PANI sensor for monitoring the oxidative degradation of wine using cyclic voltammetry

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Abstract

Redox species in wine are altered by pH and some wines are easily degraded due to oxidation and sulfur dioxide (SO_2) reduction. There is a need for quick, easy, simple, and economical methodologies for pH and wine-oxidized products (acetaldehyde) analysis. This study aimed to measure pH and degradation of wines that were electrochemically analyzed using polyaniline (PANI) sensor. Gas chromatography (GC) and fourier transform infrared spectrometer (FT-IR) were also used. Electrochemical analysis showed that oxidation was accelerated and peak currents ($I_{p,a}$) and potentials ($E_{p,a}$) shifted to negative direction due to acetaldehyde formation. PANI sensor achieved a limit of detection (LOD) of 7×10^{-1} ppm and a sensitivity of 5.20 µA ppm^{-1} cm^{-2}. Acetaldehyde formation was confirmed by GC (30%) and FT-IR spectra at 1647 cm^{-1} to the C=O vibration of aldehyde. These results suggested that acetaldehyde degraded the taste of wine after remaining open.

Keywords

Polyaniline sensor; Wine; Cyclic voltammetry; Degradation of wine

1. Introduction

Wine exposure to air/oxygen (O_2) can change wine from decent to inconsumable, and its color can change from vibrant to brown-tinged, which is a sign of oxidation. The pH of wine is another important factor, as it influences the stability of the wine's microorganisms, protein solubility, affects color and oxidative reactions, and determines the effectiveness of sulfur dioxide (SO_2) (Sarmento et al., 2000). The alteration of color, flavour, and taste are significantly influenced by polyphenols. Polyphenols can be grouped into two families: (i) flavonoids (anthocyanidins, tannins, flavonols, flavanols, flavanones, flavones) and (ii) non-flavonoids (hydroxycinnamic acids, hydroxybenzoic acids, stilbenes etc). Polyphenols and organic acids readily oxidize into their corresponding quinone in the presence of hydrogen per oxide (H_2O_2). Quinones affect the color of wine, enhance its bitterness, and impair its flavor and nutritional value (Marrufo-Curtido et al., 2022). Quinones can first undergo decarboxylation and then hydrolysis to form an aldehyde. Quinones can also polymerize with flavonoids and anthocyanins and form pigmented polymers, similar to acetaldehyde (Fowler et al., 2011). Acetaldehyde is the major byproduct of wine oxidation and leads to changes in color and flavor (Tarko et al., 2020). Researchers established that high temperatures and

excessive O_2 exposure cause wine to lose its rich flavors, color and taste (Ontañón, et al., 2020). Acetaldehydes are well-known irritants that can cause headaches and dizziness if inhaled over long periods, rapidly attach to proteins and DNA, and possibly even cause cancer (Mizumoto et al., 2017). As a result, acetaldehyde is considered hazardous to the environment, making its detection crucial. Unfortunately, consumers frequently ignore these dangers. There are some time-consuming, expensive techniques used for the detection of oxidized products (acetaldehyde.), such as high performance liquid chromatography (HPLC), liquid chromatography-electrospray mass spectrometry (LC-ES-MS), enzyme assay (Ontañón, et al., 2020, McCloskey and Mahaney, 1981), spectroscopic techniques (ultraviolet (UV), infrared (IR)), etc.; those require trained personnel. However, there aren't quick and easy ways to figure out how vulnerable chemical composition of wine is to O_2 exposure or being left open for a long time. Therefore, a quick, easy-to-use procedure that can reveal information about a wine's susceptibility is required.

The formation of acetaldehyde (a carcinogen) in wine is well-known and favored by exposure but can also develop in properly stored wines. This study aims to apply the

newly designed electrochemical PANI sensor to immediately understand the deterioration of wine.

2. Materials and methods

2.1. Wine samples and reagents

Wines were procured from a local supermarket in Sapporo, Japan (Table 1). Acetaldehyde causes a range of toxic, pharmacological, and behavioral responses (Guo and Ren 2010) and is formed by the oxidation of ethanol in wine. After opening the wine bottle, 50 mL of each wine was poured into a 100-mL beaker and remained open at room temperature (±25 °C) for 96 h to produce acetaldehyde, which was then measured by a PANI sensor. Aniline was purchased from Sigma-Aldrich Co. LLC (Tokyo, Japan), Sodium hydroxide (NaOH) and hydrochloric acid (HCl) (Wako Pure Chem. Osaka, Japan)

Table 1. here

2.2. Methods

2.2.1. Polyaniline sensor preparation

The sensing electrode was a polyaniline-modified Au electrode prepared previously described electro-polymerization method (Begum et al., 2021). A planar-type electrochemical sensor chip (3.5 cm × 1.2 cm) developed by Hitachi Chem was cleaned by ashing treatment using UV (172 nm, 10 $mWcm^{-2}$) for 1 min. Aniline and perchloric acid ($HClO_4$) (Wako Pure Chem. Osaka, Japan) were used to modify the chip. The chip was modified via the electro-polymerization of PANI on the surface of the Au electrode by applying a potential step of -0.025 V for 150 s in 1 M of aniline and 2 M of an $HClO_4$ solution (Scheme SI-1). PANI can prevent the non-specific adsorption of organic compounds onto the electrode.

2.2. 2. Measurement of physiochemical parameter, CV, GC and FT-IR

We measured the physiochemical parameter of the wine samples using OenoFoss (Fourier Transform Infrared (FTIR)) (Web address). Table 1 showed the information of wines accompanied with appearance/color and physiochemical parameters (pH, total acid, volatile acid and total sugar) of red, rose, and white wines after 24 hours of the opening using OneoFoss. The experimental configuration for CV measurement included a planar-type electrochemical sensor chip with three electrodes—PANI/Au working, Au counter, and Au pseudo-reference—all connected to a potentiostat, an IVIUM

COMPACTSTAT electrochemical interface, through a USB interface. Next, 50 µL of wine (without any treatment) was dropped onto the sensing area at the working electrode for CV measurement. All measurements were conducted at room temperature (±25 °C), with a scanning range of -0.1–0.7 V at the scan rate of 0.05 Vs^{-1}. The same chip was used more than 100 times after being thoroughly washed with MilliQ water (Begum et al., 2021). To create various pH wine solutions, NaOH and HCl were utilized. The degradation of wines was electrochemically investigated using a PANI sensor and analyzed them using CV. To test the PANI electrode's signal strength in the presence of acetaldehyde, acetaldehyde (30, 35 and 40 ppm) and white wine were mixed and the CV was recorded. The formation of acetaldehyde was confirmed by GC (SHIMADZU GC-2025) according to the method (see supplementary information) reported by Hübschmann. The formation of acetaldehyde was also determined by FT-IR (Nicolet iS 10, Thermo Scientific) following the procedure described by Kauffman et al.

