Effect of Different Glass Shapes and Size on the Time Course of Dissolved Oxygen in Wines during Simulated Tasting

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Abstract: The different shapes and sizes of wine glass are claimed to balance the different wine aromas in the headspace, enhancing the olfactory perception and providing an adequate level of oxygenation. Although the measurement of dissolved oxygen in winemaking has recently received much focus, the role of oxygen in wine tasting needs to be further disclosed. This preliminary study aims to explore, for the first time, the effect of swirling glasses of different shapes and sizes on the oxygen content of wine. Experimental trials were designed to simulate real wine tasting conditions. The O_2 content after glass swirling was affected to a considerable extent by both the type of wine and the glass shape. A lack of correlation between the shape parameters of five glasses and the O_2 content in wine was found which suggests that the nonequilibrium condition can occur during wine tasting. The International Standard Organisation (ISO) glass—considered to be optimal for the wine tasting—allowed less wine oxygenation than any other glass shapes; and the apparent superiority of the ISO glass is tentatively attributed to the more stable oxygen content with time; i.e., less variability in oxygen content than any other glass shape.

Keywords: glass swirling; glass shape; nonequilibrium conditions; oxygen sensor; wine tasting

1. Introduction

Although the critical role of oxygen in enology has recently been disclosed from a chemistry [1] and winemaking point of view [2–4], little information is available from the sensory perspective.

Before tasting, the glass of wine is usually "swirled" by holding the glass by the stem and gently rotating it. This action, technically called 'orbital shaking', increases the surface area of the wine by spreading it over the inner part of the glass and consequently enabling some evaporation to take place [5]. Moreover, it is also expected to draw in some oxygen from the air. The ingress estimated on the undisturbed surface of a wine is about 200 mg/h/m^2 [6].

The physics of wine swirling was recently investigated with an elegant fluid dynamic approach, which modelled the pumping mechanism induced by the wave propagation along the glass wall [7]. Three factors seemed to determine whether the team spotted one big wave in the wine or several smaller ripples: (i) the ratio of the level of wine poured in to the diameter of the glass; (ii) the ratio of the diameter of the glass to the width of the circular shaking; (iii) and the ratio of the forces acting on the wine. From a practical point of view, these findings suggest that the mixing and oxygenation may be optimized with an appropriate choice of shaking diameter (d) and rotation speed (rpm). In this view, the glass shape parameters (Figure S1) can play a key role as they may influence the perceived

volume of wine [8], and the perception of wine odors [9–11], and color [12–14], and therefore the consumer's preference [15,16] as well. Moreover, with time, the glass shape affects the change of headspace chemical composition of wine poured inside, and the D ratio (i.e., maximum diameter divided by opening diameter) seems to be the most important parameter relating glass shape to headspace composition [17].

Considering that both consumers and professional wine tasters usually swirl the glass of wine for approx. 10 to 20 s to unlock odors, there is a need for information to disclose the effect of glass shape on the oxygen content of wines during simulated tasting condition.

This preliminary trial aimed to study whether the glass shape can affect the oxygen content in wine under both static and dynamic conditions (i.e., swirling), the latter to simulate the standard procedure of sensory evaluation of wine. The use of optical oxygen sensors (also called minisensors) allowed for the first time the on-line non-invasive and non-destructive oxygen measurements in a glass under dynamic conditions.

2. Materials and Methods

2.1. Samples

Both red and white wines were selected for this study, including (i) a Rebola 'Nita' white wine Colli di Rimini DOP 2013, (ii) a Sangiovese red wine Carlo Leo Romagna DOP 2013, and (iii) a Cabernet Sauvignon 'Tano' Colli di Rimini DOP 2013 (Az. Agric. Le Calastre, Rimini, Italy). Sangiovese is the main red grape in Italy, Cabernet Sauvignon is a well know international grape variety, and Rebola is an emerging local white grape variety of great interest as well. The bottled wines were provided by the producer and were stored at room temperature (20 ± 1 °C) until the swirling trials. Preliminary characterization of wine composition (Table S1) was carried out according to endorsed methods (RESOLUTION OIV/OENO 390/2010).

