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Polymeric chemosensor for the colorimetric determination of the total polyphenol index (TPI) in wines

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Abstract

We have developed a new method for the rapid and inexpensive determination of the total polyphenol index (TPI) in wines by simply immersing our sensory film in red or white wines and visually checking the colour change (qualitative analysis) or by analysing a photo taken of the film with a smartphone (quantitative analysis). This sensory material is straightforward and inexpensively prepared; it requires no monomer synthesis, is based on 100% commercially available monomers, and contains benzenediazonium salt motifs, which in the presence of phenols and/or polyphenol-based structures produce coloured diazo compounds. These sensory motifs are chemically anchored to the polymeric structure, and, accordingly, no migration of organic substances from the material occurs in the sensing process. Our method needs neither reagents nor sample pretreatment and has been contrasted with the standard TPI determination, i.e., measuring the absorbance of diluted wine at 280 nm, obtaining reliable data for white and red wines.

Keywords: Polymeric sensors, solid phase reactions, colorimetric sensors, polyphenol sensors, TPI

1. Introduction

Polyphenols are organic compounds present in many vegetables, fruits, dietary spices and herbs (Chan, Gan, Shah, & Corke, 2018; Manach, Scalbert, Morand, Rémésy, & Jiménez, 2004; Mayer & Harel, 1979; Scalbert & Williamson, 2000). They are characterized by having at least two phenol groups per molecule (Bravo, 2009), which exhibit well-known antioxidant activity, have an important role in the prevention of

some illnesses, such as cancer and cardiovascular diseases (Khan & Mukhtar, 2018; Manach et al., 2004; Quiñones, Miguel, & Aleixandre, 2012; Scalbert, Manach, Morand, Rémésy, & Jiménez, 2005; Xing, Zhang, Qi, Tsao, & Mine, 2019), and exhibit other properties, such as antimicrobial activity (Fei et al., 2018). Other benefits have been attributed to polyphenols, for example, the inhibition of the oxidation process of LDL cholesterol, a decrease of the inflammatory process in an atheroma plaque, the inhibition of platelet aggregation, astringency, the stimulation of nitric oxide synthesis, the stabilization of collagen fibres of the arterial wall, and their performance as phytoestrogens, such as isoflavones and lignans (Boulet et al., 2016; Creus, 2004; Meyer, A. S., Yi, O., Pearson, D. A., Waterhouse, A. L., Frankel, 1997; Shrikhande, 2000). These compounds are synthetized by plants as secondary metabolites and assume a role as a very important protecting agent (Gutiérrez Maydata, 2002). Polyphenols are present in grapes at high concentrations, and specifically, the concentration in red grapes is considerably higher than that in white grapes. A large part of the grape's polyphenols transfers to the wine in the fermentation process, which converts wine into a polyphenol-rich matrix containing flavonoids (e.g., catechin) and non-flavonoids (e.g., gallic acid or resveratrol) (Cavallini, Straniero, Donati, & Bergamini, 2016; Gutiérrez Maydata, 2002).

In addition to the antioxidant properties, polyphenols are also related to the colour of the wines (Cejudo-Bastante et al., 2016; El Darra et al., 2016). Thus, the control of the concentration of these compounds in wines is very relevant. In fact, the determination of polyphenols in wines is one of the most common analyses in wineries (Cerezo et al., 2008; Pérez-Lamela, García-Falcón, Simal-Gándara, & Orriols-Fernández, 2007). There are many methods for calculating this concentration, including the total polyphenol index (TPI) and the Folin-Ciocalteu method (Cetó et al., 2012; Kedrina-Okutan et al., 2018; Tsao & Yang, 2003), both of which are spectrophotometric methods. The first is based on the measurement of the polyphenol absorbance band at 280 nm to obtain the I_{280} parameter, and the second is related to the composition of polyphenols as a reducing agent (Singleton et al., 1999). High-