2.3. Statistical analysis

Each experiment was conducted in triplicate. Statistical analysis was performed using Student's t-test, with $P \leq 0.01$ (1 tail) considered significant. The experimental results are presented as mean ± SD (standard deviation).

3. Results and discussion

3.1. Effect of pH on the PANI sensor

The electrochemical parameters extracted from CV curve were the anodic and cathodic peak currents ($I_{p,a}$ and $I_{p,c}$, respectively); anodic and cathodic peak potentials ($E_{p,a}$ and $E_{p,c}$, respectively); peak-to-peak separation (ΔE_p); peak ratio and half-wave potential. As shown in Fig. 1, both the oxidation and reduction peak potentials gradually shift negatively with increasing pH, accompanied by a decrease in the peak area, which is a consequence of the lower proton transfer involved in the oxidation process with increasing pH. At high pH, the electrochemical potential of the wine solution was low, and accordingly, an oxidation/reduction process occurred at a lower potential concerning the PANI electrode. However, increasing the release of protons led to acidification, increasing the electrical potential. These results are consistent with those

Fig. 1. here

of previous studies (Yakovleva et al. 2007). Yakovleva et al. (2007) observed that the anodic peak voltage decreased with increasing pH, which was a consequence of the decrease in the degree of antioxidant protonation and resulted in negative values. The $E_{p,a}$ values for red wine (Fig. 1a) at pH 2 was 0.43 V, while the $E_{p,a}$ values of rosé (Fig.

1b) and white (Fig. 1c) wines were 0.25 and 0.36 V, respectively. Red wine contains anthocyanins (red pigments), which have high reactivity under acidic conditions due to the acidic character of the phenolic groups. A Reversible process was observed in all cases. The electrochemical parameter E^0 shifted to more positive potentials as pH decreased (Table SI-1). Anodic peak current decreased with increasing pH of red and white wine as shown in Table (SI-1). At pH 2, 3, and 4, the oxidation and reduction peaks were evident, however at pH 5 and even more so at pH 6, the electrochemical reactions of the system were subdued. Thus, it is possible to explain the observed pH-dependent redox reactions, in agreement with previous studies (Bourourou et al., 2014).

The relationship between $E_{p,a}$ and the pH values in red wine was examined. The linear regression equation was obtained as $E_{p,a}$ (mV) = 0.5294 - 0.055 pH, (n=3, R^2=0.9772) (Fig. 1d). Value of the slope was close to the predicted value of 59 mV/pH, demonstrating that the number of electrons and protons is equal (Murthy et al., 2019). The relationship between E^0 and the pH values in rose and white wines were studied. The plots produced showed a linear regression relationship with an equation E^0 (mV) = 0.2658 - 0.0289 pH, (n=3, R^2=0.9897) and E^0 (mV) =0.4242 - 0.0571 pH, (n=3,

R^2=0.9997) for rose and white wines respectively (Fig. 1e and 1f). The values (0.0289 (rose) and 0.0571 (white)) produced from the slope of E^0/pH of the regression line are near to theoretical value/Nernstian value of 29.5 mV/pH and 59 mV/pH respectively (Hong et al., 2006, Zhang et al., 2014), indicating that the number of electron and protons involved in oxidation/reduction reaction for two-electron/one-proton and a similar number of electron-proton process respectively. We used PANI sensor to measure pH with Au electrode as a reference to avoid contamination of the main electrolyte by the reference electrolyte, used at room temperature and no need to equilibrate PANI sensor before use each time.

3.2. CV measurement of red, rosé, and white wines immediately after opening

First, the CV of six red, two rosé, and four white wines were measured immediately after opening the bottle; the results are shown in Fig. 2. One anodic peak

Fig. 2. here

($E_{p,a}$) was observed at around 0.35 V to 0.42 V and one cathodic peak ($E_{p,c}$) appeared at around 0.11 V to 0.17 V on the first CV scan. The peak current and potential depend on the concentration of redox-active molecules present in wine (Pwavodi et al., 2021). A slight difference was observed in anodic/cathodic peak current and cathodic peak

potential from CV (Table SI-2). Alcohol and phenolic/organic components are the main compounds in wines that may be expected to show redox activity towards PANI electrode. Redox-active species in wine (such as flavanols, flavanol derivatives, phenolic acids, SO_2, and ascorbic acid) interfere with the responses of CV. Phenolic compounds in wines oxidized at a potential of less than 500 mV (Beer et al., 2004). Organic acids in wine such as ascorbic acid, malic acid, tartaric acid, and caffeic acid showed a large positive voltage range of 0.55 to 0.70 V with a height of the current peak at 9.2 to 10.2 µA (Zhang et al., 2017). Makhotkina et al. (2010) demonstrated that the $E_{p,a}$ greater than 0.35 V is owing to the presence of free SO_2 and with a further contribution from catechol-containing phenolics such as caffeic acid derivatives and catechin also possible. Catechol, one of the polyphenols found in wines did not show redox activity toward PANI electrode (Begum et al., 2021). In a previous paper, we showed that the anodic peak at around 0.35 V to 0.42 V and the cathodic peak at around 0.11 V to 0.17 V for the preservative, SO_2 (Begum et al., 2021). H_2S and organic components were non-specifically deposited on the surface of the electrode; it is challenging to obtain a stable electric signal for the measurement of wine. Wine non-specific adsorption can be avoided using PANI (Begum, et al., 2019). The different pH of the wine solutions also affected the oxidation/reduction on the surface of PANI

electrode. There was also no significant difference observed according to the FTIR (OenoFoss) data (total acid, Table 1). $I_{p,a}$ value decreased with increasing pH of wine as shown in Table 1 and Table (SI-2).

3.3. CV measurement of red, rosé, and white wines after being open for several hours

Fig. 3 shows the CVs of (a) red, (b) rosé, and (c) white wines after opening for several hours. After opening at room temperature (±25 °C), each wine lost its alcohol concentration. Several wines open for 48–72 h showed little change, but most wines lost their alcohol concentration quickly after opening, which caused the taste to subtly change and become less vibrant after the first day; this was especially the case for white wines, which tend to oxidize more quickly. Under the presence of O_2 for several hours (24–72 h) at room temperature, white wines degrade easily. This leads to decreased wine quality (e.g., a noticeable increase in sugar content) that affects public health. It is well known that white wines are adversely affected by oxygen exposure, although many red wines benefit from a certain degree of oxidation (Danilewicz, 2003). CV (Fig. 3d) analysis suggested that the red wines did not change as much as white wines, which may be because of the high amounts of tannin, polyphenol, and antioxidant present in red wine that protects them from degradation even after 72 h. White wines are produced

186 by fermenting solely the grape juice, whereas red wines are produced using the skins
187 and seeds of the grapes. However, minor oxidation of the phenolic compounds in red
188 wine can help stabilize the color (Lopes et al., 2009). Acetaldehyde is produced as a
189 result of oxidation. This aldehyde formation provides the chemical bridge to bind
190 anthocyanins and tannins together in red wine. Tannins stabilize anthocyanins by
191 binding to form larger polymeric pigments.

