An Assessment of the Performance of the Coravin Wine System for Different Types of Stoppers

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Abstract: The Coravin Wine System is a device used to pour wine from a bottle and any number of times without pulling out the cork. This study demonstrates that the device can be used to pour wine out of a bottle, under the protection of argon gas, with no ill-effects in the first month. After the first month, there is considerable oxygen ingress through the hole created by the Coravin Wine System needle, and that test wines reach critical oxygen levels within 6 months and exceed thresholds within one year. After one year, the test wine under the natural cork stopper had excessive ethyl acetate (nail polish remover smell), a markedly deeper color compared to the control wine, and was completely depleted of free SO_2; it was spoiled. The test wine under the twin-disc stopper had suffered in quality; it displayed a deeper color and was almost completely depleted of free SO_2. The test wine under the microagglomerate stopper performed best although oxygen levels also reached critical thresholds by the end of one year but considerably less than other stopper types, by one to two orders of magnitude. The test wine under the polymer stopper was removed from the study once the stopper was pierced with the Coravin Wine System as it leaked excessively; this stopper type is clearly stated as not supported by Coravin. All stopper types in control bottles performed very well with very low TPO levels and normal SO_2 losses recorded at the end of one year; the control wine under the polymer stopper had the lowest TPO. When using the Coravin Wine System it is highly recommended to sanitize the needle with a 70% v/v ethanol solution to minimize the risk of wine spoilage by acetic acid bacterial infection.

Key words: Coravin Wine System, volatile acidity (VA), acetaldehyde, sulfur dioxide (SO_2), headspace oxygen (HSO), dissolved oxygen (DO), total package oxygen (TPO**)**

Introduction. Wine enthusiasts often wonder how that special bottle of wine is evolving but do not wish to uncork it as the wine cannot be saved for more than a day or two. Wine drinkers may also know that they will not finish a bottle and would like to save the leftover wine for a later date.

The Coravin™ Wine System was designed to meet the needs of such wine enthusiasts and drinkers. It allows pouring wine from a bottle without removing the capsule or pulling the stopper. The device is designed for stoppers made of natural cork material or from cork particles; it is not designed for synthetic stoppers or screw caps.

The main components of the device include a thin hollow needle, a dispensing lever, and an argon gas capsule. To pour wine, the Coravin Wine System is placed over the bottle, the needle is pushed down and inserted through the capsule and stopper, the bottle is then inverted and the lever is depressed. The bottle becomes pressurized with argon, an inert gas, which starts the flow of wine into a glass. When done, the bottle is returned to an upright position and the needle is pulled out. The extra headspace in the bottle remains filled with argon to protect the wine from oxygen, which can spawn oxidative reactions and impact wine quality. The stopper is said to "reseal" the hole created by the needle to prevent wine leakage and oxygen ingress while the bottle is re-cellared. As long as no oxygen penetrates the bottle, the argon gas fully protects the wine. If oxygen is allowed to reach the wine through the hole created by the needle or around the stopper as in any other bottle of wine, argon cannot protect the wine.

The objective of this study was to assess the performance of the Coravin Wine System and its ability to keep oxygen out of bottles and protect wine from oxidation once stoppers would be pierced with the needle.

Four different stoppers were selected: a 100% natural cork stopper, two technical stoppers (twin-disc and microagglomerate), and a synthetic stopper. Although the Coravin Wine System cannot be used with synthetic stoppers because they do not reseal the hole, a synthetic stopper was included in this study to observe the behavior once punctured and to assess and compare oxygen-barrier capabilities with other stopper types.

To monitor oxygen ingress and any potential oxidation or spoilage impacts, various parameters were measured, monitored and correlated based on autoxidation reactions shown in Figure 1. These included headspace oxygen (HSO), dissolved oxygen (DO), total package oxygen (TPO), pH, total acidity (TA), volatile acidity (VA), ethanol concentration as a ratio of volume to volume (ABV), free sulfur dioxide (FSO2), total sulfur dioxide (TSO2), color intensity (IC), hue (H), and total phenol content (TPC). Acetaldehyde concentration would be an important parameter to monitor but it was not included due to limitations in instrumentation and analytical methods.

This study spanned one year. Wine was poured using a Coravin Wine System from test bottles after one week, one month, 90 days, 6 months, and one year. Parameters were measured and compared to control bottles.

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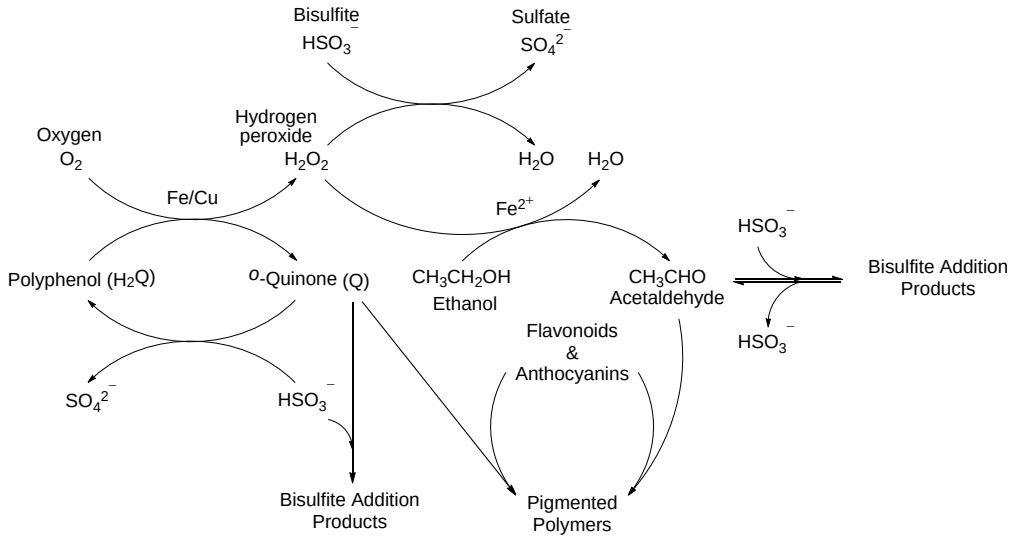

Figure 1: Overview of the autoxidation reactions in wine (adapted from Schmidtke et al. 2011; Vivas 1999; Biondi Bartolini et al. 2008)

Materials and Methods

Test Equipment and Instrumentation. A Coravin 1000 System was purchased from Coravin Inc. (coravin.com), Burlington, Massachusetts. Extra Coravin Capsules of pure argon gas were purchased from Vinum Design (vinumdesign.com), Montréal, Québec.

