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Portable Photometer for Procyanidins Quantitation in Red Wine

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***Abstract*— The present work introduces a portable photometer to estimate tannin content in red wines. The theoretical premises are based on the known reactivity of wine tannins (procyanidins) with proteinaceous matter which reaction results in a turbid formation of floating procyanidin-protein complexes. The optical device operating with a wavelength-sensitive pulsed electromagnetic source enabled to measure the degree of turbidity, combining the different intensity and spectral emission of a light source with the photodiode wavelength sensitivity. Twenty-seven red wines (tannins content range: 6-1904 mg/L) were optically analyzed soon after adding a saturated solution of gelatin (12% ethanol, pH 3.5). The photometer output signal is a waveform (voltage, V) produced and modified as a function of peak intensity, amplitude, and curvature which depends on the turbidity. Nonlinear correlation fitted the relationship between signal waveform and tannins content (R^2 up to 0.966). The proposed photometer is easy to use, cost-effective and provides a reliable alternative to the time-consuming analyses for fast in-line and off-line analysis of procyanidins in wine.**

Keywords—Portable photometer, procyanidins analysis, red wine, rapid measurement, quality control

I. Introduction

Wine industry traditionally benefits from tannins use, naturally present in grapes and extracted during the alcoholic fermentation process [1, 2]. Tannins also play a fundamental role in sensory characteristics of wine. Natural condensed tannins are abundant in red wines [3, 4]. A suitable content can provide oxidative stability and better chemical-physical properties, whereas their excess can produce precipitates and unpleasant perceptions of bitterness/astringency affecting consumer acceptability [5].

In this view, winemakers aim at improving the quality of their wines to boost the consumer preference [6, 7]. This aim can be performed by using tools to control the process and the products.

Quantification of tannin content can be quite complex, as it requires the preliminary treatment of the samples, or the use of expensive instruments, which require highly specialized employees [8, 9]. Many "user-friendly" approaches have been developed to monitor the quality parameters of food products (e.g. dissolved gases, sugar content, alcohol content, organic acids, total polyphenols, antioxidant activity), through the use of devices easily usable, portable, which provide data that can be easily interpreted by technicians working in the supply chain; however, no rapid and economical techniques have been developed for the measurement of tannins, available either on a laboratory or process scale, for oenological and beverage industry, particularly.

The solution proposed is an innovative analytical method for tannins quantification in oenological products and beverages of vegetable origin; this method exploits the selective reactivity of tannins in a mixture containing gelatine, the result of which is the formation of a turbidity solution. The reactivity of procyanidins toward proline-like proteins contained in the human saliva is also the basis for the astringency perceived during wine tasting [10]. The innovative technique named Spectral-Sensitive Pulsed Photometry (SSPP) has been successfully applied in previous experiment to exploit key optical properties of commercial milk samples, such as light scattering according to the Mie theory for the prediction of fat content in milk [11]. The SSPP technique proposed by the authors maintains a sensitivity to the wavelength of the radiation used and the optical response depends on the material under test to a pulsed source of radiation (tungsten filament bulb lamp). When the source is progressively lighted, the output voltage pulse takes a characteristic shape (peak, amplitude, curvature) as function of interposed medium; by exploiting the changing wavelength distribution during lighting and the spectral sensitivity of photodiodes, the device enables to measure the relevant optical phenomena involved in the attenuation of the source intensity, such as light scattering, but also molecular vibrational absorbance [11].

Based on these premises, the proposed SSPP method provides the direct measure of the optical turbidity instantly generated by mixing the red wine with a saturated solution of gelatine dissolved in a hydroalcoholic "wine like" buffer. The extent of turbidity is measured with optical infrared sensing, typically operating in the near-infrared (NIR) spectral region; radiations over 700 nm interact with suspended particles, with variable yield according to the particles' dimensions [12]. To maximize the optical response generated by turbidity and to overcome interferences related to wine colour during the analysis, the SSPP was equipped with a photodiode operating in the 650-1200 nm region, with a maximum sensitivity peak around the wavelength where the red wines do not display absorbance (875 nm).