50 performance liquid chromatography (HPLC) is another alternative (Fracassetti, Gabrielli, Costa, Tomás-
51 Barberán, & Tirelli, 2016; Lamuela-raventos & Waterhouse, 1994; Revilla & Ryan, 2000; Schoedl,
52 Forneck, Sulyok, & Schuhmacher, 2011) that is more precise and able to distinguish between different
53 polyphenols. Finally, other indirect calculation methods related to the antioxidant activity of the
54 polyphenols can be found in the bibliography. In these methods, the polyphenols react with different
55 compounds, such as 2,2-azino-bis(3-ethylbenz-thiazoline-6-sulphonic acid) (ABTS) (Pérez-Jiménez &
56 Saura-Calixto, 2008), 2,2-diphenyl-1-picrylhydrazyl (DPPH) (Kabir, Sultana, & Kurnianta, 2015), or *N*,*N*-
57 dimethyl-*p*-phenyldiamine dihydrochloride (DMPD) (Sendamangalam, Choi, Seo, & Kim, 2011). All of
58 these methods require reagents, measuring equipment such as spectrophotometers, and usually a
59 pretreatment of the wine sample (dilution, dealcoholisation, pH adjustment, extraction with different
60 solvents, etc.).

61 In this study, we developed a sensory material for the easy and direct colorimetric quantification
62 of phenols in red and white wines. The detection and quantification are carried out without
63 pretreatment of the sample. The experimental procedure is simple: the sensory material is immersed in
64 the wine for some minutes and the colour evolution is processed by taking a picture with a smartphone
65 and further analysing the digital colour definition using the RGB colour model (RGB stands for red, green
66 and blue, respectively), as previously described (Bustamante et al., 2019).

67 **2. EXPERIMENTAL**

68 **2.1. Materials**

69 All materials and solvents were commercially available and used as received unless otherwise indicated.
70 The following materials and solvents were used: 2,2'-azobis(2-methylpropionitrile) (AIBN) (Aldrich, 98%);
71 1-vinyl-2-pyrrolidone (VP) (Aldrich, 99%); methyl methacrylate (MMA) (Aldrich, 99%); 4-aminostyrene
72 (Aldrich, 99%); sodium nitrite (VWR, 99.5%); absolute ethanol (VWR, >99.9%); D-glucose (VWR, 99.5%);

D-fructose (Aldrich, >99%); iron (III) nitrate nonahydrate (Aldrich, >98%); copper (II) nitrate trihydrate (Aldrich, 99%); and sodium sulphite (Aldrich, >98%).

Six red wines (**RWs**) and 6 white wines (**WWs**) were chosen for the analysis. They were used without pretreatment, and they are listed in Table S1 (Electronic Supplementary Information, ESI). They have different appellations with an origin from Spain.

2.2. Measurements and instrumentation

The sensory film was punched to obtain 8 mm diameter discs, which were dipped into different wines for 20 minutes. The quantitative method was carried out by taking a digital photo of these sensory discs in the presence of a colour reference. This reference reduces the errors related to the different illumination conditions in different photos (Bustamante et al., 2019; Pascual et al., 2019; S. Vallejos, Reglero, García, & García, 2017; Saúl Vallejos et al., 2018). The photographs were taken with the iPhone SE smartphone, and the R (red) component of the RGB parameters was used for the quantification of the polyphenol concentration. Ambient light usually affects the image quality and repeatability of the analysis. To overcome this, the procedure was optimized by taking images in a homemade retro-illumination box that broadly maintained the illumination conditions. Moreover, a colour reference, in our case, a small piece of coloured poly(methyl methacrylate), was also used to further normalize the colour response with conventional image processing software (see ESI S5, Figure S3) (S. Vallejos et al., 2017).

Additionally, the UV-Vis spectrum of each wine was recorded using a Hitachi U-3900 UV/Vis spectrophotometer.

Thermogravimetric analysis of the starting materials was carried out both under a synthetic air atmosphere and under a nitrogen atmosphere, with a TA Instruments Q50 TGA analyser at 10 °C min^{-1}, using 10-15 mg of sample. Differential scanning calorimetry spectra were recorded at 20 °C min^{-1} in a TA

Instruments Q200 DSC analyser under a nitrogen atmosphere, using 10-15 mg of sample. Tensile property analysis was carried out on a Shimadzu EZ Test Compact Table-Top Universal Tester using 5 × 9.44 × 0.122 mm samples at a testing speed of 1 mm min^{-1}.

