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Author(s)	Begum, Parvin; Yang, Liu; Morozumi, Tatsuya; Sone, Teruo; Kawaguchi, Toshikazu
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1	PANI sensor for monitoring the oxidative degradation of wine using cyclic
2	voltammetry
3	Parvin Begum ^{a*} , Liu Yang ^b , Tatsuya Morozumi ^a , Teruo Sone ^{b,c} , Toshikazu Kawaguchi ^{a,}
4	b
5	^a Faculty of Environmental Earth Sciences, Hokkaido University, Sapporo 060-0810,
6	Japan
7	^b Graduate School of Global Food Resources, Hokkaido University, Sapporo 060-8589,
8	Japan
9	^c Faculty of Agriculture, Hokkaido University, Sapporo 060-8589, Japan
10	*Corresponding author
11	Email: parvinchy@ees.hokudai.ac.jp
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1 Abstract

Redox species in wine are altered by pH and some wines are easily degraded due to 2 oxidation and sulfur dioxide (SO_2) reduction. There is a need for quick, easy, simple, 3 and economical methodologies for pH and wine-oxidized products (acetaldehyde) 4 analysis. This study aimed to measure pH and degradation of wines that were 5 electrochemically analyzed using polyaniline (PANI) sensor. Gas chromatography (GC) 6 7 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 8 $(E_{p,a})$ shifted to negative direction due to acetaldehyde formation. PANI sensor achieved 9 a limit of detection (LOD) of 7×10^{-1} ppm and a sensitivity of 5.20 μ A ppm⁻¹ cm⁻². 10 Acetaldehyde formation was confirmed by GC (30%) and FT-IR spectra at 1647 cm⁻¹ to 11 the C=O vibration of aldehyde. These results suggested that acetaldehyde degraded the 12 taste of wine after remaining open. 13

14

15 Keywords

16 Polyaniline sensor; Wine; Cyclic voltammetry; Degradation of wine

1. Introduction

19	Wine exposure to air/oxygen (O_2) can change wine from decent to inconsumable,
20	and its color can change from vibrant to brown-tinged, which is a sign of oxidation. The
21	pH of wine is another important factor, as it influences the stability of the wine's
22	microorganisms, protein solubility, affects color and oxidative reactions, and determines
23	the effectiveness of sulfur dioxide (SO ₂) (Sarmento et al., 2000). The alteration of color,
24	flavour, and taste are significantly influenced by polyphenols. Polyphenols can be
25	grouped into two families: (i) flavonoids (anthocyanidins, tannins, flavonols, flavanols,
26	flavanones, flavones) and (ii) non-flavonoids (hydroxycinnamic acids, hydroxybenzoic
27	acids, stilbenes etc). Polyphenols and organic acids readily oxidize into their
28	corresponding quinone in the presence of hydrogen per oxide (H ₂ O ₂). Quinones affect
29	the color of wine, enhance its bitterness, and impair its flavor and nutritional value
30	(Marrufo-Curtido et al., 2022). Quinones can first undergo decarboxylation and then
31	hydrolysis to form an aldehyde. Quinones can also polymerize with flavonoids and
32	anthocyanins and form pigmented polymers, similar to acetaldehyde (Fowler et al.,
33	2011). Acetaldehyde is the major byproduct of wine oxidation and leads to changes in
34	color and flavor (Tarko et al., 2020). Researchers established that high temperatures and

35	excessive O ₂ exposure cause wine to lose its rich flavors, color and taste (Ontañón, et al.,
36	2020). Acetaldehydes are well-known irritants that can cause headaches and dizziness if
37	inhaled over long periods, rapidly attach to proteins and DNA, and possibly even cause
38	cancer (Mizumoto et al., 2017). As a result, acetaldehyde is considered hazardous to the
39	environment, making its detection crucial. Unfortunately, consumers frequently ignore
40	these dangers. There are some time-consuming, expensive techniques used for the
41	detection of oxidized products (acetaldehyde.), such as high performance liquid
42	chromatography (HPLC), liquid chromatography-electrospray mass spectrometry
43	(LC-ES-MS), enzyme assay (Ontañón, et al., 2020, McCloskey and Mahaney, 1981),
44	spectroscopic techniques (ultraviolet (UV), infrared (IR)), etc.; those require trained
45	personnel. However, there aren't quick and easy ways to figure out how vulnerable
46	chemical composition of wine is to O_2 exposure or being left open for a long time.
47	Therefore, a quick, easy-to-use procedure that can reveal information about a wine's
48	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 50

newly designed electrochemical PANI sensor to immediately understand thedeterioration of wine.