2.2. Oxygen Measurement

Non-invasive dissolved oxygen (DO) in wine was measured using an OXY-4 oxygen meter (PreSens GmbH, Regensburg, Germany) equipped with a polymer optical fiber and PSt3 spot, also called minisensor (Presens GmbH). The PSt3 spot had a thickness of 1 mm, a diameter of 4 mm, and a response time (t_{90}, the time for 90% of the change in signal to occur) of 10 s. In each glass, one minisensor was glued 5 mm below the wine level and calibrated with water at a controlled temperature according to the manufacturer's instructions (Figure S2). In each bottle, once uncorked, the dissolved O_2 content of wine was directly measured with an oxygen-dipping probe (Presens GmbH) placed in the middle of the bottle in a dynamic regime (i.e., with stirring). Before bottling the wines, three glass bottles (750 mL) were equipped with two minisensors each to ascertain both the headspace and the dissolved O_2 content in static regime (i.e., bottled wines).

2.3. Glasses

Six different wine glasses were selected for this study, including the ISO official-tasting glass (Bormioli, Parma, Italy) (Table 1; Figure 1). Glass parameters were measured according to the literature (Hirson, Heymann and Ebeler 2012) and each glass was filled with a fixed volume of wine (50 mL) to fit the conditions commonly used during professional wine tasting [18].

2.4. Swirling Trials

To simulate the gesture of hand swirling during wine tasting, each glass of wine was placed onto an orbital shaker (model 709/R ASAL, Cernusco s/N, Italy) with a shaking diameter of 3 cm and a shaking speed of 150 rpm (this value was optimized with preliminary screening trails from 100 to 250 rpm). Each glass of wine was swirled for 10, 20 and 40 s, using independent wine samples.

Table 1. Glass shape parameters, sample volumes and mass transfer coefficient (k_{La}) for dissolved oxygen trials.

No.	Glass Name	Opening Diameter (mm)	Maximum Diameter (mm)	Wine Diameter (mm)	Height (mm)	Headspace Height (mm)	D Ratio *	Fill (mL)	Headspace Volume (mL)	k_{La} (s^{-1})
1	ISO	45.2	63.9	63.5	94.5	68.1	1.41	50	165	0.0001
2	Fresh	49.7	79.0	71.7	116.1	89.2	1.59	50	330	0.0003
3	Mature	53.8	83.2	73.9	128.3	100.7	1.55	50	440	0.0002
4	Rich	67.6	89.8	78.2	130.6	105.7	1.33	50	540	0.0005
5	Reserve	73.0	95.8	81.6	142.5	115.8	1.31	50	710	0.0005
6	Super800	73.4	116.1	89.6	107.7	85.8	1.58	50	750	0.0003

* Maximum diameter divided by opening diameter.

Figure 1. Glasses tested for the experimental trials (see Table 1 for details).

2.5. Experimental Design and Statistical Analysis

The four variables (6 glass types, 3 wines, 3-time readings, 3 replicates for each glass) required 162 independent measurements. Statistical analysis was based on a paired *t*-test (*p*-level < 0.05) using the Unscrambler X (v. 10.3, Camo ASA, Oslo, Norway).

3. Results and Discussion

The oxygen content was measured (i) before and after opening the bottle of wine and (ii) before and during the glass swirling trails, for which protocol was designed to simulate the usual wine tasting by consumers and experts. As expected, the concentration of oxygen in bottled wine was very low with an average range from 4 to 14 µg/L for headspace O_2, and in the range of 3 to 29 µg/L for dissolved O_2 in wine. In bottled wine, the rate of O_2 dissolution was less than the consumption; however, once the bottles are opened the wine comes into contact with air and the oxygen content is expected to rise. In fact, soon after opening the O_2 content in bottled wine increased regularly up to 0.99 mg/L in 15 min (Figure 2). These findings are consistent with the initial oxygen absorption capacity of Madiran red wines with pH 3.78 [19]. The O_2 accumulation in wine implied that the rate of oxygen dissolution was higher than the rate of its uptake. The latter can be (indirectly) measured by the drop in SO_2. According to Boulton [20], the oxygen consumption reactions in wine involve the phenolic compounds as the main substrates and the oxygen consumption is the rate-limiting reaction. The rates of this reaction are first order in oxygen concentration and catalyzed by ferrous ion; therefore, the rate constant would be related to the ferrous ion concentration, but the rate law would depend only on the oxygen concentration. The amount of oxygen found after 15 min most likely increases the wine redox value of ca. 25 mV and will theoretically consume ca. 4 mg/L of sulfur dioxide [21]; both parameters could affect the sensory properties of wines to some extent [4,13].
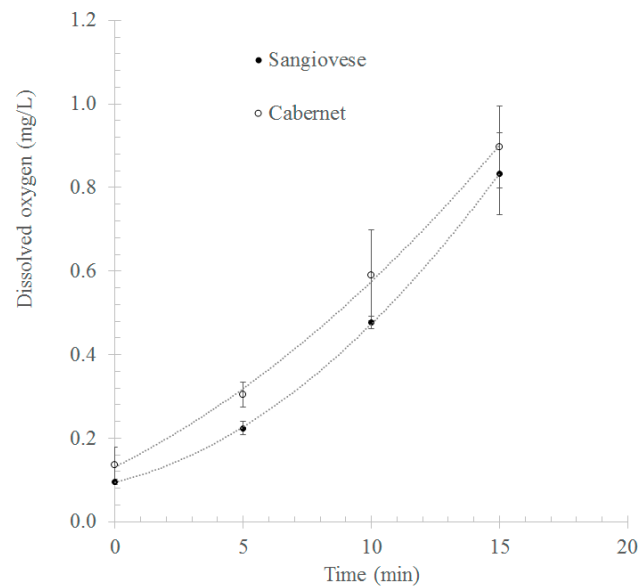
Figure 2. Time course of dissolved oxygen in wine after opening (time zero).