A Hanna Instruments HI 902C Automatic Titration System was used to measure pH and for titrating for total acidity (TA) and volatile acidity (VA) using a pH electrode. The unit was equipped with a temperature probe for auto-temperature compensation. For TA determination, 10-mL wine samples were titrated with a 0.1*N* NaOH (sodium hydroxide) solution to a fixed endpoint of 8.2.

An RD80 Volatile Acid Still, a modified version of a standard Cash Still, purchased from Research & Development Glass Products & Equipment, Berkeley, California, was used to distill 10-mL wine samples into 100-mL distillates, which were then titrated similarly to TA. Wine samples to be distilled were treated with pharmacy-grade hydrogen peroxide to bind free SO_2 to prevent its distillation.

A 10-mL Class A pipette was used to obtain samples for acidity titration measurements.

The Hanna Instruments HI 902C Automatic Titration System was also used for free SO_2 (FSO2) and total SO_2 (TSO2) determination using the Orienting Ripper Method with an ORP electrode. The unit was equipped with a temperature probe for auto-temperature compensation. 50-mL wine samples were obtained using a 50-mL Class A pipette and were treated with a 25% sulfuric acid solution (HI 70444) and stabilized with potassium iodide (KI) powder (HI 70404) and then titrated using a 0.02*N* stabilized iodine solution (HI 70440). For TSO2 determination, wine samples were first treated with a 5.0M NaOH solution (HI 70435). All chemicals identified with an HI prefix are Hanna Instruments products and were purchased from Hanna Instruments, Laval, Québec, and used within their expiry dates.

A Hanna Instruments HI 83742 Color and Total Phenols Determination Photometer for Wine, purchased from Prolab Scientific, Laval, Québec, was used to measure color intensity (IC), hue (H) and total phenol content (TPC). IC and H are measured at wavelengths of 420 and 520 nm; TPC is measured at a wavelength of 610 nm. 2-mL wine samples were obtained using a 2000-µL pipettor and were treated with a wine solvent (HI 83742-0) for determination of IC and H. For TPC determination, diluted wine samples were prepared by adding 0.2 mL of each wine obtained using a 200-µL pipettor to 2 mL of distilled water. Then, 0.2 mL of each of the diluted wine samples were added to 5 mL of acid reagent (HI 83742A-0) followed by the addition of 6 drops of Folin & Ciocalteu's reagent (HI 83742B-0) and sufficient carbonate buffer (HI 83742C-0) to bring the total reacted volume to 10 mL. TPC was measured following a 2-hour reaction wait period. IC, H and TPC measurements were taken by first zeroing the instrument with distilled water. All chemicals identified with a HI prefix are Hanna Instruments products and were purchased from Hanna Instruments, Laval, Québec, and used within their expiry dates.

A NomaSense O_2 P300 unit, purchased from Nomacorc LLC, Zebulon, North Carolina, was used in conjunction with 5-mm PSt3 oxygen-sensitive spots (PreSens GmbH, Germany) to measure headspace oxygen (HSO), dissolved oxygen (DO) and total package oxygen (TPO) in bottles and wines. This unit uses oxo-luminescence technology to measure oxygen in liquid or gas phases. Two PSt3 oxygen-sensitive spots were glued inside each control and test bottle: one spot in the headspace (ullage) and one spot at the bottom of bottles to ensure that the volume of wine left over after one year would be above the spot in order to measure DO. HSO was measured in hPa by first entering the bottle opening diameter and headspace length into the unit for each bottle. When wine (150 mL) was poured using the Coravin Wine System, the bottle opening diameter and headspace length were calculated and entered to factor in the headspace created by each pouring. For example, the actual bottle opening diameter and headspace length readings entered after bottling were 18 mm and 18 mm, respectively, then 18 mm and 608 mm after the first 150-mL pour,

and 36 mm and 299 mm after the second 150-mL pour. The unit converts hPa measurements into mg/L, according to Equation (1), and then adds DO measurements, also in mg/L, to display TPO in mg/L. A temperature probe was inserted into an empty bottle or a 750-mL bottle of water that had reached the same temperature as the wines under test to allow for proper measurements.

$$HSO\ (mg/L) = HSO\ (hPa) \times \frac{\pi d^2 \times HS \times 32}{8.314 \times (T+273) \times 40{,}000 \times V} \quad (1)$$

A pour volume of 150 mL was chosen based on the total amount (125 mL) of wine needed to perform all tests on each test day.

A Dujardin-Salleron traditional ebulliometer, purchased from Elnova, Rougement, Québec, was used to measure ethanol content, as % volume by volume (ABV). 25-mL samples were obtained using a 25-mL Class A pipette and then diluted to 50 mL. ABV measurements were multiplied by a factor of 2.

Calibration and Standardization. The HI 902C pH electrode was cleaned and calibrated prior to each test session using a 3-point calibration process with 4.01, 7.01 and 10.01 buffers purchased from Hanna Instruments, Laval, Québec.

The 0.1*N* NaOH solution was prepared fresh if the period between uses exceeded 3 months. The solution was standardized with a 0.1*N* KHP (potassium hydrogen phthalate) solution prior to each test session. A 5% by volume acetic acid solution was used prior to each test session to validate VA measurements.

The HI 902C ORP electrode was cleaned and calibrated prior to each test session and then verified with a redox solution (HI 7020) to confirm a reading in the range 200–275 mV measured at 20°C/77°F. Standards were prepared using a 10% sulfite solution to validate FSO2 and TSO2 measurements. Bound SO_2 (BSO2) were not measured analytically but, rather, calculated as the difference between TSO2 and FSO2.

Prior to each test session, oxygen was measured with the NomaSense O_2 P300 unit in an empty bottle equipped with an oxygen-sensitive spot to ensure that the unit was properly calibrated; readings of approximately 21% were recorded, as expected.

Ebulliometric measurements were calibrated by first determining the boiling temperature of distilled water at atmospheric pressure.