192 Fig. 3. here

193 Antioxidants, anthocyanins in red wine can stabilize the beverage through
194 co-pigmentation, acetylation, and self-association (Kharadze et al., 2018). Acylated
195 anthocyanins, according to the researcher, can make red wine more stable (Alcalde-Eon
196 et al., 2006). Red wine's anthocyanin content is influenced by the grape's initial
197 anthocyanin profile and the winemaking methods used (Gonzalez-San Jose et al., 1990).
198 When being transported, stored, or left open, oxygen exposure and high temperatures
199 can have an impact on the quality of wines, particularly white wine (Ricci et al., 2017).
200 The anodic peak current of the red, rosé and white wines decreased with increasing time
201 of opening. Such decreases may be related to the formation of acetaldehyde.
202 Acetaldehyde is produced in wines when ethanol is oxidized in the presence of oxygen

from the atmosphere (Danilewicz, 2003). In nonenzymatic oxidation (enzyme removed or inactivated), under the catalytic effects of iron (Fe^{2+}) and copper (Cu^{+}) ions, molecular oxygen is reduced to its major radical, H_2O_2. Iron is a natural component in wines that are involved in metabolism as an enzyme activator and solubilizer. When H_2O_2 is present, polyphenols and organic acids spontaneously oxidize into their corresponding quinine (Voelker et al., 1996). Quinones can be converted to aldehydes via hydrolysis after being first decarboxylated (Fowler et al., 2011). Naturally occurring substances (eg, isobutanol) in wine are quickly oxidized to the corresponding aldehydes and then transformed into acetic acid/vinegar. Acetaldehyde is a key potential toxin for the development of alcoholic illnesses and causes a range of toxic, pharmacological and behavioral responses (Guo and Ren 2010). As shown in Fig. 3d, white wines showed significant changes. Thus, we checked several types of white wines after being left at room temperature for a few days.

3.4. CV of white wines after several hours of being open

As shown in Fig. 4, the $I_{p,a}$ and $E_{p,a}$ values of (a) Chardonnay, (b) Niagara, (c) Reisling, and (d) Sauvignon Blanc shift in a negative direction with time (0–96 h)

because of the decreasing number of electroactive functional groups and the increasing number of oxidized products, such as acetaldehyde, in the wine solution; this result is in agreement with those of previous literature (Makhotkina et al., 2010, Feng et al., 2014). Depending on the wine composition, the peak potential and current values vary for various wines. The new peak in the CV may be caused by the product of the oxidation or reduction of the original wine components during the opening.

Fig. 4. here

In addition to the redox molecules of wine, the CV peak also depends on the pH level of the wine (Makhotkina et al., 2010, Feng et al., 2014). With time after opening, the pH of rose wine dropped (pH 3.28 after immediately opening and 3.00 after 72h). At lower pH, pairs of peaks appeared to migrate closer and merge into a single broad peak at higher pH (Feng et al., 2014). The combination of numerous phenolic antioxidants in wine with various formal potentials may also have contributed to the broadness of the peaks (Piljac et al., 2004). The larger-sized phenolic compounds that result from the original wine phenolics' oxidation during storage—which is what causes the brown colors to appear—could also undergo a different type of oxidation and contribute to the

second peak in the CV of wines. After being left open for several hours, white niagara and white sauvignon blanc displayed (Figs. 4b and 4d, respectively) a decrease in the anodic current and a modest increase in the cathodic current. According to Makhotkina et al. (2010), the quick interaction of all the free SO_2 with acetaldehyde causes the anodic current to diminish and the cathodic current to slightly increase. CV is a quick way to assess the susceptibility of wine that will give the wine drinker useful information and can become an alternative to traditional spectrophotometric techniques (Makhotkina et al., 2010).

3.5. Detection of acetaldehyde

Acetaldehyde and the wine preservative SO_2 have a strong binding relationship, as previously described (Schneider et al., 2014). After many hours of opening the wine, a noticeably decreased sensing current was seen, which may be related to SO_2 binding to acetaldehyde. Previously reported that aldehyde was formed by wine oxidation. The formation of aldehyde depends on the oxidation time, pH, and chemical composition of wine (Bueno et al., 2018 and Marrufo-Curtido et al., 2022). As demonstrated in Fig. SI-1, when white wine and acetaldehyde were mixed, the $I_{p,a}$ value increased with decreasing acetaldehyde content. The behavior is influenced by the composition of wine

252 and the research environment. Fig. 5 shows the results of the calibration curve of the
253 PANI sensor at acetaldehyde concentrations of 30–40 ppm versus anodic peak
254 current: $I_{p,a}$ (μAcm^{-2})=2.1541 - 0.0411C (R^2=0.9977).

255 Fig. 5. here

256 Alcohol undergoes oxidation reactions that produce acetaldehydes, which can
257 then be further oxidized to produce acetic acid. The presence of the acetaldehyde band
258 in GC chromatogram confirmed the formation of acetaldehyde (after 12 h (30%), 24 h
259 (21%) and decreased to 5% after 48 h) in wine. The presence of the band at 1647 cm^{-1}
260 in FT-IR spectra was assigned to the C=O vibration of aldehyde which confirmed the
261 formation of acetaldehyde in wine (after 24 h). Acetic acid content becomes more
262 significant at higher pH levels (Agatonovic-Kustrin et al., 2013). pH and volatile acid
263 increased with time, according to FTIR (OneoFoss) measurements. The CV of grape
264 juice that contained acetic acid was used to investigate the influence on the
265 electrochemical in the PANI sensor. CV of grape juice and white wine (after 96 h)
266 showing similar oxidation or reduction peaks; the acetic acid (data not shown) may have
267 been produced in white wine (after 96 h).

3.5.1. Repeatability, reproducibility, limit of detection (LOD), and sensitivity

Repeatability was determined by replicate CV analysis using the PANI sensor of one original white wine (immediately after opening, n = 3) and the relative standard deviations (RSD) of the peak currents were found to be 0.7%, indicating adequate repeatability. The reproducibility of the sensor was investigated by the CV analysis of the same wine using three different chips (n = 3). The low RSD value (1.1%) of the peak currents indicates that the PANI electrode is highly reproducible. The LOD of 7×10^{-1} $mol.L^{-1}$ of the current sensor was determined from the calibration curve (Figure 5). This was calculated using the value of the slope of the curve and standard deviation (SD, n=3) (LOD = 3*SD / slope). The sensitivity toward acetaldehyde is evaluated by measuring the slope of the calibration curve (Fig. 5) and dividing it by the area of PANI electrode. The sensitivity of 5.20 µA ppm^{-1} cm^{-2} is obtained for PANI sensor for the detection of acetaldehyde. The obtained LOD with PANI electrode is comparable to recent works (Table SI-3) (Ahammad et al., 2016, Zhang et al., 2014, Ocampo et al., 2018, Hosseini et al., 2005, Zhang et al., 2016, Do and Wang, 2013).