As time progresses, the dissolved oxygen content in wine is expected to reach a plateau approaching the saturation value of ca. 8.6 mg/L at 20 °C [22]. This postulate was confirmed by monitoring with time the dissolved O_2 in a wine glass under firm conditions, i.e., unstirred, unshaken, directly after pouring (Figure 3). The glass n. 5 showed a very fast O_2 intake followed by the glass n. 4, whereas the wine poured on the ISO glass (No. 1), commonly used in professional wine tasting, showed the lowest and most stable O_2 content. Although dissolved oxygen mostly depends on the surface area of wine exposed and the exposure time, a lack of significant correlation was found between the glass shape parameters and the O_2 content in wine. To explain this result, the hypotheses of nonequilibrium conditions and complex interaction among parameters were formulated.
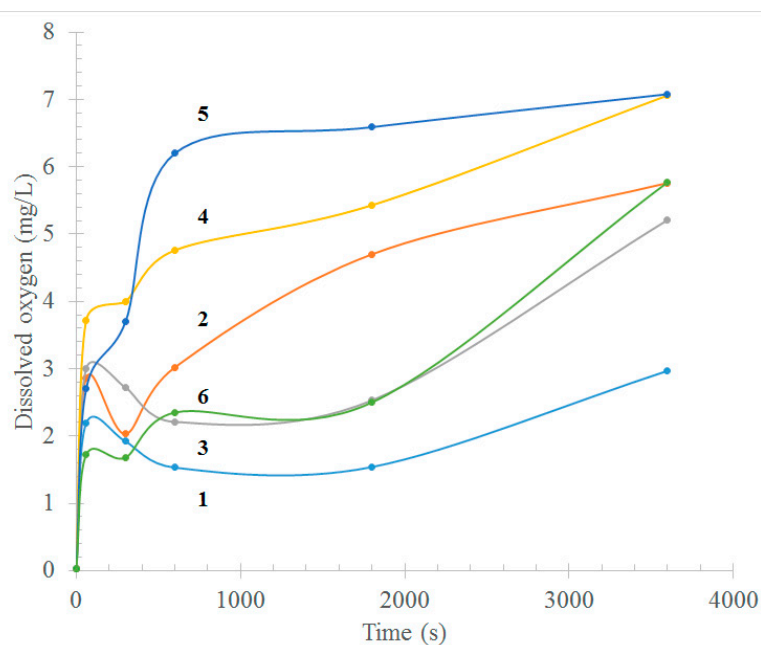

Figure 3. Time course of oxygen dissolution in wine glass under firm conditions. Legend: lines 1–6 refer to different glass shapes (see Table 1 for details).

For any specific wine, the variation of the dissolved oxygen concentration with time can be arranged as:

$$\frac{dO_2}{dt} = k_L a \cdot (O_2^* - O_2)$$

where: $k_L a$: volumetric mass transfer coefficient (T^{-1}); O_2 Dissolved oxygen concentration in wine (mg O_2 L^{-1}); O_2^* Oxygen equilibrium concentration in wine (mg O_2 L^{-1}).

Therefore, the volumetric mass transfer coefficient is the aggregate result of both contributions: the resistance to mass transport in the liquid side (k_L) and the interfacial area (a).