Wine Samples. Wine was vinified in September 2014 using California (Vittoria brand) Pinot Noir grapes from the 2014 harvest. Fermentation was carried out in a small plastic vat and then held in a 23-L carboy to complete malolactic fermentation. French, medium-toast oak chips were added at a rate of 4 g/hL and left in contact with the wine for 4 months. The FSO2 level was adjusted to 0.5 mg/L molecular SO_2 according to pH. The wine was then filtered down to 1.8 microns before bottling in 750-mL flint bottles equipped with oxygen-sensitive spots and then corked with a floor corker. Prior to corking, headspace was flushed with a mix of argon, nitrogen and carbon dioxide gases from a can of Private Reserve™ Wine Preserver. No capsules were used to allow observation of any potential leakage through stoppers once pierced with the Coravin Wine System. Flint bottles were required to allow oxygen measurements with the NomaSense O_2 P300 through the glass material. Bottles were left to stand upright for 5 days to allow stoppers to re-expand to their original forms, and then laid horizontally in the cellar at 13°C/55°F. This was DAY -10 (DAY 0 is the day stoppers are first pierced). Table 1 lists measured values on DAY -10.

pH	TA (g/L)	VA (mg/L)	FSO2 (mg/L)	TSO2 (mg/L)	IC	H	TPC (g/L)
3.91	4.85	828.9	50.3	82.1	2.90	0.98	1.72

Table 1: Wine parameters measured on DAY -10.

Stoppers. Wine bottles were corked with one of four (4) different stoppers: a Cork Supply 45×24 Super Select, Alpha Wash natural cork with paraffin/silicone coating; a Cork Supply 44×23 1+1 (twin-disc) technical stopper; a Vapex 44×24 Alpha, Bopsil chamfered microagglomerate technical stopper with an effective length of 40 mm; and a Nomacorc Select Series 900 44.5×22 polymer cork. All stoppers were obtained as samples from Vines to Vintages, Jordan, Ontario. Two (2) bottles of each (a CONTROL and a TEST bottle) were prepared.

Although the Coravin Wine System is not designed for use with polymer-type stoppers, this stopper was included in this study to observe its behavior in the control bottle and when pierced in the test bottle.

Test Procedure. Bottles were taken out of the cellar and into the lab at least 2 hours prior to tests to allow for bottles to stabilize at room temperature for measurements and for SO_2 to reach equilibrium between the wine and headspace.

On DAY -10, bottle opening diameter and headspace length for all bottles were measured and entered into the NomaSense O_2 P300 to measure HSO. HSO, DO and TPO were measured in all wines and bottles. Temperature readings were obtained and recorded for all oxygen-related measurements. All bottles were then returned to the cellar for storage, horizontally, for five more days.

On DAY -5 and on DAY 0, HSO, DO and TPO were again measured in all wines and bottles. Temperature readings were obtained and recorded for all oxygen-related measurements. On DAY 0, the stopper of each TEST bottle was pierced with the Coravin Wine System and then retrieved *without* pouring any wine. The needle was inserted as per product instructions, which involves purging air from the needle prior to insertion through the stopper. All bottles were then returned to the cellar for storage, horizontally, for seven more days.

On DAY 7 (end of first week following piercing), HSO, DO and TPO were again measured in all wines and bottles. Temperature readings were obtained and recorded for all oxygen-related measurements. The Coravin Wine System was then used to pour exactly 150 mL of wine from each TEST bottle into a graduated cylinder (±1.0 mL) and then transferred and sealed into a glass flask. pH, TA, VA, FSO2, TSO2, IC, H and TPC were measured for all TEST wines. Samples were degassed by nitrogen sparging prior to distillation for VA determination. All bottles were returned to the cellar for storage, horizontally, until the next test session.

This procedure and tests were repeated on DAY 30 (end of first month), DAY 90 (end of third month), and DAY 180 (end of sixth month). Bottle opening diameter and headspace length were

re-calculated as outlined above and then entered into the NomaSense O_2 P300 for HSO measurements.

On DAY 360 (end of first year), this procedure and tests were repeated now including CONTROL wines. ABV in CONTROL and TEST wines were also measured.

Results and Discussion

Test results. Tables 2, 3 and 4 list HSO, DO and TPO values measured in control and test wines on DAY -10, DAY -5 and DAY 0, respectively.

Stopper type	HSO (mg/L)	DO (mg/L)	TPO (mg/L)
Natural - C	0.225	0.602	0.827
Natural - T	0.174	0.694	0.868
Twin-disc - C	0.192	0.578	0.770
Twin-disc - T	0.171	0.657	0.828
MicroAgglo - C	0.171	0.565	0.736
MicroAgglo - T	0.246	0.656	0.902
Polymer - C	0.148	0.432	0.580
Polymer - T	0.131	0.495	0.626

Table 2: HSO, DO and TPO values measured in control (C) and test (T) wines on DAY -10.

Stopper type	HSO (mg/L)	DO (mg/L)	TPO (mg/L)
Natural - C	0.270	0.011	0.281
Natural - T	0.163	0.014	0.177
Twin-disc - C	0.425	0.011	0.435
Twin-disc - T	0.483	0.014	0.497
MicroAgglo - C	0.269	0.015	0.284
MicroAgglo - T	0.348	0.013	0.361
Polymer - C	0.196	0.006	0.202
Polymer - T	0.290	0.016	0.306

Table 3: HSO, DO and TPO values measured in control (C) and test (T) wines on DAY -5.

Tables 5, 6, 7, 8 and 9 list HSO, DO and TPO values measured in control and test wines and pH, TA, VA, FSO2, TSO2, IC, H and TPC values measured in test wines on DAY 7, DAY 30, DAY 90, DAY 180 and DAY 360, respectively. Table 9 also lists ethanol levels in control and test wines measured on DAY 360.

Stopper type	HSO (mg/L)	DO (mg/L)	TPO (mg/L)
Natural - C	0.028	0.007	0.034
Natural - T	0.013	0.001	0.014
Twin-disc - C	0.037	0.004	0.041
Twin-disc - T	0.038	0.012	0.050
MicroAgglo - C	0.015	0.005	0.020
MicroAgglo - T	0.026	0.004	0.031
Polymer - C	0.028	0.004	0.032
Polymer - T	0.027	0.011	0.038

Table 4: HSO, DO and TPO values measured in control (C) and test (T) wines on DAY 0.

General observations. HSO, DO and TPO levels in all bottles (control and test) on DAY -10 were at desired levels with TSO in the range 0.58–0.90 mg/L and below the recommended 1 mg/L threshold and well below the maximum of 2 mg/L to minimize oxidation effects and maintain product quality. The relatively low HSO levels in the range 0.13–0.25 mg/L demonstrate that nitrogen sparging of bottles at bottling had some positive effect but still illustrate the challenge in keeping air out with manual bottling and corking.