4. Conclusions

In conclusion, data from CV confirm that wine undergoes vital changes after being continuously open at room temperature (±25 °C) for several hours (72–96 h). As expected, the differences induced by the availability of oxygen and temperature are strongly linked to the oxidation reaction, which triggers the accumulation of the oxidized product (e.g., acetaldehyde, confirmed by GC and FTIR) that readily binds with SO_2 and can be detected with our PANI sensor. This method provides a simple one-step technique to create a very low-cost electrode compared to other sensors being used to analyze wine, eliminates any post-processing steps, easy to use and more sensitive and selective than spectrometric methods. These results would be informative for wine drinkers. Further study is required for visualizing the changes in wine components using PANI sensor.

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Supplementary Data

All datasets generated for this study are included in the article/supplementary material.

Author contributions. Toshikazu kawaguchi and Parvin Begum conceived and planned the experiments. Parvin Begum carried out the experiment, performed the analysis, drafted the manuscript, and designed the figures. Liu Yang helped to experiment. All authors discussed the results and commented on the manuscript.

Ethical approval This article does not contain any studies with human and/or animal participants performed by any of the authors.

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447 Web address: Wine analysis instrument measures more than 10 process parameters

448 (fossanalytics.com)

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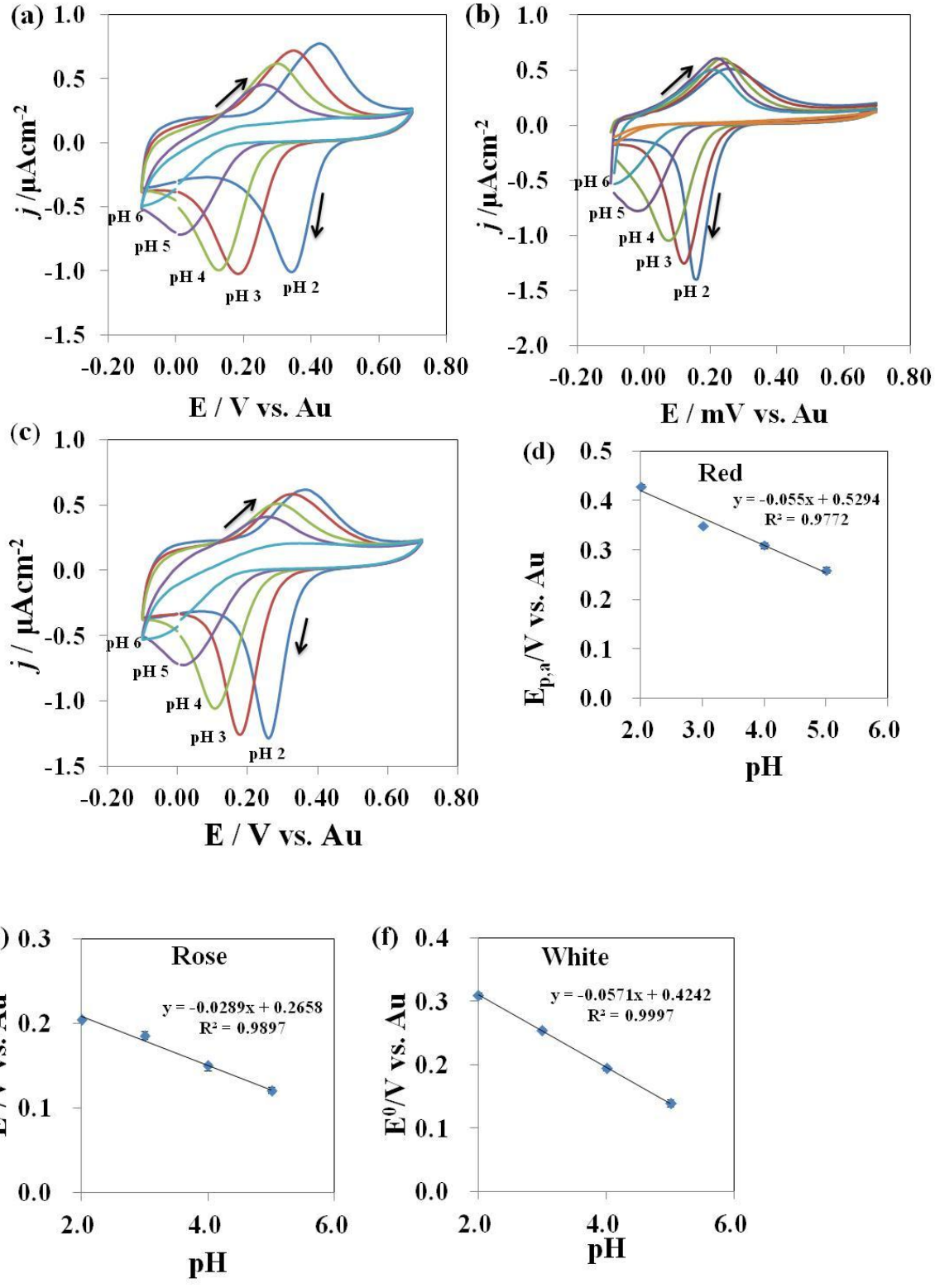
(a)
j /µAcm-2
E / V vs. Au
pH 6
pH 5
pH 4
pH 3
pH 2
(b)
j /µAcm-2
E / mV vs. Au
pH 6
pH 5
pH 4
pH 3
pH 2
(c)
j / µAcm-2
E / V vs. Au
pH 6
pH 5
pH 4
pH 3
pH 2
(d)
Red
y = -0.055x + 0.5294
R² = 0.9772
Ep,a/V vs. Au
pH
(e)
Rose
y = -0.0289x + 0.2658
R² = 0.9897
E0/V vs. Au
pH
(f)
White
y = -0.0571x + 0.4242
R² = 0.9997
E0/V vs. Au
pH

Fig. 1. CV at different pH (2~6) of (a) red, (b) rosé, and (c) white wines, recorded at a 0.0079 cm^2 PANI electrode at 0.05 vs. $^{-1}$. The first scan of the CV was recorded each time. The pH was adjusted by adding NaOH /HCl to each wine. Calibration curve of (d) $E_{p,a}$ versus pH (red wine); (e) E^0 versus pH (rose wine) and (f) E^0 versus pH (white wine). Respective calibration curve made from CV.