53 **2.** Materials and methods

54 2.1. Wine samples and reagents

55 Wines were procured from a local supermarket in Sapporo, Japan (Table 1). Acetaldehyde causes a range of toxic, pharmacological, and behavioral responses (Guo 56 and Ren 2010) and is formed by the oxidation of ethanol in wine. After opening the 57 58 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 59 measured by a PANI sensor. Aniline was purchased from Sigma-Aldrich Co. LLC 60 61 (Tokyo, Japan), Sodium hydroxide (NaOH) and hydrochloric acid (HCl) (Wako Pure Chem. Osaka, Japan) 62

63 Table 1. here

64 *2.2. Methods*

65 *2.2.1. Polyaniline sensor preparation*

66	The sensing electrode was a polyaniline-modified Au electrode prepared
67	previously described electro-polymerization method (Begum et al., 2021). A planar-type
68	electrochemical sensor chip (3.5 cm \times 1.2 cm) developed by Hitachi Chem was cleaned
69	by ashing treatment using UV (172 nm, 10 mWcm ⁻²) for 1 min. Aniline and perchloric
70	acid (HClO ₄) (Wako Pure Chem. Osaka, Japan) were used to modify the chip. The chip
71	was modified via the electro-polymerization of PANI on the surface of the Au electrode
72	by applying a potential step of -0.025 V for 150 s in 1 M of aniline and 2 M of an
73	HClO ₄ solution (Scheme SI-1). PANI can prevent the non-specific adsorption of
74	organic compounds onto the electrode.

75 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

83	COMPACTSTAT electrochemical interface, through a USB interface. Next, 50 μ L of
84	wine (without any treatment) was dropped onto the sensing area at the working
85	electrode for CV measurement. All measurements were conducted at room temperature
86	(±25 °C), with a scanning range of -0.1–0.7 V at the scan rate of 0.05 Vs ⁻¹ . The same
87	chip was used more than 100 times after being thoroughly washed with MilliQ water
88	(Begum et al., 2021). To create various pH wine solutions, NaOH and HCl were utilized
89	The degradation of wines was electrochemically investigated using a PANI sensor and
90	analyzed them using CV. To test the PANI electrode's signal strength in the presence of
91	acetaldehyde, acetaldehyde (30, 35 and 40 ppm) and white wine were mixed and the CV
92	was recorded. The formation of acetaldehyde was confirmed by GC (SHIMADZU
93	GC-2025) according to the method (see supplementary information) reported by
94	Hübschmann. The formation of acetaldehyde was also determined by FT-IR (Nicolet iS
95	10, Thermo Scientific) following the procedure described by Kauffman et al.

96 2.3. Statistical analysis

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

100 **3. Results and discussion**

101 *3.1. Effect of pH on the PANI sensor*

The electrochemical parameters extracted from CV curve were the anodic and 102 cathodic peak currents ($I_{p,a}$ and $I_{p,c}$, respectively); anodic and cathodic peak potentials 103 ($E_{p,a}$ and $E_{p,c}$, respectively); peak-to-peak separation (ΔE_p); peak ratio and half-wave 104 potential. As shown in Fig. 1, both the oxidation and reduction peak potentials gradually 105 106 shift negatively with increasing pH, accompanied by a decrease in the peak area, which 107 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, 108 and accordingly, an oxidation/reduction process occurred at a lower potential 109 concerning the PANI electrode. However, increasing the release of protons led to 110 acidification, increasing the electrical potential. These results are consistent with those 111 Fig. 1. here 112

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.