The infrared spectra of the membranes (FT-IR) were recorded using a JASCO FT-IR 4200 (4000–400 cm^{-1}) spectrometer.

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were recorded on an Agilent 7500 ICP-MS spectrometer.

The water swelling percentage (**WSP**) of the films in water was calculated using the weight of a dry sample (ω_d, dried at 60 °C for 1 hour) and the weight of a water-swelled sample (ω_s, immersed in distilled water for 1 hour) using the following expression: $\mathbf{WSP} = 100 \times [(\omega_s-\omega_d)/\omega_d]$.

2.3. Polymer synthesis

The preparation of the starting material ($\mathbf{F_0}$) was previously described (Bustamante et al., 2019), and its structure is based on 100% commercially available monomers (vinylpyrrolidone (**VP**), methyl methacrylate (**MMA**) and 4-aminostyrene ($\mathbf{SNH_2}$), in a molar ratio of 49.5/49.5/1, as shown in Scheme 1a). The aniline pendant groups can be easily converted to benzenediazonium salt pendant groups by immersion in an aqueous acid solution of sodium nitrite (1M of HCl, 0.05M of $NaNO_3$). The resulting sensory material ($\mathbf{F_1}$) reacts with phenols, and its polymeric structure is shown in Scheme 1b.

Scheme 1

3. RESULTS AND DISCUSSION

The reactivity of benzenediazonium salts has been widely studied for decades (Colbert, Lacy Vol, C Colbert, & Lacy, 1890; Lewis & Miller, 1953), and the diazo compounds formed in the presence of a phenol structure are currently used for the preparation of dyes and pigments. In this work, we have

taken advantage of this reaction, adapting it for use in the solid phase within the solid sensory material. In comparison with the most commonly used methods for the determination of TPI (Tsao & Yang, 2003), the proposed material makes the analysis faster, easier and less expensive.

In our previous work, we studied this solid phase reaction with a number of phenols, providing different colours for each studied phenol (Bustamante et al., 2019). We also studied the formed solid phase compounds by FT-IR, where a band centred at 1576 cm^{-1} could be observed due to the formation of the azo compounds. Due to the high concentration of polyphenols in wines, the limit of detection is not relevant for this application, but it should be noted that this limit is quite low at the ppb level. The lack of stability of the benzenediazonium salts in solution is also well known due to their high reactivity. However, this behaviour was not observed inside the polymeric structure, and our material is stable for weeks without special care under ambient conditions. This fact is mandatory for their hypothetical use as a polyphenol sensor in wineries, making the control of these substances more direct (no pretreatment of samples), easier, less expensive and not dependent upon measurement equipment (such as a spectrophotometer).

3.1. Water uptake

Our goal is to have this material work in water media with organic compounds. Thus, we carried out the detection of target chemical species in water using organic chemosensors, which are usually not soluble in aqueous media. For this purpose, we anchored the organic sensing motifs to a hydrophilic crosslinked material (hydrogel-like polymer network). The water swelling percentage (**WSP**) of the network is a critical parameter. The higher the WSP, the lower the response time (because the water-swelled target species enter the network by diffusion). On the other hand, an increase in the WSP impairs the mechanical properties (manageability). Thus, as lower response times and good mechanical properties are key parameters, a balance is necessary. Accordingly, **WSP** values between 50 and 100% are usually

found to be appropriate for these kinds of materials for their application as solid sensors for water environments. This parameter is controlled by the feed ratio between monomers, which in this case is the molar ratio between **VP** (hydrophilic) and **MMA** (hydrophobic).

Accordingly, we tuned the chemistry of the starting material to ha a **WSP** of 53%. This is a manageable material that can be handled without care under ambient conditions by unskilled personnel (the material can be handled, bent, exposed to moisture and light, etc.). At the same time, the sensory materials derived show reasonable response times, as described later. However, the ratio of feed monomers in the material preparation could be further optimized chemically to obtain faster sensors by increasing the water uptake or physically by diminishing the thickness of the sensory films.

