0.9343	2.0109	0.8956	2.6001	2
	Folin-C.	0.9276	1.8972	0.8944	2.3496	3
Glories color parameters	**CD**	0.9726	0.0371	0.9497	0.0525	3
	CI	0.9712	0.0440	0.9475	0.0620	3
	H	0.9873	0.0121	0.9689	0.0198	3
	dA%	0.9885	0.5301	0.9720	0.8631	3
	Y%	0.9869	0.3806	0.9707	0.5944	3
	R%	0.9822	0.4188	0.9623	0.6355	3
	B%	0.9701	0.1292	0.9558	0.1640	3
CIELab color parameters	**a***	0.9893	0.8141	0.9800	1.1590	3
	b*	0.9845	0.4963	0.9625	0.8061	3
	L*	0.9754	0.9232	0.9496	1.3800	3
	C*	0.9927	0.6063	0.9813	1.0137	3
	h*	0.9905	0.8160	0.9793	1.2577	3
	ATR-FTIR data					
	Parameter	**R^2_C (a)**	**$RMSE_C$ (b)**	**R^2_P (c)**	**$RMSE_P$ (d)**	**Factors**
	TPI280	0.9195	2.2255	0.8908	2.7049	3
	Folin-C.	0.9029	2.1966	0.8538	2.8123	4
Glories color parameters	**CD**	0.9649	0.0420	0.9416	0.0566	4
	CI	0.9635	0.0495	0.9392	0.0667	4
	H	0.9305	0.0284	0.9125	0.0332	3
	dA%	0.9490	1.1164	0.9339	1.3264	3
	Y%	0.9441	0.7871	0.9289	0.9265	3
	R%	0.9645	0.5912	0.9487	0.7419	4
	B%	0.9579	0.1533	0.9162	0.2258	5
CIELab color parameters	**a***	0.9234	2.1737	0.9071	2.4988	3
	b*	0.9611	0.7864	0.9401	1.0183	4
	L*	0.9749	0.9323	0.9603	1.2252	4
	C*	0.9762	1.0964	0.9634	1.4179	4
	h*	0.9713	1.4192	0.9553	1.8506	4

(a), (c) Squared correlation coefficients in calibration and prediction.

(b), (d) Root mean square errors in calibration and prediction.

Figure 1

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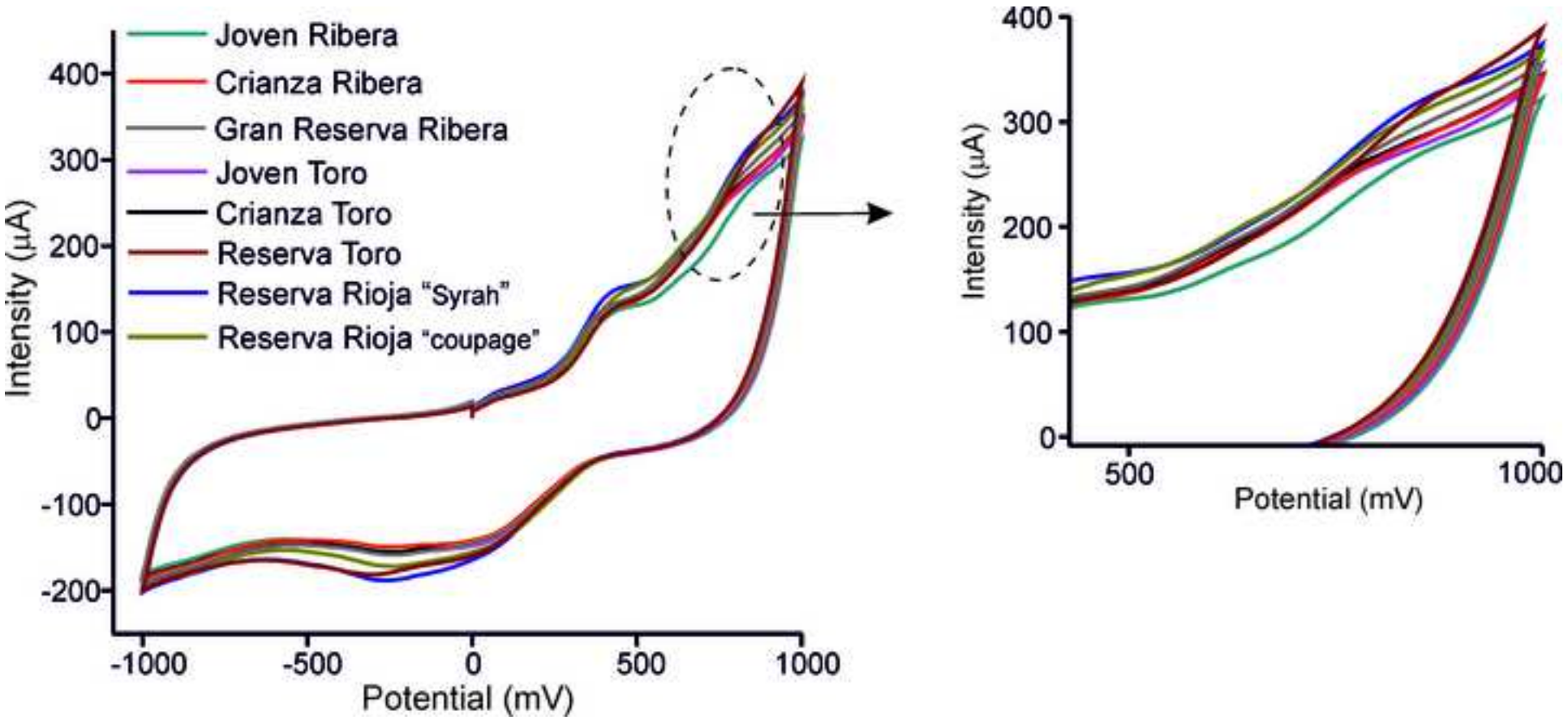