117	1b) and white (Fig. 1c) wines were 0.25 and 0.36 V, respectively. Red wine contains
118	anthocyanins (red pigments), which have high reactivity under acidic conditions due to
119	the acidic character of the phenolic groups. A Reversible process was observed in all
120	cases. The electrochemical parameter E^0 shifted to more positive potentials as pH
121	decreased (Table SI-1). Anodic peak current decreased with increasing pH of red and
122	white wine as shown in Table (SI-1). At pH 2, 3, and 4, the oxidation and reduction
123	peaks were evident, however at pH 5 and even more so at pH 6, the electrochemical
124	reactions of the system were subdued. Thus, it is possible to explain the observed
125	pH-dependent redox reactions, in agreement with previous studies (Bourourou et al.,
126	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, R²=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, R²=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) 134 (rose) and 0.0571 (white)) produced from the slope of $E^{0/pH}$ of the regression line are 135 near to theoretical value/Nernstian value of 29.5 mV/pH and 59 mV/pH respectively 136 (Hong et al., 2006, Zhang et al., 2014), indicating that the number of electron and 137 protons involved in oxidation/reduction reaction for two-electron/one-proton and a 138 similar number of electron-proton process respectively. We used PANI sensor to 139 measure pH with Au electrode as a reference to avoid contamination of the main 140 electrolyte by the reference electrolyte, used at room temperature and no need to 141 142 equilibrate PANI sensor before use each time.

143 *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



potential from CV (Table SI-2). Alcohol and phenolic/organic components are the main 151 compounds in wines that may be expected to show redox activity towards PANI 152 electrode. Redox-active species in wine (such as flavanols, flavanol derivatives, 153 154 phenolic acids, SO₂, 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). 155 156 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 157 at 9.2 to 10.2 µA (Zhang et al., 2017). Makhotkina et al. (2010) demonstrated that the 158 $E_{p,a}$ greater than 0.35 V is owing to the presence of free SO₂ and with a further 159 contribution from catechol-containing phenolics such as caffeic acid derivatives and 160 161 catechin also possible. Catechol, one of the polyphenols found in wines did not show 162 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 163 0.11 V to 0.17 V for the preservative, SO₂ (Begum et al., 2021). H₂S and organic 164 components were non-specifically deposited on the surface of the electrode; it is 165 challenging to obtain a stable electric signal for the measurement of wine. Wine 166 non-specific adsorption can be avoided using PANI (Begum, et al., 2019). The different 167 pH of the wine solutions also affected the oxidation/reduction on the surface of PANI 168

169 electrode. There was also no significant difference observed according to the FTIR

- 170 (OenoFoss) data (total acid, Table 1). $I_{p,a}$ value decreased with increasing pH of wine as
- 171 shown in Table 1 and Table (SI-2).
- 172 *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 173 several hours. After opening at room temperature (±25 °C), each wine lost its alcohol 174 concentration. Several wines open for 48-72 h showed little change, but most wines lost 175 their alcohol concentration quickly after opening, which caused the taste to subtly 176 change and become less vibrant after the first day; this was especially the case for white 177 wines, which tend to oxidize more quickly. Under the presence of O_2 for several hours 178 179 (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 180 well known that white wines are adversely affected by oxygen exposure, although many 181 red wines benefit from a certain degree of oxidation (Danilewicz, 2003). CV (Fig. 3d) 182 183 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 184 red wine that protects them from degradation even after 72 h. White wines are produced 185

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

192 Fig. 3. here

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

from the atmosphere (Danilewicz, 2003). In nonenzymatic oxidation (enzyme removed 203 or inactivated), under the catalytic effects of iron (Fe^{2+}) and copper (Cu^+) ions, 204 molecular oxygen is reduced to its major radical, H_2O_2 . Iron is a natural component in 205 wines that are involved in metabolism as an enzyme activator and solubilizer. When 206 H₂O₂ is present, polyphenols and organic acids spontaneously oxidize into their 207 corresponding quinine (Voelker et al., 1996). Quinones can be converted to aldehydes 208 209 via hydrolysis after being first decarboxylated (Fowler et al., 2011). Naturally occurring 210 substances (eg, isobutanol) in wine are quickly oxidized to the corresponding aldehydes 211 and then transformed into acetic acid/vinegar. Acetaldehyde is a key potential toxin for 212 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 213 significant changes. Thus, we checked several types of white wines after being left at 214 room temperature for a few days. 215

216 *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)

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

225 Fig. 4. here

In addition to the redox molecules of wine, the CV peak also depends on the pH 226 level of the wine (Makhotkina et al., 2010, Feng et al., 2014). With time after opening, 227 228 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 229 230 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 231 peaks (Piljac et al., 2004). The larger-sized phenolic compounds that result from the 232 233 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 234

second peak in the CV of wines. After being left open for several hours, white niagara 235 and white sauvignon blanc displayed (Figs. 4b and 4d, respectively) a decrease in the 236 anodic current and a modest increase in the cathodic current. According to Makhotkina 237 238 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 239 way to assess the susceptibility of wine that will give the wine drinker useful 240 information and can become an alternative to traditional spectrophotometric techniques 241 242 (Makhotkina et al., 2010).