3.2. Thermal and mechanical characterization of F_0

To be considered manageable, a film must have different characteristics: at least reasonably good mechanical properties and thermal stability under ambient conditions (temperature and light). This manageability is essential for sensing applications where the detection process (TPI analyses within minutes) can also be carried out by non-trained personnel.

Regarding the thermal behaviour of the film **F_0**, the thermal resistance was determined by TGA by calculating the temperature at which 5% (T_5) and 10% (T_{10}) weight loss of the film was observed, under both inert and oxidant atmospheres. In nitrogen, T_5 and T_{10} were 353°C and 367°C, respectively, and in synthetic air, the temperatures were 328°C and 344°C, respectively. On the other hand, the material was further characterized by analysing its glass transition temperatures (*Tg*) by DSC, obtaining a value of 140°C. Both TGA and DSC graphs are shown in Section S2 (electronic supplementary information, ESI).

The mechanical properties were tested with testing strips cut from $\mathbf{F_0}$. Young´s modulus was 571 MPa. These data, and the well above room temperature degradation temperatures analytically confirm the manageability visually observed upon film handling.

3.3. Comparison with other methods

The figure of merit of the methods used in wineries for the determination of the TPI (Table 1) shows the advantages of using our sensory films. Visual detection, response time and cost are considered. The cost is mainly related to the need for trained personnel, pretreatment of the samples, and use of analytical equipment. The preparation time of the samples is not depicted in the table, as it is not published data and it is difficult to estimate. However, this time is usually high when conventional techniques are used. In our case, neither pretreatment nor preparation of the sample are needed, and the cost to prepare a disc for one analysis is very low, approximately 0.002 euros. Additionally, non-skilled personnel can carry out the analysis.

174 **Table 1**

175 **3.4. Total Polyphenol Index (UV-Vis method)**

176 Red and white wines were diluted with distilled water 100- and 25-fold, respectively, to obtain
177 absorbance values below 1. The absorbance of the samples was checked at 280 nm (Tsao & Yang,
178 2003)[Error! Bookmark not defined.] and was measured 5 times. The absorbance at this specific wavelength is
179 characteristic for all the polyphenols, including single ring phenolic acids (hydroxybenzoic acid and
180 hydroxycinnamic acid derivatives), procyanidins (flavan-3-ols), flavonols, tannins, anthocyanidins, and
181 dihydrochalcones. The TPI was calculated by multiplying the obtained absorbance at 280 nm (average)
182 and the dilution factor (I_{280}). This method has been selected as the reference method for this work, and
183 the results are shown in Table 2.

184 Table 2

3.5. Total Polyphenol Index, proposed RGB method

The chosen wines have different appellations of origin and were manufactured in different years. This wide variety of samples was specifically selected to study the influence of different types of grapes from different regions of Spain in the proposed method.

F_1 discs were directly immersed in each wine at 20°C for 20 minutes. The measurements were performed in triplicate, and the discs were washed with a mixture of water:ethanol (88:12) before being photographed. The R parameter obtained from the digital photo (RGB colour parameters) was used for the graphical representation *vs.* the I_{280} (Figure 1). The fitting equations and the RGB parameters are depicted in Section S3 (ESI).

Figure 1

3.6. Interference study

We know that any phenol structure can be a chemical interferent for the measurement because the material in this method was designed to detect the total amount of phenol-based structures.

However, wines contain other species, such as metals. Accordingly, all the wines were measured in duplicate in an ICP-MS spectrometer and the complete analysis report is shown in Section S7 (ESI). We observed large differences between the samples; some of the most remarkable differences in red wines were the concentration of phosphorous between RW1 and RW3 (87.67 and 170.56 ppm, respectively), the concentration of silicon between RW1 and RW2 (30.46 and 72.83 ppm, respectively), the concentration of iron between RW4 and RW6 (6.21 and 0.87 ppm, respectively) and the concentration of cooper between RW4 and RW6 (57.4 and 16.3 ppb, respectively). Additionally, differences were observed in white wines, such as the concentration of potassium between WW1 and WW3 (653.46 and

208 2195.52 ppm, respectively), the concentration of iron between WW1 and WW3 (0.48 and 5.84 ppm,
209 respectively) and the concentration of cooper between WW3 and WW4 (43.2 and 15.2 ppb,
210 respectively). Despite these results, the measurement of the total polyphenol concentration was not
211 affected, since no interference was observed in the curve fitting shown in Figure 1.