The invention is particularly suitable for determining the concentration of tannins on liquid samples and it was initially proposed with the intention of supporting the wine industry through quantification of the tannin content present in red wines. In addition, the method can assist in monitoring the extractability of tannins over time in the industrial processes of maceration of plant substances, to evaluate their effectiveness under specific process conditions (e.g., tea, coffee, or beer).

Accordingly, the proposed analytical method is intended for industrial applications, as it allows rapid monitoring of supply chain processes. The measured parameter did not show significant interferences due to the physical and compositional characteristics of the tested samples, and this feature makes the technique potentially applicable to a wide range of products, from beverages, juices, extracts and food supplements. The current prototype and advanced research state would allow the direct industrialization of the measurement system. The interest of the final user is achieved by the simplicity of use and by the low cost.

II. MATERIAL AND METHODS

A. Photometer

The photometer and acquisition setting up are previously reported in Ragni [11] and briefly described herein. The prototype is composed by a bulb lamp (tungsten incandescent filament) with a lent to focalize the radiation, a photodiode (OPTEK Technology Inc., model OP993, operating in NIR-B range with peak sensitive of 890 nm) and interposed a glass cuvette with a path of 10 mm as sample holder. The lighting is progressive (applied voltage up to 1.2V) and controlled by Arduino ® Uno Rev. 3 board. Acquisitions were conducted by using the software tool PLX-DAQ (Parallax ®).

Wines were directly mixed with a saturated solution of gelatine (30 g/L in model wine buffer) in ratio 1:1 (v/v) to enable the reaction with formation of the colloidal suspension, then immediately put in the device sample holder and irradiated with the pulsed lighting source, as shown in Figure 1.

The proposed method exploits the selective reactivity of tannins in a mixture containing gelatine, the result of which is the formation of turbidity that is measured with high accuracy by using an optical prototype detector, which operates with a pulsed light electromagnetic source, in a specific wavelength not sensitive to colour and media composition.

For each wine-gelatine mixture, five subsequent voltage pulses were acquired and averaged.

B. Sample tested

Twenty-seven red wines of different Italian regions were selected to cover a wide range of tannin content, as reported in Table 1. Bottles were opened immediately before the optical analysis. Wines were assessed in duplicate by the well-known Adams-Harbertson colorimetric assay [1]. Calibration was performed using (+)-catechin as a reference standard and results were expressed as mg/L (+)-catechin equivalents (mg/L CE) (Ricci et al. 2020).

C. Statistical analyses

Waveforms are characterized by 187 points, used as x variable to build simple linear model with tannins (mg/L) as f(x). Models with different functions were explored to fit the data set and estimate tannin contents. 187 models were built, one for each of the waveform's points. The best results in terms of coefficient of determination show that the quadratic model is the best estimation model. Adjusted R^2, p-level of each function coefficient, 95% confidence and prediction limits were calculated and reported for a comprehensive regression characterization.

III. RESULTS AND DISCUSSION

Average values and standard deviation of the procyanidin content of red wines are reported in Table 1. As expected, the amount of tannins in red wines was highly variable.

The voltage signals for the different wines characterized by different tannins content, as a function of the lighting time of the lamp (time during which the lamp lights up, becomes brighter and suddenly blow out) are shown in Figure 2 [13]. As expected, the raise of tannins content enhances the turbidity reaction and a less intensity signal was revealed. The voltage peak values and the voltage at the most sensitive points (at the time giving the highest R^2 value) were used to create models for predicting the tannins content by fitting with a quadratic regression.

Figures 3 show the quadratic regression between tannins content and the voltage peak the highest coefficient of determination was obtained [13].

The nonlinear correlation between tannins and detected light signal could be attributed to a certain amount of saturation of the turbidity increasing with the tannins content. Previous work also reported nonlinear relation among light signal and quality parameters of dairy products [11].