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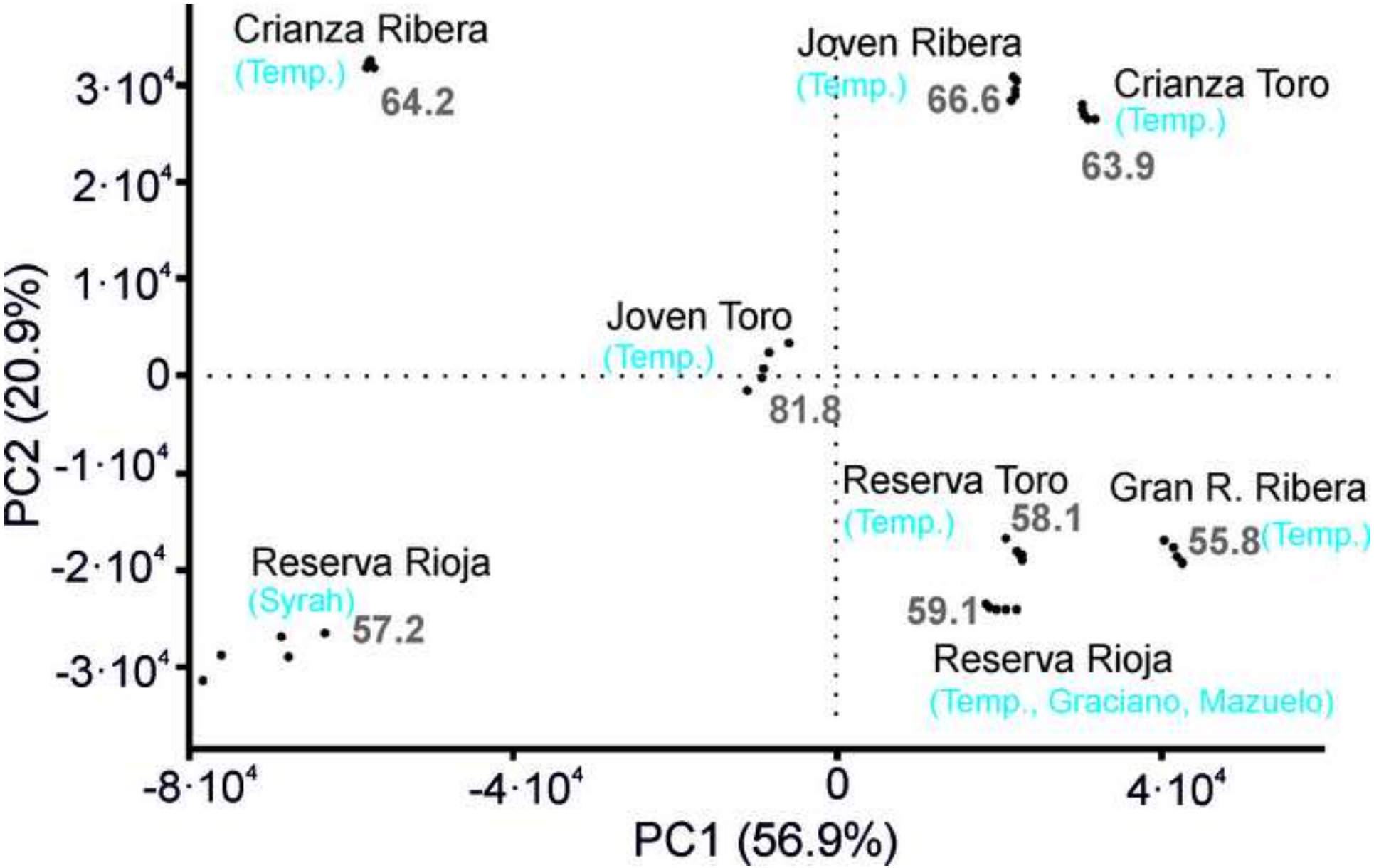