212 Additionally, we carried out an interference study with 5 of the most abundant species in wines,
213 including glucose, fructose, sulphites, Fe(III), and Cu(II). Two wines were randomly chosen (WW3 and
214 RW5), and 6 discs of $\mathbf{F_1}$ were dipped in pure wine and wine spiked with each interferent species (at 10^{-2}
215 M concentration). The discs were submerged for 20 minutes, washed with water:ethanol (88:12), and
216 photographed. As shown in Figure 2, no remarkable interference was observed in the obtained R
217 parameter of the digital photograph.

218
219
220 **Figure 2**
221
222 **4. Conclusions**

223 In short, we have developed a new method for the direct determination of the total polyphenol index in
224 wines by using a film-shaped polymeric sensor made from 100% commercially available monomers. The
225 proposed experimental procedure requires no reactants, no expensive equipment, and can be easily
226 carried out by unskilled personnel by simply immersing the material in the wine and taking and
227 analysing a photo. The sensor works both in white and red wines, and some characteristics of the
228 material (such as the response time or the hydrophilicity) could be adapted “a la carte” to specifications
229 by modifying the molar ratio of the monomers to tune its colour response towards polyphenols or its
230 hydrophilicity. Additionally, no interference was observed with the addition of 5 of the most abundant

231 species in wines (glucose, fructose, Cu(II), Fe(III), sulphites) or between wines with different appellations
232 of origin.

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237 **Conflict of interest**

238 The authors declare that they have no conflict of interest.

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1 **Tables**

2

3 **Table 1.** Comparative table of different polyphenol analytical methods.

4 **Table 2.** The absorbance data for the diluted red (RW) and white (WW) wines and the I_{280} value.

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Table 1. Comparative table of different polyphenol analytical methods.

Method name	Detection method	Low cost	Response time (min)	Naked eye detection	Reference
TPI (reference method)	UV-Vis	No	0.5 – 1	No	(Kuskoski, Asuero, Troncoso, Mancini-Filho, & Fett, 2005)
Folin-Ciocalteu	Redox reaction & UV-Vis	No	15	No	(Kuskoski et al., 2005)
Price & Butler	Redox reaction & UV-Vis	No	15	No	(Graham, 1992)
CUPRAC	Redox reaction & UV-Vis	No	60	No	(Apak et al., 2007)
HPLC	HPLC	No	30	No	(Lamuela-raventos & Waterhouse, 1994)
	UPLC –MS/MS	No	5	No	(Lamuela-raventos & Waterhouse, 1994)
	HPLC - DAD	No	18	No	(Türköz Acar, Celep, Charehsaz, Akyüz, & Yeşilada, 2018)
Cerium nanoparticles	Redox reaction & colorimetry (RGB)	No	10	Yes	(T. A. Cenusa, n.d.)
Capillary electrophoresis	Electrophoresis	No	110	No	(Arribas et al., 2014; Godoy-Navajas, Aguilar-Caballos, & Gómez-Hens, 2015)
Laccase enzyme & nanoparticles	Laccase/Tb_2O_3 nanoparticles & fluorimetry	No	51	No	(Godoy-Navajas et al., 2015)
	Lacasse/silver nanoparticles & amperometry	No	-	No	(Chawla, Rawal, Kumar, & Pundir, 2012)
Flow injection analyser	Microfluidic flow injection analyser with embedded optical fibres	No	0.33	No	(Oscar, Olguín-Contreras, & Cañizares-Macías, 2017)
F_1	Digital picture (RGB parameters defining the digital colours)	Yes	20	Yes	This work

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Table 2. The absorbance data for the diluted red (RW) and white (WW) wines and the I_{280} value.