243 *3.5. Detection of acetaldehyde*

244 Acetaldehyde and the wine preservative SO₂ have a strong binding relationship, as previously described (Schneider et al., 2014). After many hours of opening the wine, 245 a noticeably decreased sensing current was seen, which may be related to SO₂ binding 246 to acetaldehyde. Previously reported that aldehyde was formed by wine oxidation. The 247 248 formation of aldehyde depends on the oxidation time, pH, and chemical composition of 249 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 250 decreasing acetaldehyde content. The behavior is influenced by the composition of wine 251

and the research environment. Fig. 5 shows the results of the calibration curve of the PANI sensor at acetaldehyde concentrations of 30–40 ppm versus anodic peak current: $I_{p,a}$ (μ Acm⁻²)=2.1541 - 0.0411C (R²=0.9977).

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

269	Repeatability was determined by replicate CV analysis using the PANI sensor of
270	one original white wine (immediately after opening, $n = 3$) and the relative standard
271	deviations (RSD) of the peak currents were found to be 0.7%, indicating adequate
272	repeatability. The reproducibility of the sensor was investigated by the CV analysis of
273	the same wine using three different chips ($n = 3$). The low RSD value (1.1%) of the
274	peak currents indicates that the PANI electrode is highly reproducible. The LOD of 7 \times
275	10^{-1} mol.L ⁻¹ of the current sensor was determined from the calibration curve (Figure 5).
276	This was calculated using the value of the slope of the curve and standard deviation (SD,
277	n=3) (LOD = $3*SD$ / slope). The sensitivity toward acetaldehyde is evaluated by
278	measuring the slope of the calibration curve (Fig. 5) and dividing it by the area of PANI
279	electrode. The sensitivity of 5.20 μ A ppm ⁻¹ cm ⁻² is obtained for PANI sensor for the
280	detection of acetaldehyde. The obtained LOD with PANI electrode is comparable to
281	recent works (Table SI-3) (Ahammad et al., 2016, Zhang et al., 2014, Ocampo et al.,
282	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 284 being continuously open at room temperature (±25 °C) for several hours (72–96 h). As 285 expected, the differences induced by the availability of oxygen and temperature are 286 strongly linked to the oxidation reaction, which triggers the accumulation of the 287 oxidized product (e.g., acetaldehyde, confirmed by GC and FTIR) that readily binds 288 with SO₂ and can be detected with our PANI sensor. This method provides a simple 289 290 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 291 292 sensitive and selective than spectrometric methods. These results would be informative for wine drinkers. Further study is required for visualizing the changes in wine 293 components using PANI sensor. 294

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302 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.

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

310 **References**

Agatonovic-Kustrin, S., Morton, D. W., & Yusof, A. P. Md. (2013). The use of

Fourier Transform Infrared (FTIR) spectroscopy and Artificial Neural Networks

- 313 (ANNs) to assess wine quality. *Modern Chemistry and Applications*, 1, 110. DOI:
- **314** 10.4172/2329-6798.1000110.
- Ahammad, A. J. S., Mamun, A. A., Akter, T., Mamun, M. A., Faraezi, S., & Monira,
- 316 F. Z. (2016). Enzyme-free impedimetric glucose sensor based on gold

- 317 nanoparticles/polyaniline composite film. *Journal of Solid State Electrochemistry*,
- 318 20, 1933–1939. DOI 10.1007/s10008-016-3199-2.
- Alcalde-Eon, C., Escribano-Bailón, M. T., Santos-Buelga, C., & Rivas-Gonzalo, J.
- 320 C. (2006). Changes in the detailed pigment composition of red wine during maturity
- and ageing: A comprehensive study. *Analytica Chimica Acta*, *563*, 238–254.
- 322 https://doi.org/10.1016/j.aca.2005.11.028.
- Begum, P., Li, S., Morozumi, T., Johmen, M., Sone, T., & Kawaguchi, T. (2019).
- 324 Electrochemical sensing for analysis of wine. Proceedings of Chemical Sensor
- *Symposium*, *35*, 49–51.
- Begum, P., Morozumi, T., Kawaguchi, T., & Sone, T. (2021). Development of an
- 327 electrochemical sensing system for wine component analysis. *ACS Food*
- *Science & Technology*, *1*, 2030–2040.
- https://doi.org/10.1021/acsfoodscitech.1c00146.
- Beer, D. De., Harbertson, J. F., Kilmartin, P. A., Roginsky, V., Barsukova, T.,
- Adams, D. O., & Waterhouse, A. L. (2004). Phenolics: A comparison of diverse
- analytical methods. *American Journal of Enology and Viticulture*, 55, 389–400.
- 333 DOI: 10.5344/ajev.2004.55.4.389.