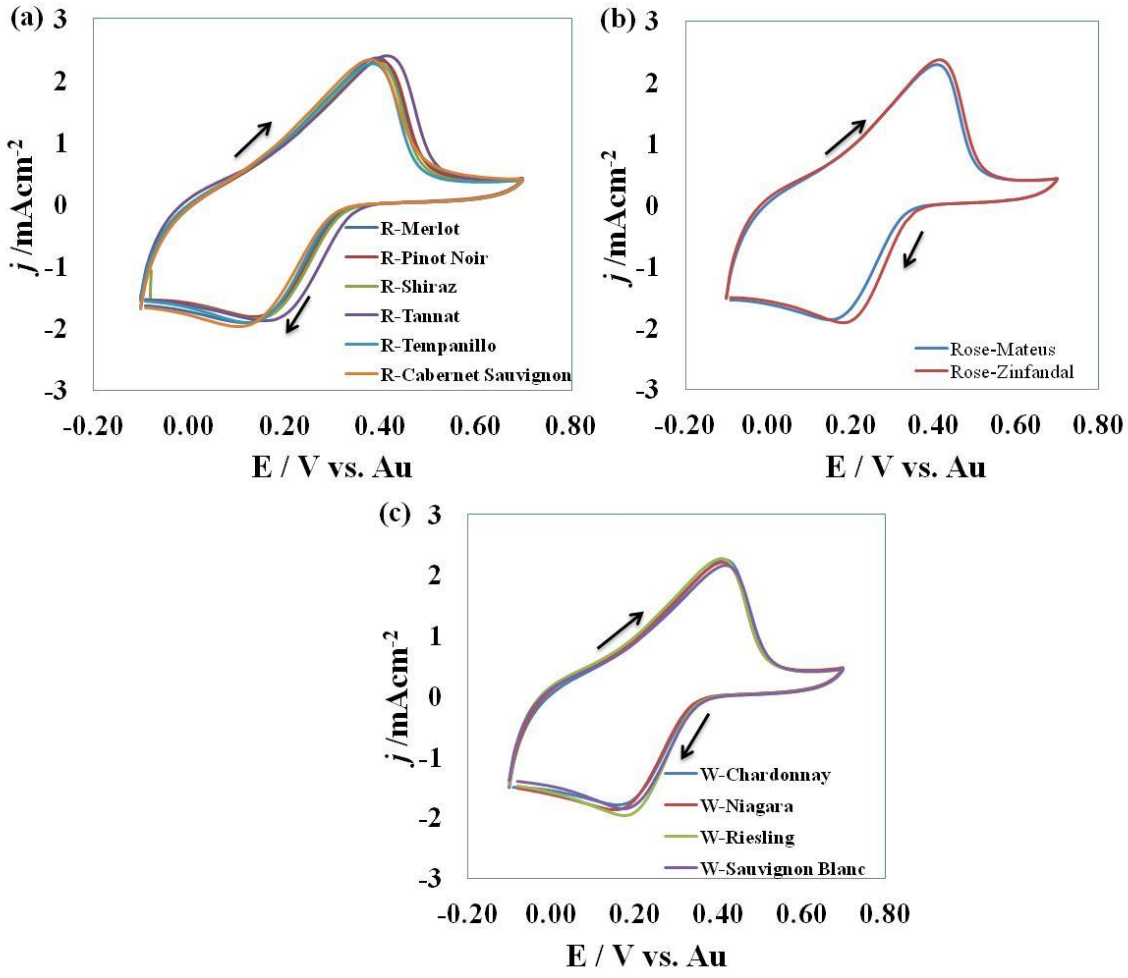

Fig. 2. Cyclic voltammograms of (a) red wines (Cabernet, Merlot, Pinor Noir, Shiraz, Tannot, Tempranillo, and Cabernet Sauvignon); (b) rose wines (Mateus and Zinfandal); (c) white wines (Chardonnay, Niagara, Riesling and Sauvignon Blanc) taken at a 0.0079

cm^2 PANI electrode at 0.05 Vs^{-1} after opening. The first scan of the cyclic voltammogram was recorded for each sample.

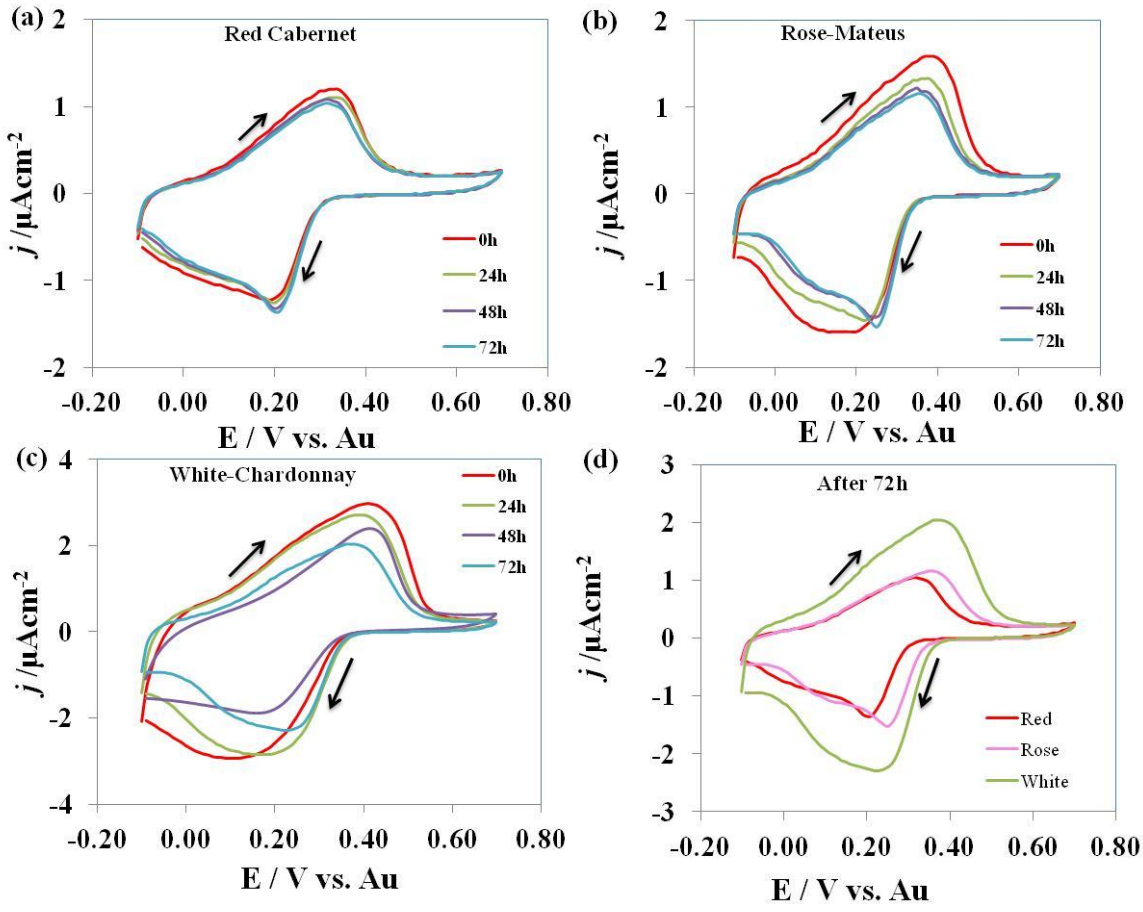

Fig. 3. CV of (a) red - Cabernate, (b) rose - Mateus, (C) white - Chardonnay, and (d) comparison of red, rose and white wines after opening at normal temperature (25 ºC); recorded at a different time interval at a 0.0079 cm^2 PANI electrode at 0.05 Vs^{-1}. First scan of the cyclic voltammogram was recorded each time.