	ABS 280 average (nm)	Dilution factor	I_{280}
RW1	0.4720	100	47.20
RW2	0.5144	100	51.44
RW3	0.5362	100	53.62
RW4	0.5400	100	54.00
RW5	0.7974	100	79.74
RW6	0.9430	100	94.30
WW1	0.3098	25	7.75
WW2	0.2814	25	7.03
WW3	0.2688	25	6.72
WW4	0.1832	25	4.58
WW5	0.2896	25	7.24
WW6	0.3264	25	8.16

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Figures and Schemes

Scheme caption

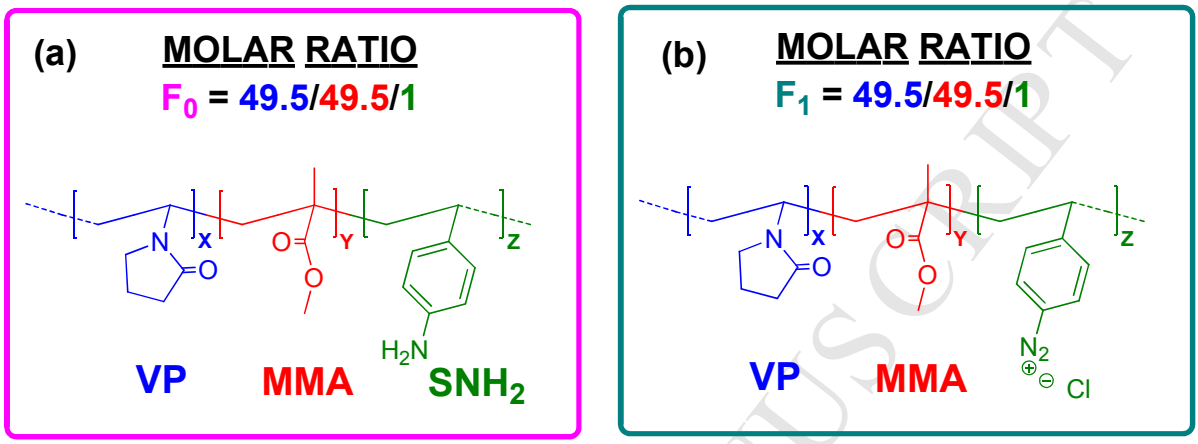
Scheme 1. Chemical structure of: **(a)** the starting material ($\mathbf{F_0}$), and (**b**) the sensory polymer $\mathbf{F_1}$ obtained after dipping $\mathbf{F_0}$ in an aqueous acid solution of sodium nitrite.

Figure captions

Figure 1. R parameter (obtained from the RGB parameters of the digital photo) *vs* I_{280} of white (left) and red (right) wines.

Figure 2. Interference analysis carried out by the RGB method with $\mathbf{F_1}$ discs after immersion in RW5 (left) and WW3 (right) with D-glucose, $Cu(NO_3)_2 \times 3\ H_2O$, $Fe(NO_3)_3 \times 9\ H_2O$, D-fructose and Na_2SO_3. The concentration of each spiked species was 10^{-2} M.

Scheme 1



Scheme 1. Chemical structure of: **(a)** the starting material ($\mathbf{F_0}$), and (**b**) the sensory polymer $\mathbf{F_1}$ obtained after dipping $\mathbf{F_0}$ in an aqueous acid solution of sodium nitrite.