334	Bourourou, M., Barhoumi, H., Maaref, A., & Jaffrezic-Renault, N. (2014).
335	Electrochemical study of modified glassy carbon electrode with carboxyphenyl
336	diazonium salt in aqueous solutions. Sensors & Transducers, 27, 22–28.
337	Bueno, M., Marrufo-Curtido, A., Carrascon, V., Fernandez-Zurbano, P., Escudero,
338	A., & Ferreira, V. (2018). Formation and accumulation of acetaldehyde and strecker
339	aldehydes during red wine oxidation. Frontiers Chemistry, 6, 20.
340	https://doi.org/10.3389/fchem.2018.00020.
341	Danilewicz, J. C. (2003). Review of reaction mechanisms of oxygen and proposed
342	intermediate reduction products in wine: central role of iron and copper.
343	American Journal of Enology and Viticulture, 54, 73–85. Corpus ID: 87659513.
344	ISSN 0002-9254.
345	Do, J. S., & Wang, S. H. (2013). On the sensitivity of conductimetric acetone gas
346	sensor based on polypyrrole and polyaniline conducting polymers. Sensors and
347	Actuators, B, 185, 39-46. https://doi.org/10.1016/j.snb.2013.04.080.
348	Feng, X., Zhang, Y., Yan, Z., Ma, Y., Shen, Q., Liu, X., Fan, Q., Wang, L., &
349	Huang, W. (2014). Synthesis of polyaniline/Au composite nanotubes and their high

- 350 performance in the detection of NADH. *Journal of Solid State Electrochemistry*, 18,
- 351 1717–1723. 10.1007/s10008-014-2407-1.
- 352 Fowler, Z. L., Baron, C. M., Panepinto, J. C., & Koffas, M. A. G. (2011).
- 353 Melanization of flavonoids by fungal and bacterial laccases. *Yeast*, 28, 181–188.
- 354 https://doi.org/10.1002/yea.1829.
- 355 Gonzalez-San Jose, M. L., Santa-Maria, G., & Diez, C. (1990). Anthocyanins as
- 356 parameters for differentiating wines by grape variety, wine-growing region, and
- 357 wine-making methods. *Journal* of *Food Composition and Analysis*, *3*, 54–66.
- 358 https://doi.org/10.1016/0889-1575(90)90009-B.
- Guo, R., & Ren, J. (2010). Alcohol and acetaldehyde in public health: from marvel to
- 360 menace. International Journal of Environmental Research and Public Health, 7,
- 361 1285–1301. doi: 10.3390/ijerph7041285.
- Hong, J., Ghourchian, H., & Moosavi-Movahedi, A. A. (2006). Direct electron
- transfer of redox proteins on a nafion-cysteine modified gold electrode.
- *Electrochemistry communications*, 8, 1572–1576.
- 365 https://doi.org/10.1016/j.elecom.2006.07.011.
- 366 Hosseini, S. H., Oskooei, S. H. A., & Entezani, A. A. (2005). Toxic gas and vapour 23

367	detection by polyaniline gas sensor. Iranian Polymer Journal, 14, 333-344. Corpus
368	ID: 97048494.
369	Hübschmann, HJ. (2015). Handbook of GC-MS: fundamentals and applications.
370	Wiley-VCH Verlag GmbH & Co. KgaA. Weinheim, Germany. ISBN:
371	9783527334742.
372	Kharadze, M., Japaridze, I., Kalendia, A., & Vanidze, M. (2018). Anthocyanins and
373	antioxidant activity of red wines made from endemic grape varieties. Annals of
374	Agrarian Science, 16, 181–184. https://doi.org/10.1016/j.aasci.2018.04.006.
375	Kauffman, K. L., Culp, J. T., Goodman, A., & Matranga, C. (2011). FT-IR study of
376	CO ₂ adsorption in a dynamic copper(II) benzoate-pyrazine host with CO ₂ -CO ₂
377	interactions in the adsorbed state. The Journal of Physical Chemistry C,115,
378	1857–1866. https://doi.org/10.1021/jp102273w.
379	Lopes, P., Silva, M. A., Pons, A., Tominaga, T., Lavigne, V., Saucier, C., Darriet, P.,
380	Teissedre, PL., & Dubourdieu, D. (2009). Impact of oxygen dissolved at bottling
381	and transmitted through closures on the composition and sensory properties of a
382	sauvignon blanc wine during bottle storage. Journal of Agricultural and Food
383	Chemistry, 57, 10261–10270. doi: 10.1021/jf9023257.