In the first few days post bottling until DAY -5, DO levels dropped substantially as dissolved oxygen was being chemically reduced into hydrogen peroxide (H_2O_2) under the catalytic effects of iron (Fe) and copper (Cu) naturally present in wine. FSO2 levels would be expected to decrease, albeit only slightly, as H_2O_2 quickly binds sulfur dioxide (SO_2). As one mole of molecular oxygen (32 g/mol) binds one mole of SO_2 (64 g/mol) and given the levels of DO in the range 0.432–0.694 mg/L on DAY -10 compared to 0.006–0.016 mg/L on DAY -5, FSO2 would decrease by less than 0.9–1.4 mg/L. Some dissolved oxygen would also have been involved in oxidizing polyphenols into their *o*-quinone forms to then regenerate their *o*-diphenols by reacting with bisulfite ions, therefore contributing to a small decrease in FSO2. Binding with other carbonyls compounds, such as acetaldehyde produced by yeast fermentation, can also contribute to a decrease in FSO2.

On DAY -5, HSO levels increased by 0.01–0.31 mg/L likely due to trapped oxygen transferred from within the stoppers. It cannot be excluded that HSO increases may be due to the quality of the stopper and its permeability to atmospheric oxygen while bottles were being stored upright in the first 5 days of the study to allow stopper materials to re-expand to their original form.

By DAY 0, just prior to stoppers being pierced with the needle of the Coravin Wine System for the first time, all bottles had reached equilibrium with HSO, DO and TPO dropping significantly and which remained very low in control bottles until the end of the study on DAY 360.

Stopper type	pH	TA (g/L)	VA (mg/L)	FSO2 (mg/L)	TSO2 (mg/L)	IC	H	TPC (g/L)	HSO (mg/L)	DO (mg/L)	TPO (mg/L)
Natural - C									0.013	0.005	0.018
Natural - T	3.88	4.47	781.1	40.5	72.4	2.92	0.98	1.63	0.005	0.004	0.009
Twin-disc - C									0.012	0.004	0.016
Twin-disc - T	3.88	4.45	793.6	39.8	71.3	2.94	0.98	1.64	0.011	0.003	0.015
MicroAgglo - C									0.007	0.004	0.011
MicroAgglo - T	3.86	4.60	788.1	41.2	73.2	2.89	0.96	1.56	0.014	0.002	0.016
Polymer - C									0.016	0.001	0.016
Polymer - T											

Table 5: HSO, DO and TPO values measured in control (C) and test (T) wines and pH, TA, VA, FSO2, TSO2, IC, H and TPC values measured in test (T) wines on DAY 7. No results are reported for the polymer stopper as the test wine was removed due to excessive leakage.

Stopper type	pH	TA (g/L)	VA (mg/L)	FSO2 (mg/L)	TSO2 (mg/L)	IC	H	TPC (g/L)	HSO (mg/L)	DO (mg/L)	TPO (mg/L)
Natural - C									0.009	0.003	0.012
Natural - T	3.86	4.77	721.3	37.2	72.6	2.98	0.99	1.58	0.153	0.001	0.155
Twin-disc - C									0.006	0.003	0.009
Twin-disc - T	3.87	4.76	707.0	37.6	70.8	2.86	0.99	1.51	0.205	0.002	0.207
MicroAgglo - C									0.005	0.001	0.006
MicroAgglo - T	3.87	4.78	730.6	38.7	70.8	2.96	0.99	1.48	0.198	0.002	0.199
Polymer - C									0.012	0.001	0.013
Polymer - T											

Table 6: pH, HSO, DO and TPO values measured in control (C) and test (T) wines and pH, TA, VA, FSO2, TSO2, IC, H and TPC values measured in test (T) wines on DAY 30. No results are reported for the polymer stopper as the test wine was removed on DAY 7 due to excessive leakage.

Stopper type	pH	TA (g/L)	VA (mg/L)	FSO2 (mg/L)	TSO2 (mg/L)	IC	H	TPC (g/L)	HSO (mg/L)	DO (mg/L)	TPO (mg/L)
Natural - C									0.010	0.013	0.023
Natural - T	3.99	4.74	741.7	30.9	61.1	2.95	0.98	1.43	0.415	0.015	0.430
Twin-disc - C									0.007	0.010	0.017
Twin-disc - T	3.98	4.83	727.7	32.6	63.3	2.95	0.98	1.44	0.352	0.003	0.356
MicroAgglo - C									0.007	0.013	0.020
MicroAgglo - T	3.99	4.83	727.5	33.6	63.3	2.92	0.98	1.46	0.457	0.011	0.468
Polymer - C									0.008	0.005	0.013
Polymer - T											

Table 7: HSO, DO and TPO values measured in control (C) and test (T) wines and pH, TA, VA, FSO2, TSO2, IC, H and TPC values measured in test (T) wines on DAY 90. No results are reported for the polymer stopper as the test wine was removed on DAY 7 due to excessive leakage.

Stopper type	pH	TA (g/L)	VA (mg/L)	FSO2 (mg/L)	TSO2 (mg/L)	IC	H	TPC (g/L)	HSO (mg/L)	DO (mg/L)	TPO (mg/L)
Natural - C									0.010	0.010	0.019
Natural - T	3.89	4.5652	694.7	29.6	60.1	3.08	0.99	1.36	0.874	0.024	0.897
Twin-disc - C									0.008	0.008	0.016
Twin-disc - T	3.88	4.4748	717.6	30.1	60.6	3.10	0.99	1.43	0.938	0.009	0.948
MicroAgglo - C									0.011	0.015	0.026
MicroAgglo - T	3.87	4.5087	720.0	30.9	61.3	3.11	1.00	1.32	0.909	0.017	0.927
Polymer - C									0.004	0.002	0.006
Polymer - T											

Table 8: HSO, DO and TPO values measured in control (C) and test (T) wines and pH, TA, VA, FSO2, TSO2, IC, H and TPC values measured in test (T) wines on DAY 180. No results are reported for the polymer stopper as the test wine was removed on DAY 7 due to excessive leakage.