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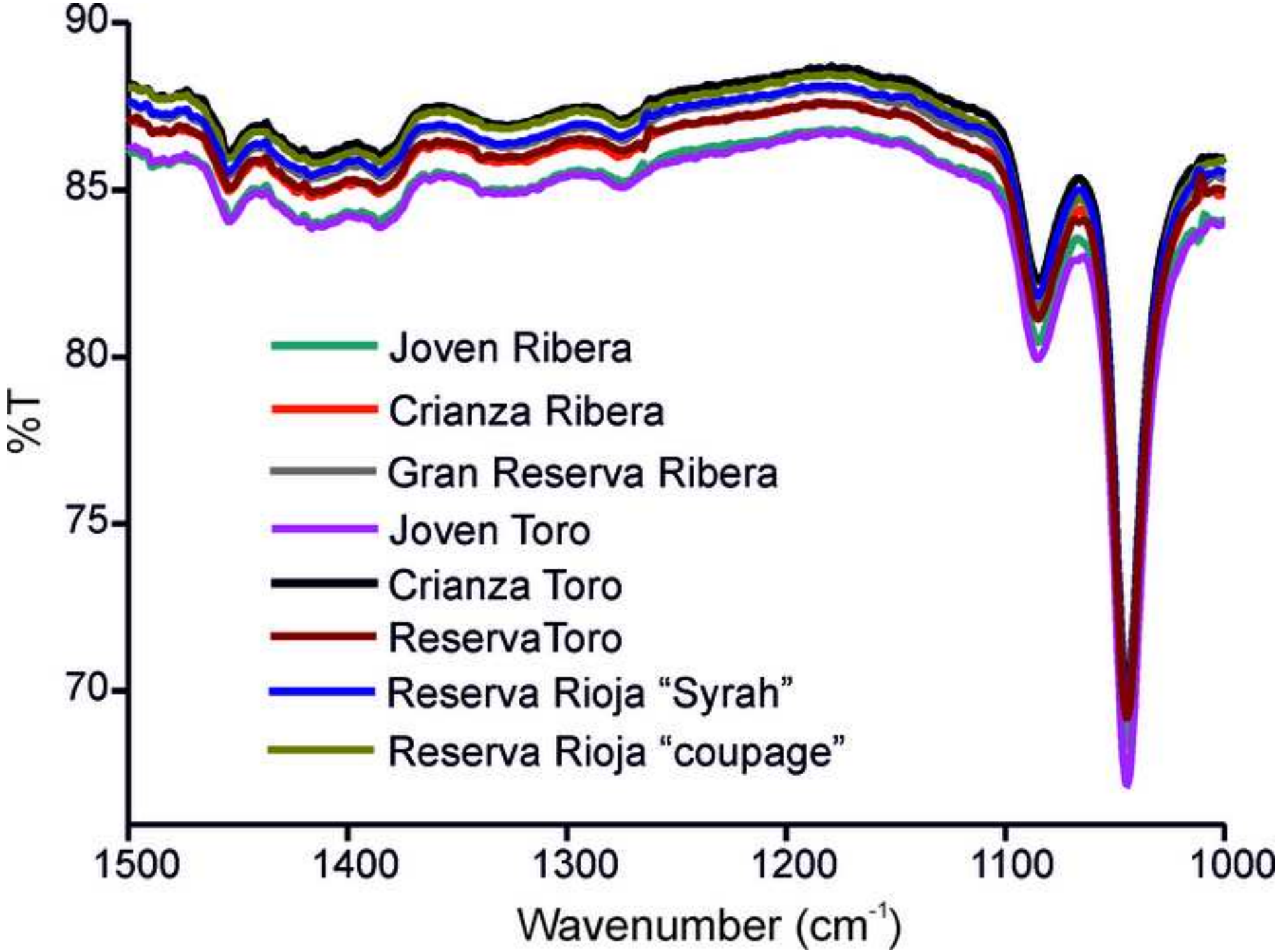