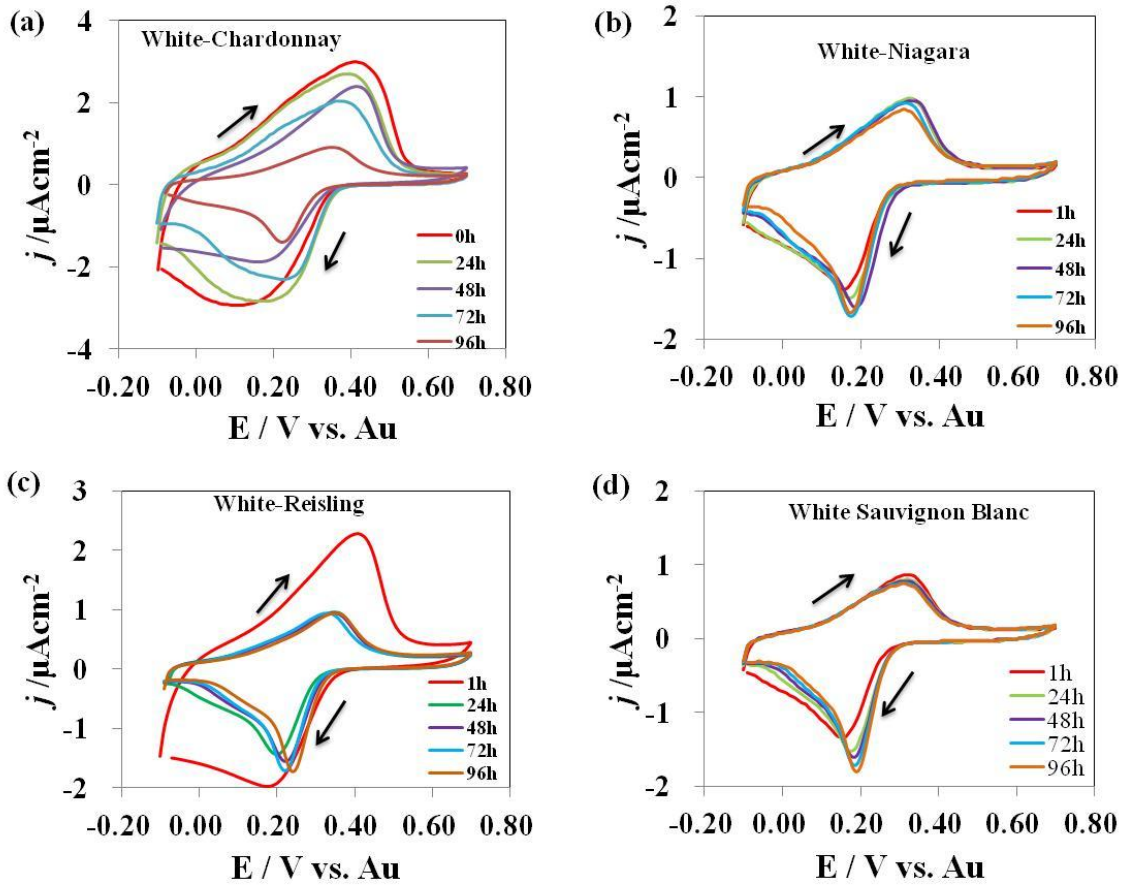

Fig. 4. CV of white wine (a) Chardonney, (b) Niagara, (C) Reisling, and (d) Sauvignon Blanc after opening at normal temperature (25 ºC); recorded at a different time interval at a 0.0079 cm^2 PANI electrode at 0.05 Vs^{-1}. First scan of the cyclic voltammogram was recorded each time.

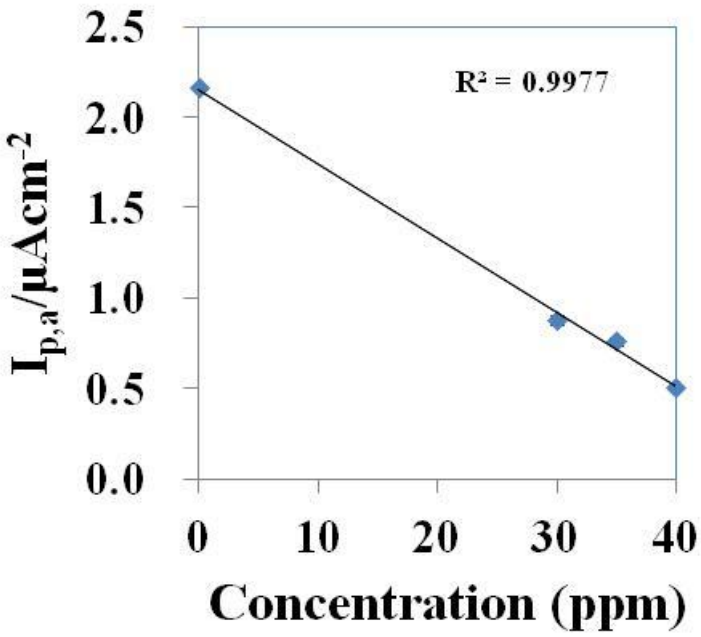

Fig. 5. Calibration curve of $I_{p,a}$ versus concentration of acetaldehyde (ppm).

Table 1. Information of wines accompanied with appearance/color and physiochemical parameters (pH, total acid, volatile acid and total sugar).