384	Makhotkina, O., & Kilmartin, P. A. (2010). The use of cyclic voltammetry for wine
385	analysis: determination of polyphenols and free sulfur dioxide. Analytica
386	Chimica Acta, 668, 155–165. https://doi.org/10.1016/j.aca.2010.03.064.
387	Marrufo-Curtido, A., Ferreira, V., & Escudero, A. (2022). Factors that affect the
388	accumulation of strecker aldehydes in standardized wines: the importance of pH in
389	oxidation. Molecules, 27, 3056; https://doi.org/10.3390/molecules27103056.
390	McCloskey, L. P., & Mahaney, P. (1981). An enzymatic assay for acetaldehyde in
391	grape juice and wine. American Journal of Enology and Viticulture, 32, 159–162.
392	Mizumoto, A., Ohashi, S., Hirohashi, K., Amanuma, Y., Matsuda, T., & Muto, M.
393	(2017). Molecular mechanisms of acetaldehyde-mediated carcinogenesis in squamous
394	epithelium. International Journal of Molecular Science. 18, 1943.
395	doi: 10.3390/ijms18091943.
396	Murthy, A. P., Duraimurugan, K., Sridhar, J., & Madhavan, J. (2019). Application
397	of derivative voltammetry in the quantitative determination of alloxan at
398	single-walled carbon nanotubes modified electrode. Electrochimica Acta, 317,
399	182–190. DOI: 10.1016/j.electacta.2019.05.163.

400	Ocampo, A. M., Santos, L. R., Julian, S., Bailon, M. X., & Bautista, J. (2018).
401	Polyaniline-based cadaverine sensor through digital image colorimetry. <i>e-Polymers</i> .
402	18, 465–471. https://doi.org/10.1515/epoly-2018-0083.
403	Ontañón, I., Sánchez, D., Sáez, V., Mattivi, F., Ferreira, V., & Arapitsas, P. (2020).
404	Liquid chromatography-mass spectrometry-based metabolomics for understanding
405	the compositional changes induced by oxidative or anoxic storage of red wines.
406	Journal of Agricultural and Food Chemistry, 68, 13367–13379.
407	https://doi.org/10.1021/acs.jafc.0c04118.
408	Piljac, J., Martinez, S., Stipèeviæ, T., Petroviæ, Z., & Metikoš-Hukoviæ, M. (2004).
409	Cyclic voltammetry investigation of the phenolic content of Croatian wines.
410	American Journal of Enology and Viticulture, 55, 4. ISSN: 0002-9254.
411	Pwavodi, P. C., Ozyurt, V. H., Asir, S., & Ozsoz, M. (2021). Electrochemical sensor
412	for determination of various phenolic compounds in wine samples using
413	Fe ₃ O ₄ nanoparticles modified carbon paste electrode. <i>Micromachines</i> (Basel),
414	12, 312. doi: 10.3390/mi12030312.

415	Ricci, A., Parpinello, G. P., & Versari, A. (2017). Modelling the evolution of
416	oxidative browning during storage of white wines: Effects of packaging and
417	closures. International Journal of Food Science & Technology, 52, 472–479.
418	https://doi.org/10.1111/ijfs.13303.
419	Sarmento, M. R., Oliveira, J. C., Slatner, M., & Boulton, R. B. (2000). Influence of
420	intrinsic factors on conventional wine protein stability tests. Food Control, 11,
421	<i>423</i> – 432.
422	Schneider, M., Türke, A., Fischer, WJ., & Kilmartin, P. A. (2014). Determination
423	of the wine preservative sulfur dioxide with cyclic voltammetry using inkjet printed
424	electrodes. Food Chemistry, 159, 428-432. doi: 10.1016/j.foodchem.2014.03.049.
425	Tarko, T., Duda-Chodak, A., Sroka, P., & Siuta, M. (2020). The impact of oxygen at
426	various stages of vinification on the chemical composition and the antioxidant and
427	sensory properties of white and red wines. International Journal of Food Science.
428	2020, Article ID 7902974, 1–11. doi: 10.1155/2020/7902974
429	Voelker, B. M., & Sulzberger, B. (1996). Effects of fulvic acid on Fe(II) oxidation
430	by hydrogen peroxide. Environmental Science & Technology, 30, 1106–1114.
431	https://doi.org/10.1021/es9502132.