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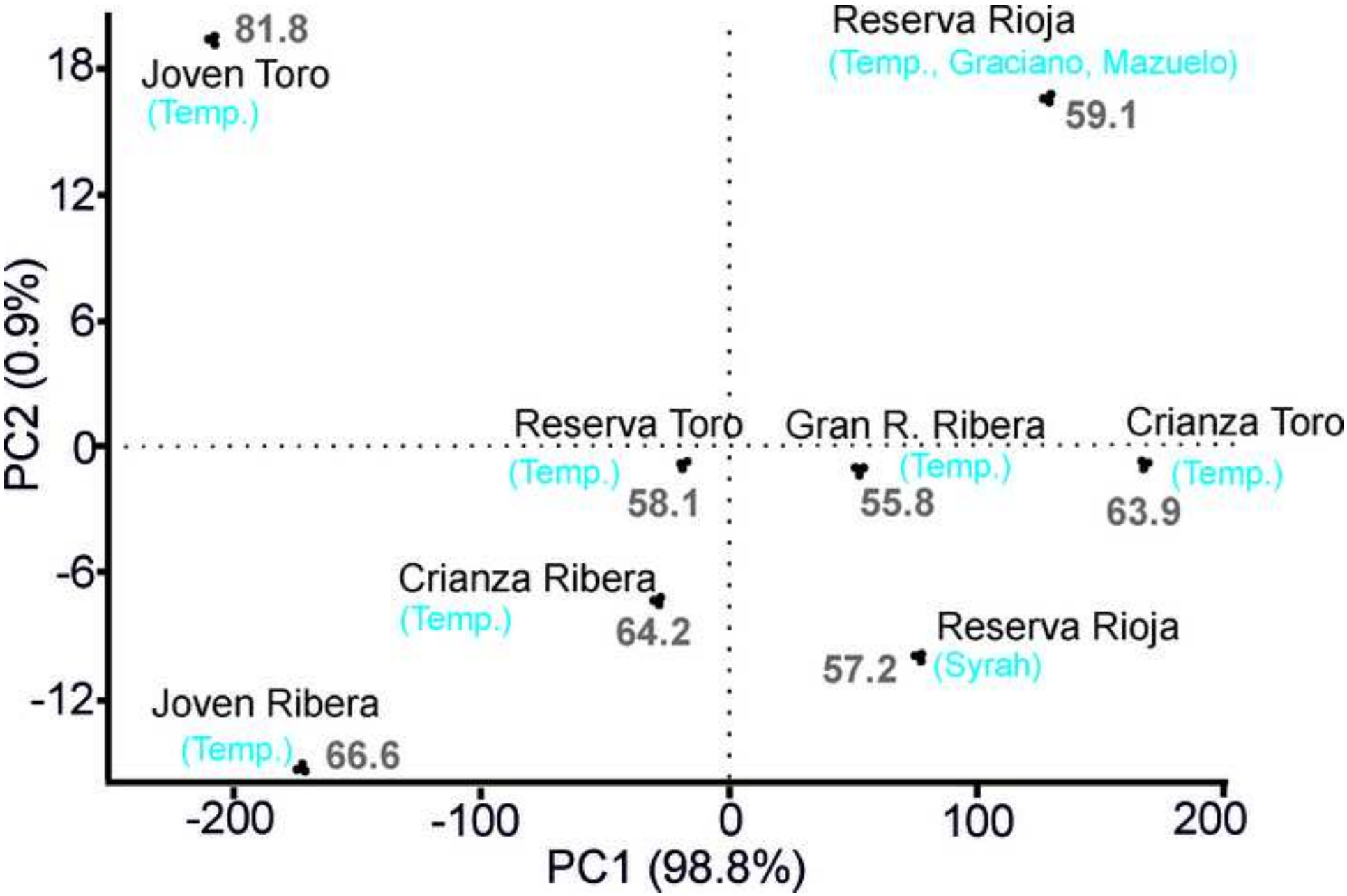