Wine	Grape variety	e	Appearance/ Color	pH	Total organic acids (g/l)	Volatile acids (g/l)	sugars (g/l)
Red	Santa Rita 3 Medallas Cabernet Sauvignon	2017	Ruby purple	3.61	3.2	0.41	2.7
	Merlot	2017	Ruby red	3.59	3.3	0.43	1.9
	Santa Helena Alpaca Pinot Noir	2017	Red purple	3.56	3.2	0.49	2.7
	Frontera Shiraz	2017	Ruby purple	3.58	3.3	0.48	5.6
	Tempranillo	2016	Ruby red	3.66	3.4	0.56	1.1
	Ascension Grand vin de Country Man Tannat	2016	Bright ruby purple	3.34	3.9	0.4	2.9
Rose	Mateus Rose	2016	Bright Rose	3.38	3.7	0.3	15.5
	Beringer White Zinfandal	2017	Rose	3.34	4.4	0.24	38.8
White	Santa Rita 3 Medallas Chardonnay	2017	Medium yellow	3.26	3.1	0.28	2
	Hokkaido Nama Wine Niagara	2017	Light yellow	3.33	4.1	0.38	3.2
	Riesling	2017	Light yellow	3.18	4.6	0.39	4.4
	Santa Helena Alpaca Sauvignon Blanc	2017	Light yellow	3.23	3.9	0.41	0.6

Highlights

- Sensing electrode was PANI modified Au electrode.
- Non-specific adsorption of organic compounds inhibited onto PANI electrode.
- Degradation of wine components observed by PANI sensor using CV.
- The $I_{p,a}$ and $E_{p,a}$ values shifted to a negative direction.

SUPPLEMENTARY MATERIAL FOR:

PANI sensor for monitoring the oxidative degradation of wine using cyclic voltammetry

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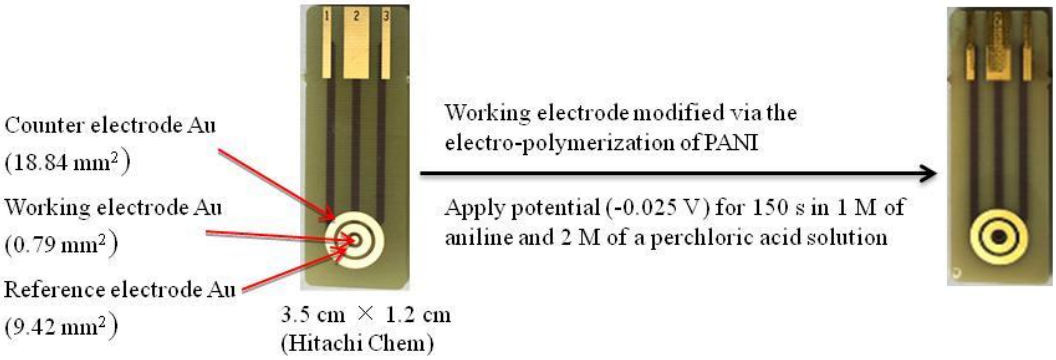
Scheme SI-1 Preparation of electrochemical sensor chip



Gas Chromatography:

The wine was analyzed on a gas chromatograph with a flame ionization detector (GC-FID) using a SHIMADZU GC-2025 chromatograph equipped with a Zebron (ZB-5 5% phenyl, 95% dimethylpolysiloxane) capillary column (30 m × 0.25 mm × 0.25 μm); an AOC-20i autosampler; and a split–splitless injector (SHIMADZU 09427). To assign the peaks of metabolized products according to mass fragmentation profiles, the system was equipped with a gas chromatograph−mass spectrometer (SHIMADZU GCMS-QP2010SE). The temperatures of the injector and detector were set at 200 and 250 °C, respectively. The oven temperature was first maintained at 40 °C for 10 min, after which it was increased at a rate of 10 °C/min to 250 °C and finally held at this temperature for 5 min. Thereafter, 1 μL of each sample was injected in the splitless mode (25 s). Helium was the carrier gas at a constant flow rate of 48.5 mL/min.

Table SI-1 The electrochemical parameters extracted from CV of red, rose and white wines at different pH

Red	pH	$E_{p,a}$ / V	$I_{p,a}$ / µAcm^{-2}	$E_{p,c}$ / V	(-) $I_{p,c}$ / µAcm^{-2}	ΔE_p/V	ΔI_p/µAcm^{-2}	$I_{p,a}/I_{p,c}$	$E_0=(E_{p,a}+E_{p,c})/$
	2	0.429 ± 0.04c	97.711 ± 0.02a	0.339 ± 0.02a	128.012 ± 0.02a	0.091	30.301	0.763	0.384
	3	0.349 ± 0.02a	91.269 ± 0.02a	0.199 ± 0.03b	126.525 ± 0.03b	0.150	35.257	0.721	0.274
	4	0.310 ± 0.04c	78.137 ± 0.02a	0.129 ± 0.03b	125.782 ± 0.03b	0.180	47.646	0.621	0.219
	5	0.259 ± 0.03b	57.819 ± 0.04c	0.019 ± 0.02a	90.846 ± 0.03b	0.240	33.027	0.636	0.139
Rose	2	0.250 ± 0.02a	64.509 ± 0.04c	0.160 ± 0.02a	177.071 ± 0.04c	0.090	112.562	0.364	0.205
	3	0.250 ± 0.02a	71.694 ± 0.02a	0.120 ± 0.04c	158.736 ± 0.04c	0.130	87.042	0.452	0.185
	4	0.240 ± 0.02a	76.650 ± 0.02a	0.060 ± 0.02a	131.976 ± 0.03b	0.180	55.327	0.581	0.150
	5	0.220 ± 0.04c	76.402 ± 0.02a	0.021 ± 0.02a	98.279 ± 0.04c	0.199	21.877	0.777	0.120
White	2	0.360 ± 0.03b	78.384 ± 0.02a	0.260 ± 0.03b	162.700 ± 0.02a	0.100	84.315	0.482	0.310
	3	0.330 ± 0.04c	73.924 ± 0.04c	0.180 ± 0.02a	159.479 ± 0.03b	0.150	85.555	0.464	0.255
	4	0.280 ± 0.02a	64.509 ± 0.02a	0.109 ± 0.03b	133.711 ± 0.04c	0.170	69.202	0.482	0.194
	5	0.260 ± 0.03b	52.120 ± 0.02a	0.019 ± 0.03b	92.085 ± 0.04c	0.240	39.965	0.566	0.139

Note: Values (means ± SD) bearing different superscripts are statistically significantly different ($P \leq 0.01$)

Table SI-2 The electrochemical parameters extracted from CV of red, rose and white wines just after opening.