The oxygen transfer rate will decrease during the period of aeration as O_2 approaches O_2^* due to the decline in the driving force ($O_2^* - O_2$). The experimental k_{La} values of wines in opened bottle and glasses were tentatively estimated upon monitoring the increase in the dissolved oxygen concentration of a wine during aeration and agitation and by plotting of oxygen deficit ($O_2^* - O_2$) versus time (t) on a semilogarithmic graph. The slope of the regression line determined the overall mass transfer coefficient ($k_L a$), which showed 5 times variation in the range 0.0001–0.0005 s^{-1} (Table 1), with k_{La} of wine in open bottle at the low value of 0.0001 s^{-1}. As the estimated k_{La} values refer to static conditions (i.e., non-agitated vessels—bottle or glass—and lack of gas supply, e.g., micro-oxygenation) the current findings are consistent with data from the literature. The mass transfer coefficient (k_{La}) in the aerated model wine solution range between 0.00145 s^{-1} [23] and 0.013 s^{-1} [24], the values of which are affected by several parameters, including the oxygen gas flow rate and the intensity of agitation. The best estimate of the rotational speeds effect is given in terms of liquid side mass transfer coefficient (k_L) which increases more than 9 times as rotational speed increases from 50 to 120 rpm [25]. Remarkably, k_{La} is found to increase following a power law with exponent rising from 0.5 to 3 due to significant increases in the interfacial area due to vortex [26].

During professional wine tasting for appellation certification, the wine is held in a glass for about 5–10 min and swirled for approx. 5–30 s before tasting. In this view, the swirling trails were designed to verify the likely occurrence of nonequilibrium conditions during the sensory evaluation of wine. The initial O_2 content at time zero (T_0) was always measured before each swirling trials for every glass shape. The O_2 content after glass swirling was affected to a considerable extent by both the type of wine and the glass shape. Short swirling time (up to 20 s) most often decreased the dissolved oxygen in glass wine (Table 2), while O_2 significantly increased at T_{40} in Rebola white and Sangiovese red wines for all glass shape, except for glass n. 1 in Sangiovese trial. In contrast, the O_2 content in Cabernet Sauvignon wine increased only in glass n. 5 and n. 6 at T_{40}. It seems that the Cabernet Sauvignon would require more time to enhance the O_2 content compared to the other two wines, which are lower in polyphenolic compounds and SO_2.

According to the Henry's law, the oxygen uptake resulting from the presence of antioxidants in wine is rapid and follows a largely exponential form [20]. The alternative hypothesis that O_2 is initially stripped out from solution by the release of CO_2 is postulated. Clearly, the ISO glass (No. 1)—usually considered to be optimal for wine tasting—allowed less wine oxygenation than any other glass shape. Considering that the O_2 content of wine most likely affects the performance of sensory evaluation, based on our findings, the apparent superiority of the ISO glass is tentatively attributed to the more stable oxygen content with time, i.e., less variable than any other glass shape.

The current results under the dynamic regime substantiate the findings of Venturi et al. [27] who also investigated the influence of glass shape on the dissolved oxygen content of a rosé wine under static conditions—using the polarographic ADI dO_2 sensor—for which equilibration time was found to be approx. 1 h.

In conclusion, the current preliminary study showed that pouring wine into a glass considerably affects the O_2 content and the likely occurrence of nonequilibrium condition requires a careful standardization procedure during a real wine tasting.

Table 2. Heatmap plot of dissolved oxygen (mg/L) in wine glasses at time zero (T_0) and after 10, 20 and 40 s (T_{10}, T_{20}, T_{40}). Legend: glass 1–6 refers to different shape (see Table 1 for details). The symbol in letters (a, b) refers to significant paired difference between samples (*p*-level = 0.05) if occurred.