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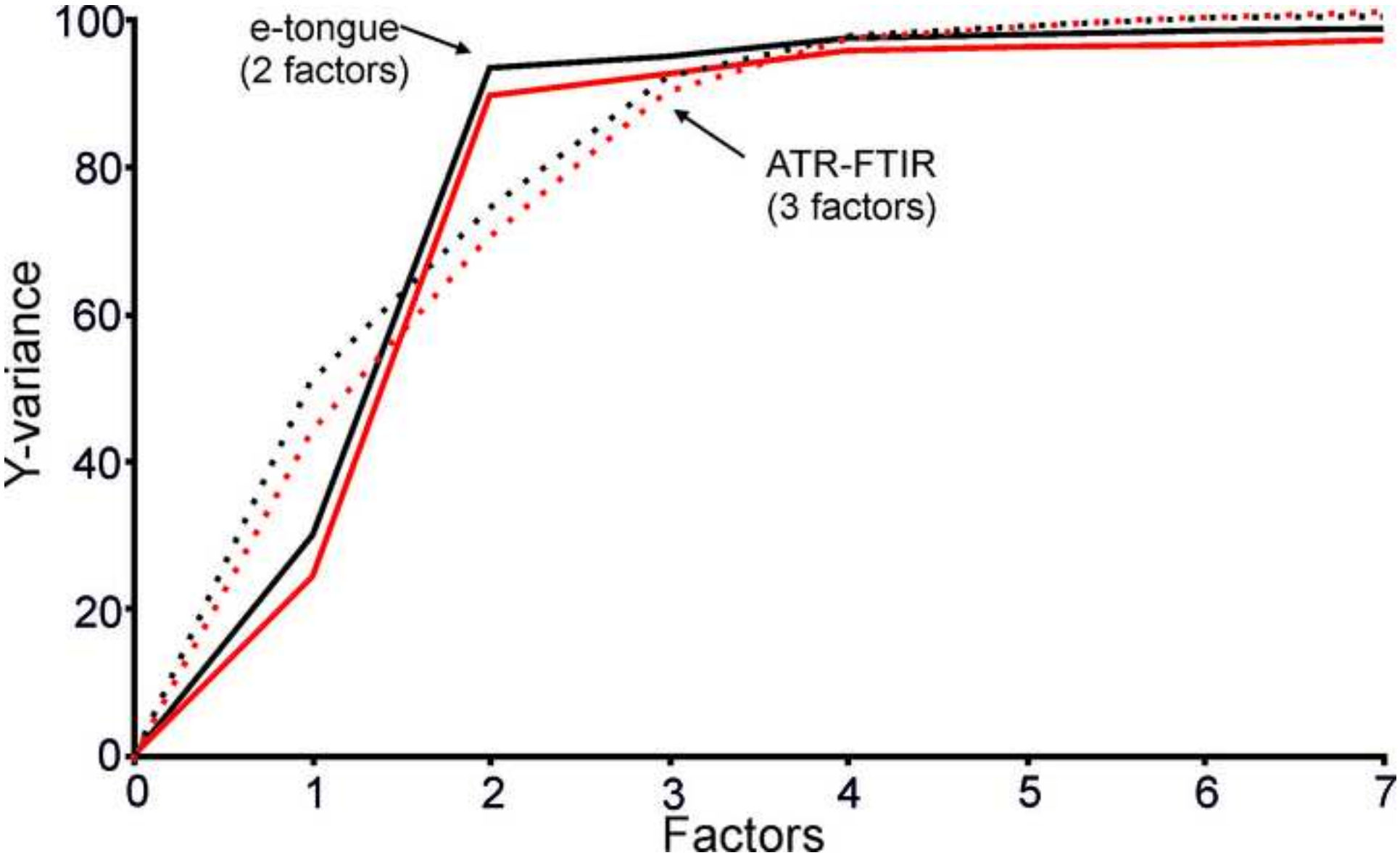

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Conflicts of Interest

The authors declare that they have no conflict of interest.