433	A., & Koroleva, O. V. (2007). Characterization of plant phenolic compounds by
434	cyclic voltammetry. Applied Biochemistry and Microbiology, 43, 661-668.
435	DOI:10.1134/S0003683807060166.
436	Zhang, J., Guan, P., Li, W., Shi, Z., & Zhai, H. (2016). Synthesis and

Yakovleva, K. E., Kurzeev, S. A., Stepanova, E. V., Fedorova, T. V., Kuznetsov, B.

- 437 characterization of a polyaniline/silver nanocomposite for the determination of
- 438 formaldehyde. *Instrumentation Science & Technology*, *44*, 249–258.
- 439 https://doi.org/10.1080/10739149.2015.1104507.

- 440 Zhang, Q., Türke, A., & Kilmartin, P. (2017). Electrochemistry of white wine
- 441 polyphenols using PEDOT modified electrodes. *Beverages*, *3*, 28.
- 442 https://doi.org/10.3390/beverages3030028.
- 443 Zhang, S., Zhang, D., Sheng, Q., & Zheng, J. (2014). PANI-TiC nanocomposite
- film for the direct electron transfer of hemoglobin and its application for biosensing.
- 445 Journal of Solid State Electrochemistry, 18, 2193–2200. DOI
- 446 10.1007/s10008-014-2462-7.

447	Web address: Wine analysis instrument measures more than	10 process parameters
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448 (fossanalytics.com)



Fig. 1. CV at different pH (2~6) of (a) red, (b) rosé, and (c) white wines, recorded at a 0.0079 cm² 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 °C); recorded at a different time interval at a 0.0079 cm² 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 °C); recorded at a different time interval at a 0.0079 cm² 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).

Wine	Grape variety	e	Appearance/ Color	pН	Total organic acids (g/l)	Volatile acids	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	2016	Bright ruby	3.34	3.9	0.4	2.9
	Country Man Tannat		purple				
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

Table 1. Information of wines accompanied with appearance/color and physiochemical

parameters (pH, total acid, volatile acid and total sugar).

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

Parvin Begum^{a*}, Liu Yang^b, Tatsuya Morozumi^a, Teruo Sone^{b,c}, Toshikazu Kawaguchi^{a, b}

^a Faculty of Environmental Earth Sciences, Hokkaido University, Sapporo 060-0810, Japan

^b Graduate School of Global Food Resources, Hokkaido University, Sapporo 060-8589, Japan

[°] Faculty of Agriculture, Hokkaido University, Sapporo 060-8589, Japan

*Corresponding author

Email: parvinchy@ees.hokudai.ac.jp

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First scan of the cyclic voltammogram was recorded each time

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 μ m); 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 μ L 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