Stopper type	pH	TA (g/L)	VA (mg/L)	FSO2 (mg/L)	TSO2 (mg/L)	IC	H	TPC (g/L)	HSO (mg/L)	DO (mg/L)	TPO (mg/L)	EtOH (%v/v)
Natural - C	3.91	7.1724	938.7	29.7	64.6	2.96	0.97	1.76	0.017	0.056	0.073	14.6
Natural - T	3.87	5.7018	846.4	0.0	12.0	7.45	0.77	1.40	142.98	2.61	145.59	14.3
Twin-disc - C	3.94	7.0563	959.2	30.1	65.0	3.01	0.99	1.48	0.016	0.047	0.064	14.6
Twin-disc - T	3.86	5.9211	909.7	2.26	14.6	4.31	1.00	1.55	72.84	3.06	75.91	14.4
MicroAgglo - C	3.93	6.97	926.1	30.1	64.6	3.11	0.96	1.59	0.013	0.056	0.069	14.6
MicroAgglo - T	3.87	6.06	975.5	24.0	56.7	3.15	1.02	1.58	2.14	0.067	2.21	14.6
Polymer - C	3.89	7.1337	981.8	27.1	66.9	3.24	0.95	1.55	0.009	0.040	0.049	14.6
Polymer - T												

Table 9: pH, TA, VA, FSO2, TSO2, IC, H, TPC, HSO, DO, TPO and EtOH values measured in control (C) and test (T) wines on DAY 360. No results are reported for the polymer stopper as the test wine was removed on DAY 7 due to excessive leakage.

Natural cork stopper. Refer to Figures 2 to 7.

The test wine behaved similarly with respect to decreasing HSO and DO levels (Figure 2), both dropping significantly from DAY -5 levels until DAY 30. There was a gradual drop in FSO2 (Figure 3) until DAY 30 from 50.3 mg/L to 37.2 mg/L, a drop of approximately 26% of its initial level. The small loss of FSO2 measured on DAY 7 was likely due to a combination of H_2O_2 binding, carbonyl binding, regeneration of *o*-quinones into their *o*-diphenols, dissipation at bottling owing to the drop in TSO2, and dissipation from pouring wine into the graduated cylinder. TSO2 then remained constant until DAY 30 with a small increase in BSO2 as SO_2 continued binding. pH, TA and VA (Figure 4) remained constant within the error range of instrumentation. IC and H (Figure 5) remained constant while TPC dropped slightly, suggesting oxidation of phenolic substances in line with observations on oxygen and SO_2 consumption.

On DAY 30 (Figure 2), there was a significant increase in HSO in the test wine but with TPO still well below acceptable levels, albeit significantly higher than in the control bottle, 0.154 vs. 0.012 mg/L; the latter was the lowest TPO level recorded in the control bottle during the study. The impacts on FSO2, TSO2, pH, TA, VA, IC, H and TPC (Figures 3, 4, 5 and 6) were limited as the headspace oxygen had likely not yet become dissolved in the wine. A small amount of leakage through the hole, where the needle pierced through, was observed. The top of the cork was wiped with 90% v/v ethanol to remove wine likely due to removal of the needle.

However, on DAY 90, HSO (Figure 2) again increased substantially from 0.153 mg/L to 0.415 mg/L, likely due to the hole in the stopper, with an increase in DO from 0.001 mg/L to 0.015 mg/L, likely due to headspace oxygen becoming dissolved and oxygen being consumed. The small increase in DO can also be attributed to instrumentation error. Both FSO2 and TSO2 (Figure 3) decreased with a small drop in BSO2, suggesting that FSO2 was likely being lost through the hole in the stopper. Some FSO2 loss may also be due to the same reasons stated above. FSO2 and TSO2 levels were down approximately 61% and 74% of their initial levels. Although there were no significant changes in TA and VA (Figure 4), pH increased by 0.13 but then dropped back down by a similar amount on DAY 180; this cannot be explained and is attributed to instrumentation or procedural error. IC and H (Figure 5) remained constant while TPC (Figure 6) dropped again, albeit slightly from 1.58 g/L to 1.43 g/L, suggesting oxidation of phenolic substances in line with observations on oxygen ingress and consumption and FSO2 depletion. TPO in the control bottle increased only slightly from 0.012 mg/L to 0.023 mg/L. And as leakage through the stopper continued, it is concluded that the stopper material does not reseal itself completely when the needle is removed.

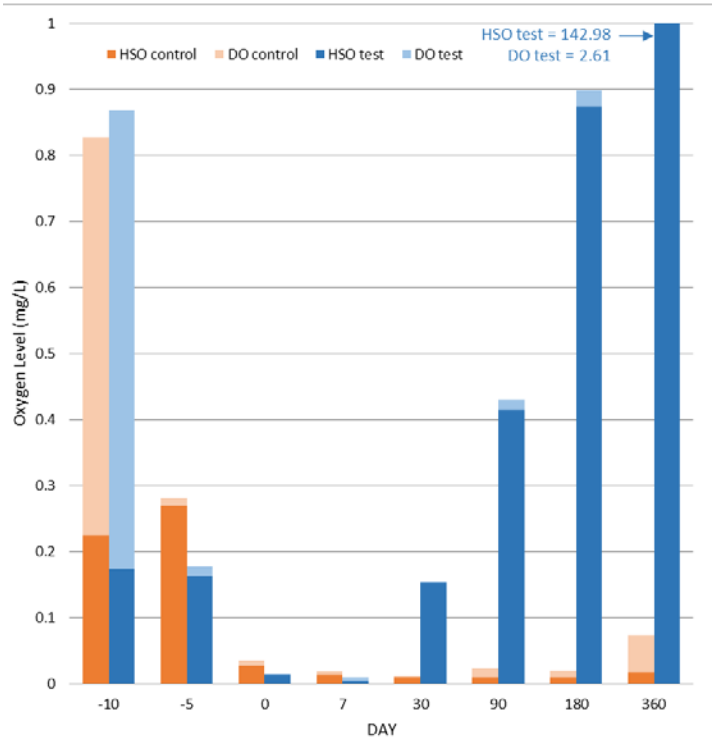

Figure 2: Oxygen evolution in wine under a natural cork stopper.

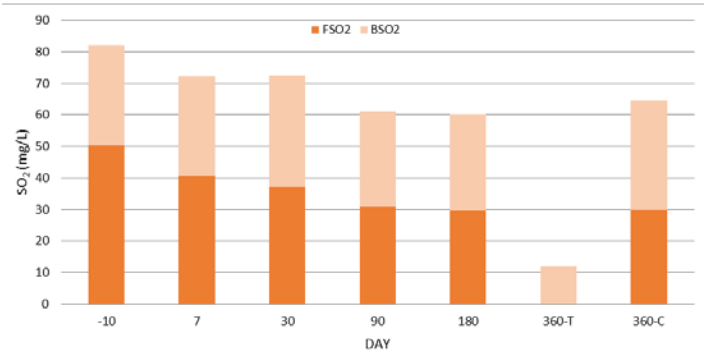

Figure 3: FSO2, BSO2 and TSO2 evolution in wine under a natural cork stopper.