	Wine Name	$E_{p,a}$ / V	$I_{p,a}$ / µAcm^{-2}	$E_{p,c}$ / V	(-)$I_{p,c}$ / µAcm^{-2}	△ E_p/V	$\triangle I_p$/µAcm^{-2}	$I_{p,a}/I_{p,c}$	E0=$(E_{p,a}+E_{p,c})/2$
Red	**Tannat**	0.409 ± 0.01a	303.797 ± 0.03c	0.159 ± 0.03c	238.024 ± 0.01a	0.250	65.772	1.276	0.284
	Merlot	0.389 ± 0.01a	299.114 ± 0.03c	0.119 ± 0.03c	240.750 ± 0.01a	0.270	58.364	1.242	0.254
	Cabernet Sauvigno	0.379 ± 0.03c	295.57 ± 0.02b	0.109 ± 0.02b	249.173 ± 0.03c	0.270	46.397	1.186	0.244
	Pinot Noir	0.399 ± 0.02a	293.418 ± 0.01a	0.129 ± 0.01a	229.104 ± 0.03c	0.270	64.314	1.280	0.264
	Shiraz	0.389 ± 0.02a	290.127 ± 0.01a	0.139 ± 0.01a	234.060 ± 0.01a	0.250	56.067	1.240	0.264
	Tempanillo	0.379 ± 0.02a	286.203 ± 0.02b	0.130 ± 0.02b	240.502 ± 0.02b	0.250	45.701	1.190	0.254
Rose	**Zinfandal**	0.409 ± 0.02b	299.367 ± 0.03c	0.179 ± 0.03c	242.980 ± 0.02b	0.230	56.387	1.232	0.294
	Mateus	0.409 ± 0.02b	290.38 ± 0.02b	0.149 ± 0.01a	236.289 ± 0.01a	0.260	54.091	1.229	0.279
White	**Riesling**	0.409 ± 0.03c	288.481 ± 0.01a	0.169 ± 0.02b	248.431 ± 0.01a	0.240	40.050	1.161	0.289
	Chardonnay	0.419 ± 0.01a	284.43 ± 0.01a	0.139 ± 0.02b	225.387 ± 0.03c	0.280	59.043	1.262	0.279
	Niagara	0.419 ± 0.03c	277.342 ± 0.03c	0.149 ± 0.01a	237.033 ± 0.03c	0.270	40.309	1.170	0.284
	Sauvignon Blanc	0.419 ± 0.02b	273.291 ± 0.01a	0.179 ± 0.03c	233.564 ± 0.02b	0.240	39.727	1.170	0.299

Note: Values (means ± SD) bearing different superscripts are statistically significantly different ($P \leq 0.01$)

Table SI-3 Comparison of the PANI electrode's determined detection limit in identifying the analytes of interest with recently published works.

Sensor	Detection limi	Analytes	Ref.
GCE/PANI/GNPs	0.1 mM	Glucose	Ahammad et al. 201
Hb/PANI–TiC/GCE	0.2 μM	H_2O_2	Zhang et al. 2014
PANI	0.8816 mM	Cadaverine	Ocampo et al. 2018
PANI	500 ppm	Toxic gas	Hosseini et al. 2005
PANI/Ag	1.24 ppm	Formaldehyde vapor	Zhang et al. 2016
PANI(IO)	29 ppm	Acetone gas	Do et al. 2013
PANI	7×10^{-1} ppm	Acetaldehyde	This work

Note: polyaniline-modified glassy carbon electrode- gold nanoparticles (GCE/PANI/GNPs) for the detection of glucose; Hemoglobin- polyaniline-titanium carbide-glassy carbon electrode (Hb/PANI–TiC/GCE) for the reduction of H_2O_2; PANI for the detection of cadaverine; polyaniline (PANI) for the detection of toxic gas; polyaniline/silver nanocomposite (PANI/Ag) for the determination of formaldehyde vapor; polyaniline/impregnated oxidation technique (PANi(IO)) for the detection of acetone gas.

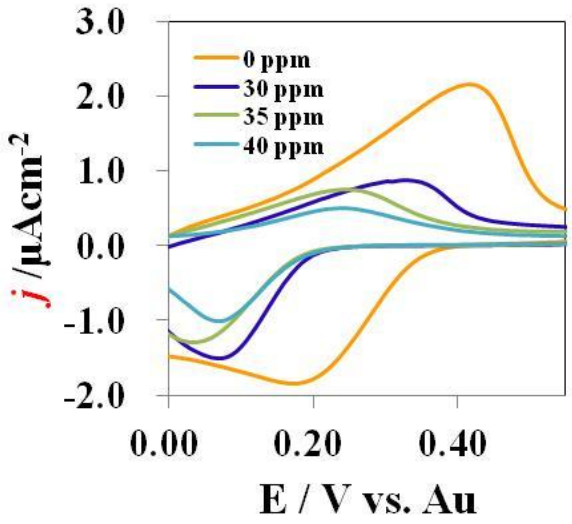


Fig. SI-1 CV of white wines (0 ppm, without acetaldehyde) and increasing amount of acetaldehyde (30 ppm, 35 ppm and 40 ppm); recorded at a 0.0079 cm^2 PANI electrode at 0.05 Vs^{-1}. First scan of the cyclic voltammogram was recorded each time.

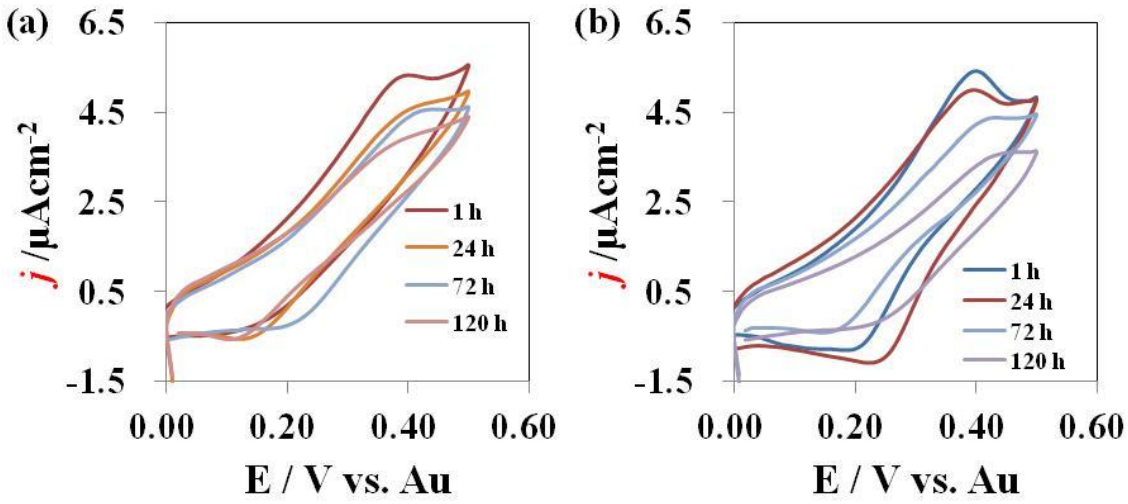


Fig. SI-2 CV of two white wines (a and b) after opening at normal temperature (25 ºC); recorded at different time interval at a 0.0079 cm^2 PANI electrode at 0.05 Vs^{-1}. First scan of the cyclic voltammogram was recorded each time.