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wines	at	different	pН

Red	pН	E _{p,a} / V	I _{p,a} / μAcm ⁻²	E _{p,c} / V	(-) I _{p,c} / µAcm	$\Delta E_p/V$	ΔI _p /μAcm ⁻²	I _{p,a} /I _{p,c}	$E_0 = (E_{p,a} + E_{p,c})/2$
	2	0.429 ± 0.046	$97.711 \pm 0.02a$	$0.339 \pm 0.02a$	$128.012\pm0.02a$	0.091	30.301	0.763	0.384
	3	$0.349\pm0.02a$	$91.269 \pm 0.02a$	0.199 ± 0.031	$126.525 \pm 0.03b$	0.150	35.257	0.721	0.274
	4	0.310 ± 0.046	$78.137 \pm 0.02a$	0.129 ± 0.031	$125.782 \pm 0.03t$	0.180	47.646	0.621	0.219
	5	$0.259\pm0.03b$	57.819 ± 0.046	$0.019 \pm 0.02a$	$90.846\pm0.03b$	0.240	33.027	0.636	0.139
Rose	2	$0.250\pm0.02a$	64.509 ± 0.046	$0.160 \pm 0.02a$	177.071 ± 0.04	0.090	112.562	0.364	0.205
	3	$0.250\pm0.02a$	$71.694 \pm 0.02a$	0.120 ± 0.046	158.736 ± 0.046	0.130	87.042	0.452	0.185
	4	$0.240\pm0.02a$	$76.650 \pm 0.02a$	$0.060 \pm 0.02a$	$131.976 \pm 0.03t$	0.180	55.327	0.581	0.150
	5	0.220 ± 0.046	$76.402 \pm 0.02a$	0.021 ± 0.023	$98.279\pm0.04c$	0.199	21.877	0.777	0.120
White	2	$0.360\pm0.03b$	$78.384 \pm 0.02a$	0.260 ± 0.031	$162.700 \pm 0.02a$	0.100	84.315	0.482	0.310
	3	0.330 ± 0.046	73.924 ± 0.046	$0.180 \pm 0.02a$	$159.479 \pm 0.03t$	0.150	85.555	0.464	0.255
	4	$0.280\pm0.02a$	$64.509 \pm 0.02a$	0.109 ± 0.031	133.711 ± 0.04	0.170	69.202	0.482	0.194
	5	0.260 ± 0.031	$52.120 \pm 0.02a$	0.019 ± 0.031	$92.085 \pm 0.04c$	0.240	39.965	0.566	0.139

Note: Values (means \pm 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 ⁻⁷	$\Delta E_p/V$	∆I _p /µAcm ^{-?}	I _{p,a} /I _{p,c}	E0=(E _{p,a} +E _{p,c})/2
Red	Tannat	$0.409\pm0.01a$	303.797 ± 0.036	$0.159 \pm 0.03c$	$238.024 \pm 0.01a$	0.250	65.772	1.276	0.284
	Merlot	$0.389\pm0.01a$	299.114 ± 0.036	$0.119 \pm 0.03c$	$240.750 \pm 0.01a$	0.270	58.364	1.242	0.254
	Cabernet Sauvigno	$0.379\pm0.03c$	$295.57\pm0.02b$	$0.109 \pm 0.02b$	249.173 ± 0.036	0.270	46.397	1.186	0.244
	Pinot Noir	$0.399\pm0.02a$	$293.418 \pm 0.01a$	0.129 ± 0.01 a	229.104 ± 0.036	0.270	64.314	1.280	0.264
	Shiraz	$0.389\pm0.02a$	$290.127 \pm 0.01a$	0.139 ± 0.01 a	$234.060 \pm 0.01a$	0.250	56.067	1.240	0.264
	Tempanillo	$0.379\pm0.02a$	$286.203 \pm 0.02b$	$0.130\pm0.02b$	240.502 ± 0.021	0.250	45.701	1.190	0.254
Rose	Zinfandal	$0.409\pm0.02b$	299.367 ± 0.036	$0.179 \pm 0.03c$	242.980 ± 0.021	0.230	56.387	1.232	0.294
	Mateus	$0.409\pm0.02b$	$290.38\pm0.02b$	$0.149 \pm 0.01a$	$236.289 \pm 0.01a$	0.260	54.091	1.229	0.279
White	Riesling	$0.409\pm0.03c$	$288.481 \pm 0.01a$	$0.169 \pm 0.02b$	$248.431 \pm 0.01a$	0.240	40.050	1.161	0.289
	Chardonnay	$0.419\pm0.01a$	$284.43\pm0.01a$	$0.139 \pm 0.02b$	225.387 ± 0.036	0.280	59.043	1.262	0.279
	Niagara	$0.419\pm0.03c$	277.342 ± 0.036	0.149 ± 0.01 a	237.033 ± 0.036	0.270	40.309	1.170	0.284
	Sauvignon Blanc	$0.419\pm0.02b$	$273.291 \pm 0.01a$	$0.179 \pm 0.03c$	233.564 ± 0.021	0.240	39.727	1.170	0.299

Note: Values (means \pm 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 limit	Analytes	Ref.
GCE/PANI/GNPs	0.1 mM	Glucose	Ahammad et al. 2010
Hb/PANI-TiC/GCE	0.2 μΜ	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 H₂O₂; 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 cm² 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 °C); recorded at different time interval at a 0.0079 cm² PANI electrode at 0.05 Vs⁻¹. First scan of the cyclic voltammogram was recorded each time.