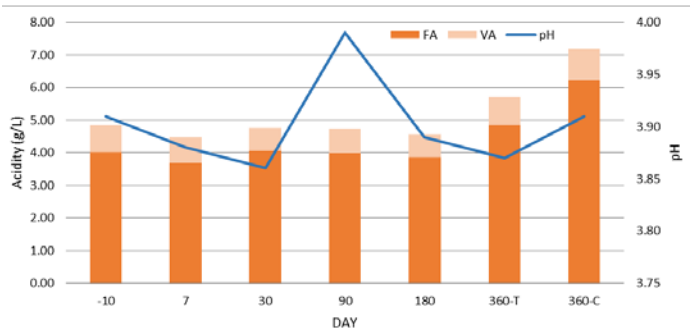

Figure 4: pH, TA and VA evolution in wine under a natural cork stopper.

On DAY 180 (Figure 2), there was another significant increase in HSO to 0.874 mg/L and a small increase in DO to 0.024 mg/L in the test wine with TPO now at 0.898 mg/L and thus very close to the 1-mg/L threshold level. There were no significant changes in SO_2 levels (Figure 3), suggesting that headspace oxygen had not yet become dissolved in the wine. There were no significant changes in TA and VA (Figure 4), although, as reported above, pH dropped back down to its DAY 30 level. IC and H (Figure 5) remained constant while TPC (Figure 6) dropped again, albeit only slightly to 1.36 g/L, suggesting continued oxidation of phenolic substances. No further leakage through the stopper was observed. TPO in the control bottle remained constant.

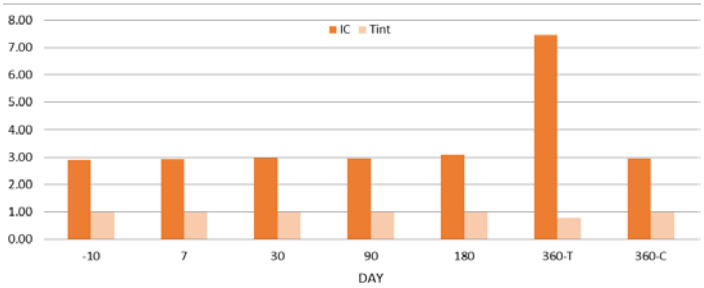

Figure 5: Color and hue evolution in wine under a natural cork stopper.

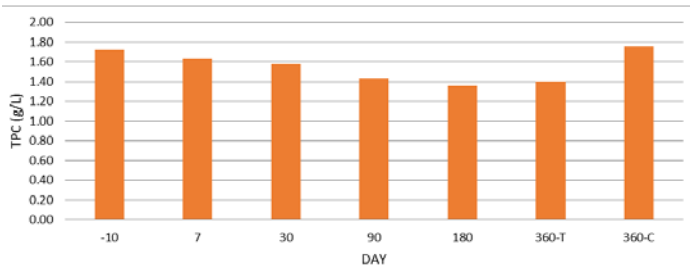

Figure 6: Total phenol content evolution in wine under a natural cork stopper.

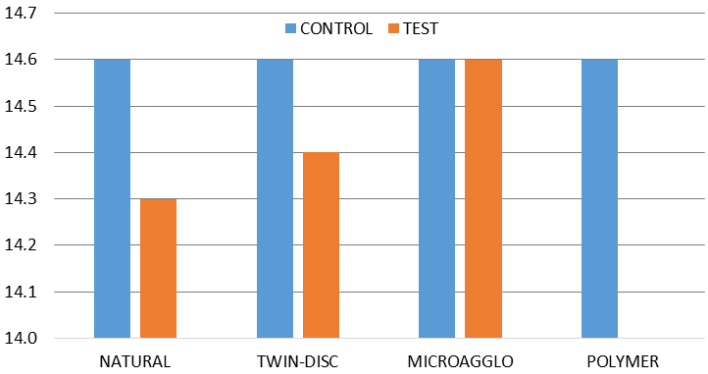

Figure 7: Ethanol changes between DAY -10 and DAY 360 in wine under different stoppers.

On DAY 360 (Figure 2), HSO had spiked to approximately 143 mg/L, well beyond spoilage levels, and DO was at 2.61 mg/L and thus above the 2-mg/L critical maximum. The test wine was completely depleted of FSO2 (Figure 3), likely due to binding with acetaldehyde from ethanol oxidation, in addition to other factors stated above, with only about 15% TSO2 remaining, all in the bound form. The control wine had the same FSO2 level as that on DAY 180 and a slightly higher TSO2. TA (Figure 4) increased from approximately 4.6 g/L to 5.7 g/L but with only an increase

in VA from 0.69 g/L to 0.85 g/L. IC (Figure 5) increased significantly from around 3.0 to 7.45 and H decreased from around 1.0 to 0.77. Color intensity and hue results suggest that both absorbance at wavelengths of 420 and 520 nm increased in similar proportions but slightly higher absorbance at 520 nm, suggesting a deeper red color. The color was in fact visibly much darker than that of the control wine. TPC (Figure 6) remained relatively unchanged given that FSO2 was completely depleted and oxygen was diverted to non-polyphenolic oxidation reactions. But the test wine had a drop of 0.3% in ethanol (Figure 7) and reeked of ethyl acetate. That is a substantial drop given that only a 0.01% v/v change in ethanol is required for it to become esterified by acetic acid and push ethyl acetate over the detection threshold of 160−180 mg/L (Ribéreau-Gayon et al. 2012). A 0.01% v/v change in ethanol (molar mass of 46 g) represents a change of approximately 79 mg/L, which reacts with 103 mg/L of acetic acid (molar mass of 60 g) to produce approximately 151 mg/L of ethyl acetate (molar mass of 88 g). Once FSO2 was all consumed, acetaldehyde was further oxidized into acetic acid to enable esterification of ethanol into ethyl acetate. It is quite possible that, within the measurement error of the ebulliometer, the same amount of acetic acid produced by acetaldehyde oxidation is consumed in ethanol esterification, therefore with no net change in VA. No further leakage through the stopper was observed. The emptied test bottle had some slight staining from anthocyanins and tannins, which was not observed in bottles under the other types of stoppers.