Figure 1

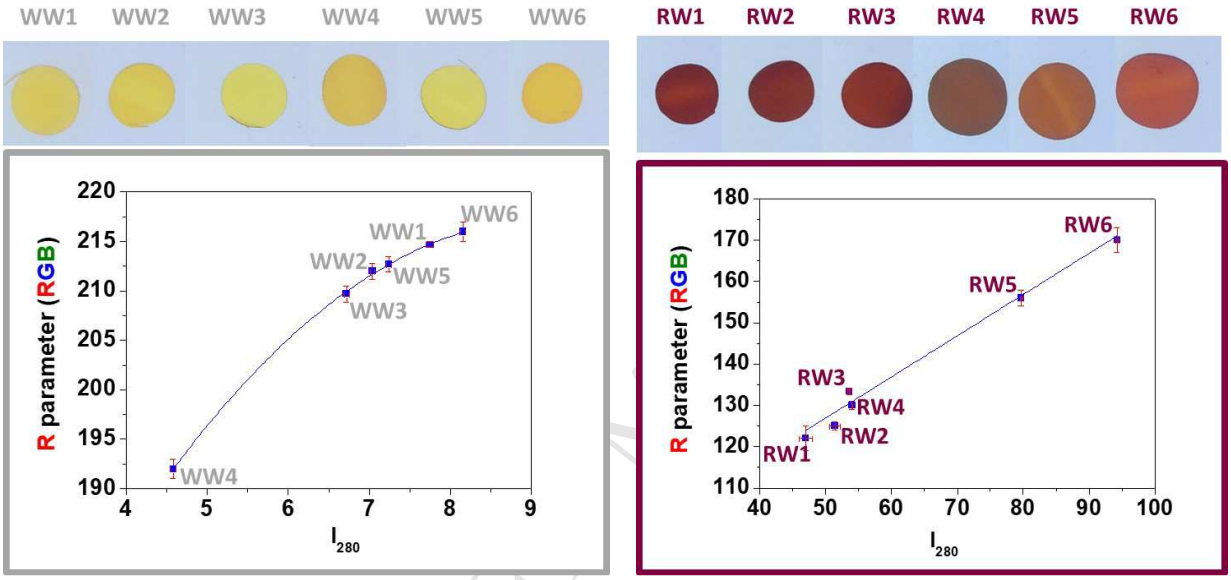
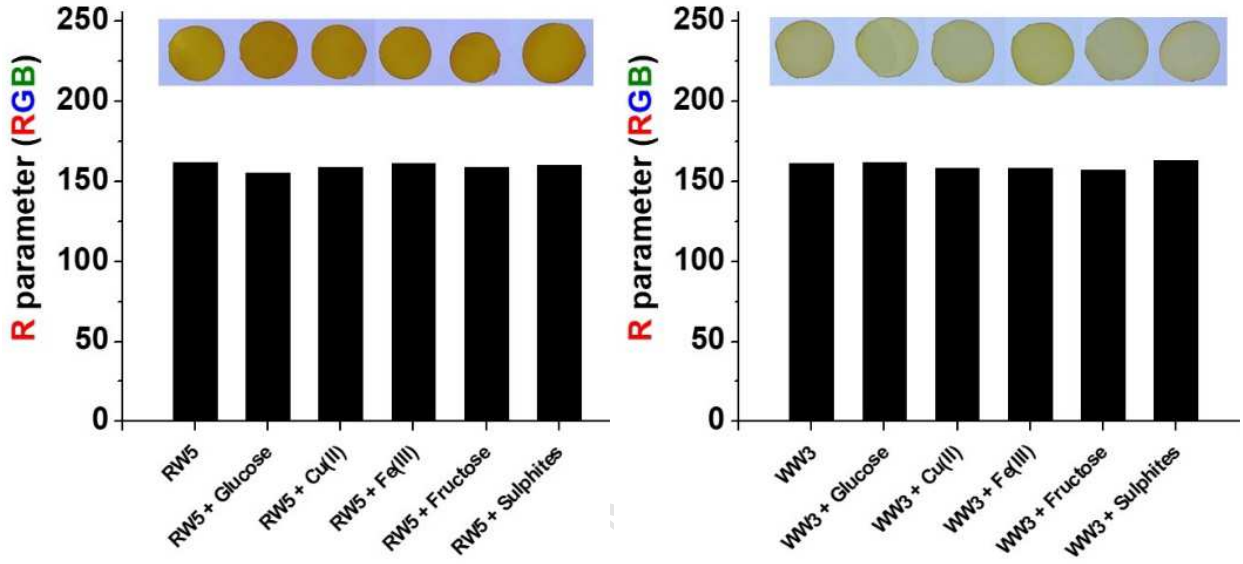


Figure 1. R parameter (obtained from the RGB parameters of the digital photo) *vs* I_{280} of white (left) and red (right) wines.

Figure 2



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Highlights

- Sensory film changes its colour after its immersion in red and white wines
- The sensory films are intelligent polymers
- The film´s colour allows for the determination of the total polyphenol index
- The determination of the total polyphenol index is rapid and inexpensive