Rebola White Wine: Dissolved O_2 (mg/L)						
Glass	T_0	T_{10}	T_0	T_{20}	T_0	T_{40}
No. 1	3.0	2.9	2.9	3.0	2.7	3.1
No. 2	3.1 [a]	2.2 [b]	4.3	4.1	3.4 [a]	4.2 [b]
No. 3	4.2	4.2	3.1 [a]	4.3 [b]	3.1 [a]	4.5 [b]
No. 4	3.0	3.0	3.1	3.2	3.8 [a]	4.7 [b]
No. 5	3.9 [a]	3.0 [b]	3.7	3.5	3.5 [a]	4.2 [b]
No. 6	2.8	2.5	3.0	3.3	4.5 [a]	6.0 [b]

Sangiovese Red Wine: Dissolved O_2 (mg/L)						
Glass	T_0	T_{10}	T_0	T_{20}	T_0	T_{40}
No. 1	2.8	2.8	2.9 [a]	2.3 [b]	3.5	3.1
No. 2	3.2	3.4	3.2	2.9	2.7 [a]	3.6 [b]
No. 3	2.8	3.3	3.3	3.0	3.3 [a]	4.0 [b]
No. 4	3.1	2.7	3.3	2.9	3.0 [a]	4.2 [b]
No. 5	3.4	2.8	3.2 [a]	4.2 [b]	3.1 [a]	4.2 [b]
No. 6	2.8	3.0	3.1	3.1	3.8 [a]	5.0 [b]

Cabernet Sauvignon Red Wine: Dissolved O_2 (mg/L)						
Glass	T_0	T_{10}	T_0	T_{20}	T_0	T_{40}
No. 1	2.8	2.8	2.9	2.3	2.9	3.0
No. 2	4.2 [a]	3.0 [b]	3.9 [a]	2.8 [b]	4.2 [a]	3.3 [a]
No. 3	3.0	2.7	4.0 [a]	3.1 [b]	4.1	3.8
No. 4	3.5	3.0	3.2	2.8	4.6	4.1
No. 5	3.2	3.1	3.8	3.4	3.8 [a]	4.5 [a]
No. 6	3.4	3.5	3.4	3.8	4.3 [a]	5.5 [a]

References

1.　Danilewicz, J.C. Review of oxidative processes in wine and value of reduction potentials in enology. *Am. J. Enol. Vitic.* **2011**, *63*, 1–10. [CrossRef]

2.　Calderón, J.F.; del Alamo-Sanza, M.; Nevares, I.; Laurie, F. The influence of selected winemaking equipment and operations on the concentration of dissolved oxygen in wines. *Cienc. Investig. Agric.* **2014**, *41*, 273–280. [CrossRef]

3.　Oliveira, V.; Lopes, P.; Cabral, M.; Pereira, H. Kinetics of oxygen ingress into wine bottles closed with natural cork stoppers of different qualities. *Am. J. Enol. Vitic.* **2013**, *64*, 395–399. [CrossRef]

4.　Ugliano, M. Oxygen contribution to wine aroma evolution during bottle aging. *J. Agric. Food Chem.* **2013**, *61*, 6125–6136. [CrossRef] [PubMed]

5.　Arakawa, T.; Iitani, K.; Wang, X.; Kajiro, T.; Toma, K.; Yano, K.; Mitsubayashi, K. A sniffer-camera for imaging of ethanol vaporization from wine: The effect of wine glass shape. *Analyst* **2015**, *140*, 2881–2886. [CrossRef] [PubMed]

6. Mueller-Spath, H. Production of white table wines with minimal SO$_2$. In Proceedings of the Second Australian Wine Industry Technical Conference Proceedings, Tanunda, South Australia, 7–9 August 1973; Australian Wine Research Institute: Tanunda, South Australia, 1973; pp. 51–52.

7. Reclari, M.; Dreyer, M.; Tissot, S.; Obreschkow, S.; Wurm, F.M.; Farhat, M. Surface wave dynamics in orbital shaken cylindrical containers. *Phys. Fluids* **2014**, *26*. [CrossRef]

8. Pechey, R.; Attwood, A.S.; Couturier, D.-L.; Munafò, M.R.; Scott-Samuel, N.E.; Woods, A.; Marteau, T.M. Does glass size and shape influence judgements of the volume of wine? *PLoS ONE* **2015**, *10*, e0144536. [CrossRef] [PubMed]

9. Delwiche, J.F.; Pelchat, M.L. Influence of glass shape on wine aroma. *J. Sens. Stud.* **2002**, *17*, 19–28. [CrossRef]

10. Hummel, T.; Delwiche, J.F.; Schmidt, C.; Hüttenbrink, K.B. Effects of the form of glasses on the perception of wine flavors: A study in untrained subjects. *Appetite* **2003**, *41*, 197–202. [CrossRef]

11. Vilanova, M.A.R.; Vidal, P.; Cortes, S. Effect of the glass shape on flavor perception of 'toasted wine' from Ribeiro (NW Spain). *J. Sens. Stud.* **2008**, *23*, 114–124. [CrossRef]