TPO in the control wine on DAY 360 (Figure 2) increased to 0.073 mg/L but with HSO and DO still at very low levels, 0.017 and 0.056 mg/L, respectively. There was a small increase in DO from 0.010 mg/L and, although well below the critical maximum, it was still an order of magnitude greater than on DAY 180. It can be concluded that, between DAY 180 and DAY 360, there was oxygen ingress around (and possibly through) the stopper, and which became dissolved but not yet consumed by wine components. TA (Figure 4) increased substantially from 4.85 to 7.17 g/L, in contrast to 5.70 g/L in the test wine. This cannot be explained and is attributed to instrumentation or procedural error. IC, H and TPC (Figures 5 and 6) remained unchanged between the start and the end of the study.

Based on oxygen and SO_2 test results, the much darker color of the test wine and the clear presence of excessive ethyl acetate, it can be concluded that the natural cork stopper provided excellent protection against oxygen ingress in the control wine but that the Coravin Wine System had a negative impact on wine parameters after 30 days and getting very close to threshold levels after 6 months and then the wine becoming spoiled within one year. As the needle was not sanitized prior to use, it is quite conceivable that it contributed to an infection by acetic acid bacteria.

Twin-disc stopper. Refer to Figures 7 and 8 to 12.

Wines under twin-disc stoppers exhibited similar behaviors as with the wines under natural cork stoppers in all parameters measured. But both the control and test wines measured higher TPO on DAY -5 (Figure 8), 0.436 and 0.497 mg/L, compared to the wines under natural cork stoppers, which measured 0.281 and 0.177 mg/L (Figure 2).

The test wine behaved similarly with respect to decreasing HSO and DO levels (Figure 8), both dropping significantly from DAY -5 levels until DAY 30. There was a gradual drop in FSO2 (Figure 9) until DAY 30 from 50.3 mg/L to 37.6 mg/L, a drop of approximately 25% of its initial level. The small loss of FSO2 measured on DAY 7 was likely due to a combination of H_2O_2 binding, carbonyl binding, regeneration of *o*-quinones into their *o*-diphenols, dissipation at bottling owing to the drop in TSO2, and dissipation from pouring wine into the graduated cylinder. TSO2 then remained constant until DAY 30 with a small increase in BSO2 as SO_2 continued binding. pH, TA and VA (Figure 10) remained constant within the error range of instrumentation. IC and H (Figure 11) remained constant while TPC (Figure 12) dropped slightly, suggesting oxidation of phenolic substances in line with observations on oxygen and SO_2 consumption.

On DAY 30 (Figure 8), there was a significant increase in HSO in the test wine but with TPO still well below acceptable levels, albeit significantly higher than in the control bottle, 0.207 vs. 0.009 mg/L; the latter was the lowest TPO level recorded in the control bottle during the study. The increase in HSO in the test wine under the twin-disc stopper was greater than that for the test wine under the natural cork stopper. The impacts on FSO2, TSO2, pH, TA, VA, IC, H and TPC (Figures 9, 10, 11 and 12) were limited as the headspace oxygen had likely not yet become dissolved in the wine. A small amount of leakage through the hole, where the needle pierced through, was observed. The top of the stopper was wiped with 90% v/v ethanol to remove wine likely due to removal of the needle.

However, on DAY 90, HSO (Figure 8) again increased substantially from 0.205 mg/L to 0.352 mg/L with a small increase in DO from 0.002 mg/L to 0.003 mg/L, likely due to headspace oxygen becoming dissolved and oxygen being consumed. The small increase in DO can also be attributed to instrumentation error. Now, the increase in HSO in the test wine under the twin-disc stopper was smaller than that for the test wine under the natural cork stopper. Both FSO2 and TSO2 (Figure 9) decreased with a small drop in BSO2, suggesting that FSO2 was likely being lost through the hole in the stopper. Some FSO2 loss may also be due to the same reasons stated above. FSO2 and TSO2 levels were down approximately 65% and 77% of their initial levels. Although there were no significant changes in TA and VA (Figure 10), pH increased by 0.11 but then dropped back down by a similar amount on DAY 180; this cannot be explained and is attributed to instrumentation or procedural error. IC and H (Figure 11) remained constant while TPC (Figure 12) dropped again, albeit slightly from 1.51 g/L to 1.44 g/L, suggesting oxidation of phenolic substances in line with observations on oxygen ingress and consumption and FSO2 depletion. TPO in the control bottle increased only slightly from 0.009 mg/L to 0.017 mg/L. No further leakage was observed through the stopper continued.

On DAY 180 (Figure 8), there was another significant increase in HSO to 0.938 mg/L with TPO now at 0.947 mg/L and thus very close to the 1-mg/L threshold level. There were no significant changes in SO_2 levels (Figure 9), suggesting that headspace oxygen had not yet become dissolved in the wine. There were no significant changes in TA and VA (Figure 10), although, as reported above, pH dropped back down to its DAY 30 level. IC

and H (Figure 11) and TPC (Figure 12) remained constant. No further leakage through the stopper was observed. TPO in the control bottle remained constant.

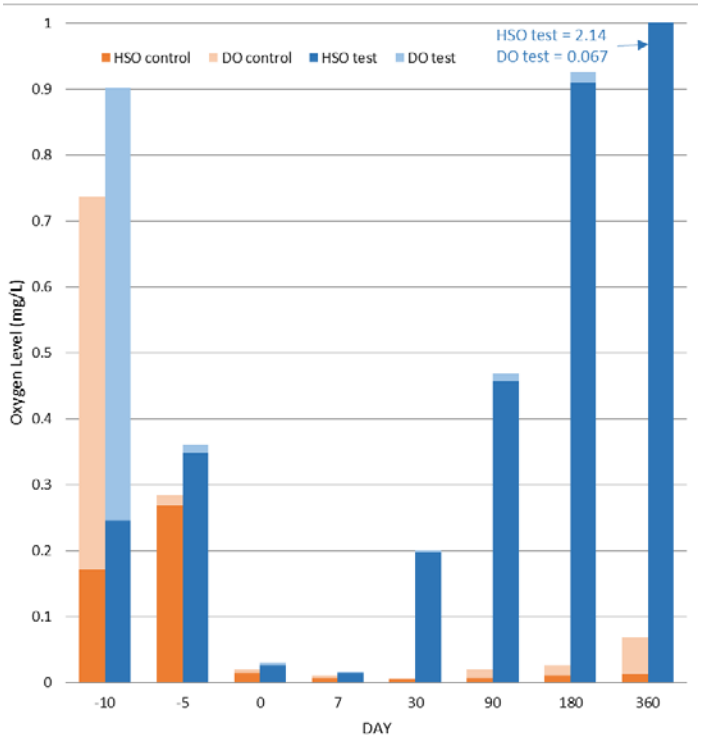

Figure 8: Oxygen evolution in wine under a twin-disc stopper.