CONCLUSION

In light of the results obtained, pulsed photometry, based on the interaction of the spectrally variable light radiation and the interposed wine, reacted with gelatine, has proven to be a technique capable of estimating the tannins content in wine with appreciable precision. The highest R^2 value, obtained with a quadratic regression function, was 0.966 with a RMSE value of 99 mg/L).

The highest correlation coefficient can be attributed to the initial lighting of the lamp, characterized by a large amount of infrared radiation.

Further samples are mandatory to perform the statistical model implementation in reason to afford the light pulsed contribution in procyanidin content assessment. Multivariate techniques, such PLS and neural network could be used to attempt to improve the model power.

The proposed method for tannins quantitation in oenological products and beverages of vegetable origin is particularly suitable for industrial applications, as it allows rapid monitoring of supply chain processes.

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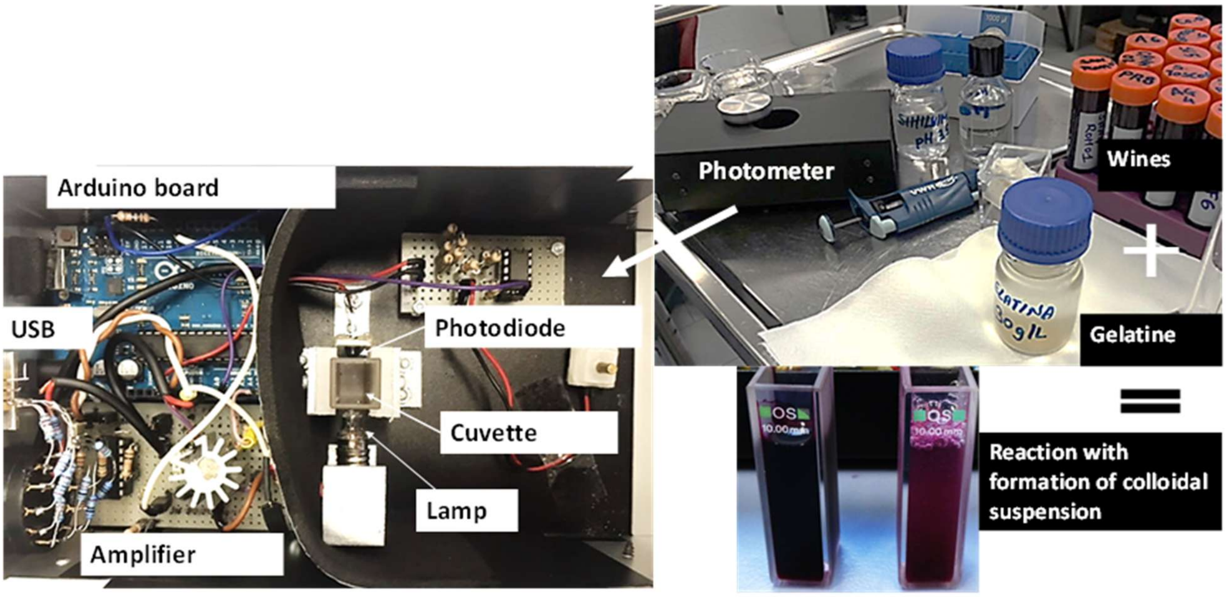

Figure 1. Layout of the photometer

Table 1 Procyanidin contents measures by the Adams-Harbertson assay, CE, equivalent of (+)-catechin.

Sample wine nr	Tannins (mg/L CE)	
	Mean	SD
1	480	22
2	443	22
3	97	5
4	246	18
5	1786	22
6	1855	76
7	1522	20
8	1005	40
9	39	1
10	740	19
11	618	41
12	1170	42
13	699	18
14	1452	44
15	976	18
16	1017	19
17	970	20
18	877	46
19	795	43
20	1164	18
21	652	47
22	820	44
23	258	17
24	6	0
25	538	22
26	1555	79
27	1904	100