12. Cliff, M.A. Influence of wine glass shape on perceived aroma and colour intensity in wines. *J. Wine Res.* **2001**, *12*, 39–46. [CrossRef]

13. Venturi, F.; Andrich, G.; Sanmartin, C.; Scalabrelli, G.; Ferroni, G.; Zinnai, A. The expression of a full-bodied red wine as a function of the characteristics of the glass utilized for the tasting. *CyTA J. Food* **2014**, *12*, 291–297. [CrossRef]

14. Wan, X.; Woods, A.T.; Seoul, K.-H.; Butcher, N.; Spence, C. When the shape of the glass influences the flavour associated with a coloured beverage: Evidence from consumers in three countries. *Food Qual. Prefer.* **2015**, *39*, 109–116. [CrossRef]

15. Spence, C.; Wan, X. Beverage perception and consumption: The influence of the container on the perception of the contents. *Food Qual. Prefer.* **2015**, *39*, 131–140. [CrossRef]

16. Spence, C.; Van Doorn, G. Does the shape of the drinking receptacle influence taste/flavour perception? A review. *Beverages* **2017**, *3*, 33. [CrossRef]

17. Hirson, G.D.; Heymann, H.; Ebeler, S.E. Equilibration time and glass shape effects on chemical and sensory properties of wine. *Am. J. Enol. Vitic.* **2012**, *63*, 515–521. [CrossRef]

18. Jackson, R.S. *Wine Tasting: A Professional Handbook*, 2nd ed.; Academic Press: San Diego, CA, USA, 2009.

19. Moutounet, M.; Mazauric, J.-P. L'oxygène dissous dans les vins. *Revue Francaise d'Oenologie* **2001**, *186*, 12–15.

20. Boulton, R. Both White Wines and Red Wines Can Consume Oxygen at Similar Rates. 2011. Available online: http://www.acenologia.com/enfoques/roger_boulton_enf0612_eng.htm (accessed on 7 December 2017).

21. Ribéreau-Gayon, P.; Glories, Y.; Maujean, A.; Dubourdieu, D. Aging red wines in vat and barrel: Phenomena occurring during aging. In *Handbook of Enology*; John Wiley & Sons, Ltd.: Hoboken, NJ, USA, 2006; pp. 387–428.

22. Kilmartin, P.A. The oxidation of red and white wines and its impact on wine aroma. *Chem. N. Z.* **2009**, *1*, 18–22.

23. Adoua, R.; Mietton-Peuchot, M.; Milisic, V. Modelling of oxygen transfer in wines. *Chem. Eng. Sci.* **2010**, *65*, 5455–5463. [CrossRef]

24. Saa, P.A.; Moenne, M.I.; Perez-Correa, J.R.; Agosin, E. Modeling oxygen dissolution and biological uptake during pulse oxygen additions in oenological fermentations. *Bioprocess Biosyst. Eng.* **2012**, *35*, 1167–1178. [CrossRef] [PubMed]

25. Hebrard, G.; Zeng, J.; Loubiere, K. Effect of surfactants on liquid side mass transfer coefficients: A new insight. *Chem. Eng. J.* **2009**, *148*, 132–138. [CrossRef]

26. Scargiali, F.; Busciglio, A.; Grisafi, F.; Brucato, A. Oxygen transfer performance of unbaffled stirred vessels in view of their use as biochemical reactors for animal cell growth. *Chem. Eng. Trans.* **2012**, *27*, 205–210.

27. Venturi, F.; Andrich, G.; Sanmartin, C.; Taglieri, I.; Scalabrelli, G.; Ferroni, G.; Zinnai, A. Glass and wine: A good example of the deep relationship between drinkware and beverage. *J. Wine Res.* **2016**, *27*, 153–171. [CrossRef]

Table S1. Chemical composition of wines.

| Parameter	Unit	Rebola	Sangiovese	Cabernet Sauvignon
Alcohol	% v/v	14.26	14.23	13.29
Residual sugars	g/L	1.2	2.6	2.3
Total acidity (H_2T)	g/l	4.81	5.16	5.43
pH	—	3.37	3.79	3.67
Volatile acidity	g/l	0.28	0.69	0.59
Glycerol	g/L	7.1	10.4	10.1
Potassium	g/l	0.73	1.60	1.41
Dry extraxct	g/l	20.1	34.9	33.7
SO2 total	mg/l	74	56	62
SO2 free	mg/l	30	10	16
Total polyphenols	mg/l	868	2812	2771
OD 420 nm	Abs.	0.19	2.61	3.20
OD 520 nm	Abs.	—	4.31	5.99
OD 620 nm	Abs.	—	0.545	0.822
CO_2	mg/l	584	400	388

Figure S1. Glass parameters.
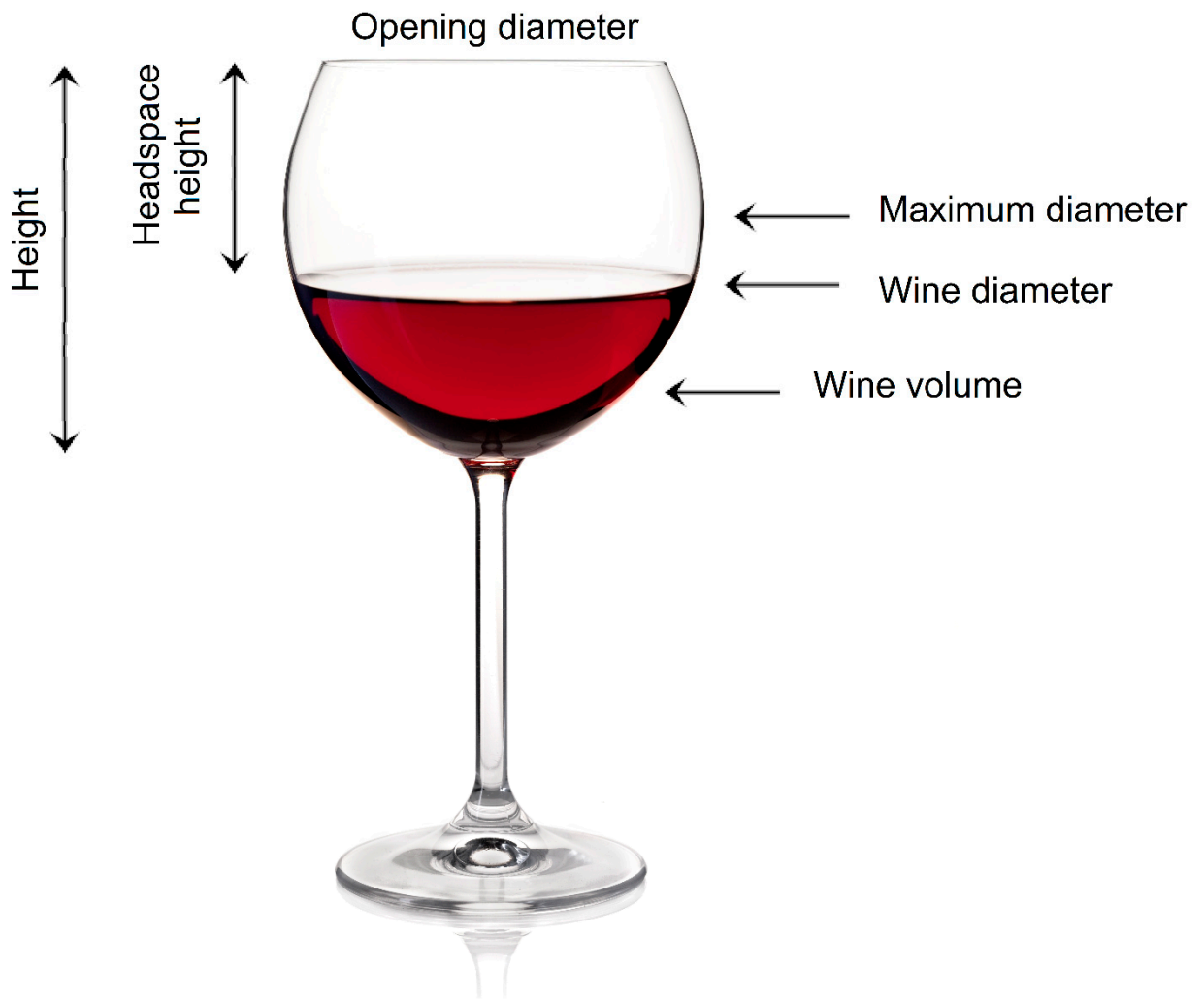
Figure S2. Experimental online measurement.

Oxygen sensor