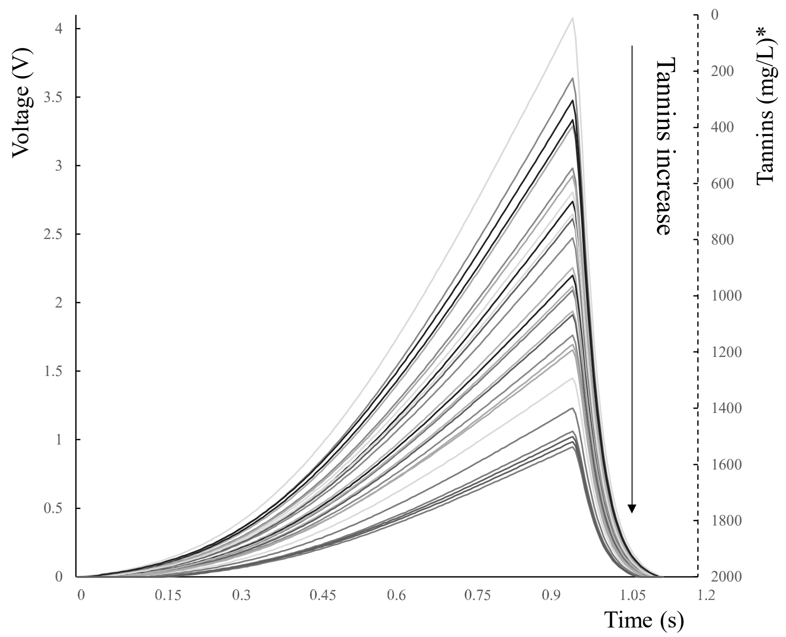

Figure 2. Voltage (V) signals vs. lighting time (s). P: maximum peak; BR: time corresponding to the highest R^2 (quadratic regression) [13].

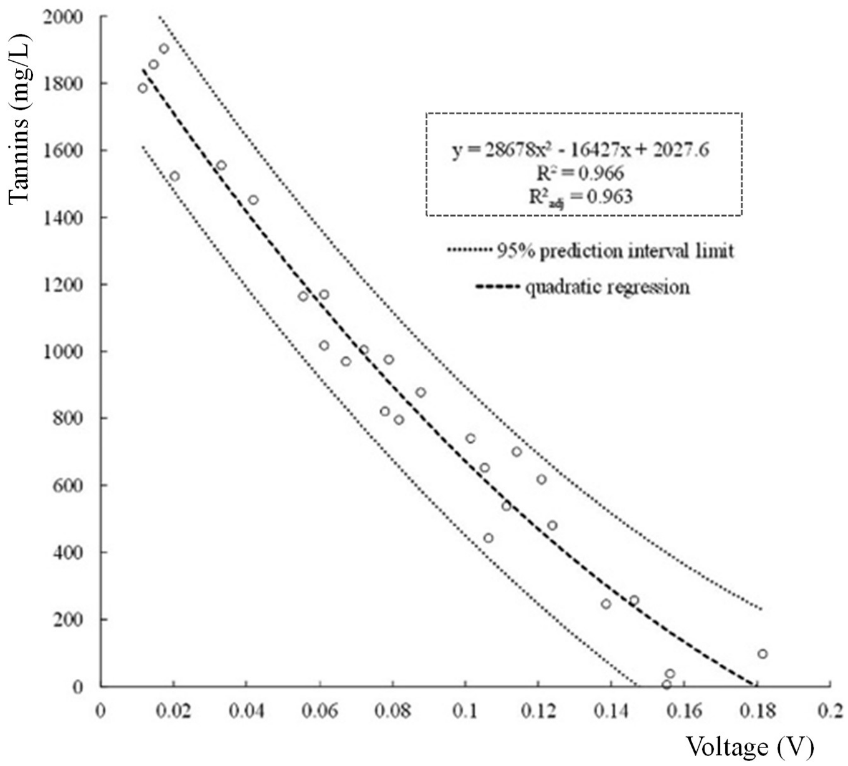

Figure 3. Tannin content vs. voltage [13].