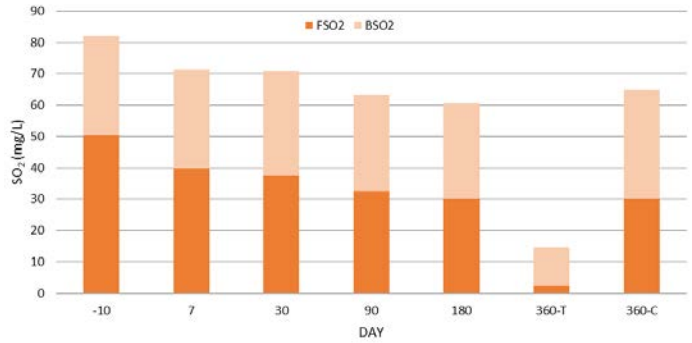

Figure 9: FSO2, BSO2 and TSO2 evolution in wine under a twin-disc stopper.

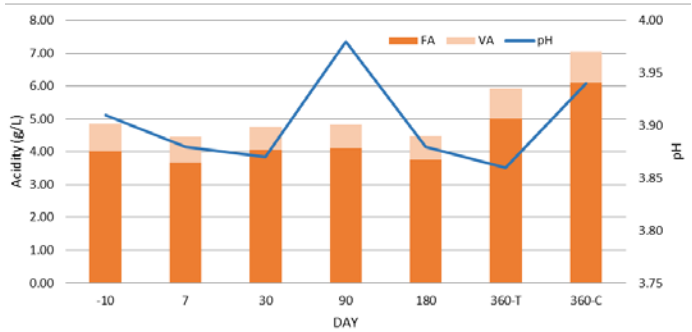

Figure 10: pH, TA and VA evolution in wine under a twin-disc stopper.

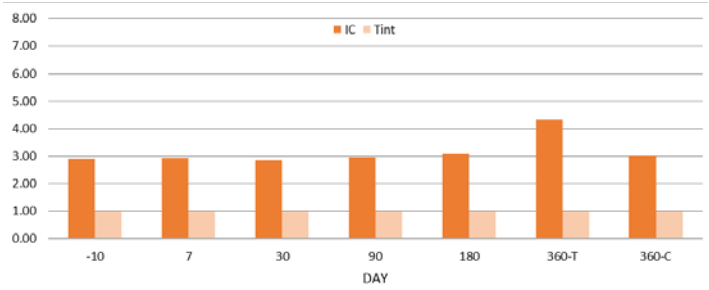

Figure 11: Color and hue evolution in wine under a twin-disc stopper.

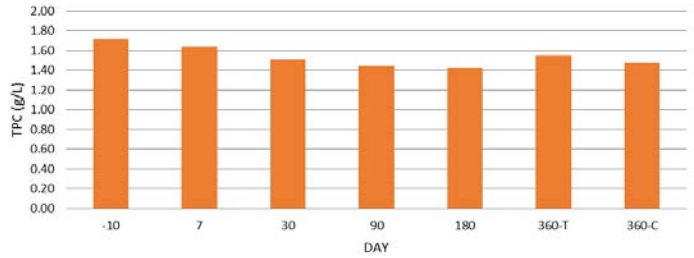

Figure 12: Total phenol content evolution in wine under a twin-disc stopper.

On DAY 360 (Figure 8), HSO had spiked to approximately 73 mg/L, well beyond spoilage levels, and DO was at 3.06 mg/L and thus above the 2-mg/L critical maximum. The test wine was almost completely depleted of FSO2 (Figure 9), likely due to binding with acetaldehyde from ethanol oxidation, in addition to other factors stated above, with only about 18% TSO2 remaining, mainly all in the bound form. The control wine had the same FSO2 level as that on DAY 180 and a slightly higher TSO2. TA (Figure 10) increased from approximately 4.5 g/L to 5.9 g/L but with an increase in VA from 0.72 g/L to 0.91 g/L. IC (Figure 11) increased from around 3.0 to 4.31 while H remained constant. Color intensity and hue results suggest that both absorbances at wavelengths of 420 and 520 nm increased in similar proportions but slightly higher absorbance at 520 nm, suggesting a deeper red color. The color was visibly darker than that of the control wine. Considering instrumentation error, TPC (Figure 12) remained relatively unchanged given that FSO2 was almost completely depleted and oxygen diverted to non-polyphenolic oxidation reactions. But the test wine had a drop of 0.2% in ethanol (Figure 7) although no ethyl acetate smell was detected, perhaps suggesting that the results were possibly within the 0.1% v/v error of the ebulliometer. Once FSO2 was all consumed, acetaldehyde was further oxidized into acetic acid to enable esterification of ethanol into ethyl acetate. It is quite possible that, within the measurement error of the ebulliometer, the same amount of acetic acid produced by acetaldehyde oxidation is consumed in ethanol esterification, therefore with no net change in VA. No further leakage through the stopper was observed.

TPO in the control wine on DAY 360 (Figure 8) increased to 0.063 mg/L but with HSO and DO still at very low levels, 0.016 and 0.047 mg/L, respectively. There was a small increase in DO from 0.008 mg/L and, although well below the critical maximum, it was still an order of magnitude greater than on DAY 180. It can be concluded that, between DAY 180 and DAY 360, there was oxygen ingress around (and possibly through) the stopper, and

which became dissolved but not yet consumed by wine components. TA (Figure 10) increased substantially from 4.85 to 7.06 g/L, in contrast to 5.92 g/L in the test wine. This cannot be explained and is attributed to instrumentation or procedural error. IC, H and TPC (Figures 11 and 12) remained unchanged between the start and the end of the study.

Based on oxygen and SO_2 test results, and the darker color of the test wine, it can be concluded that the twin-disc cork stopper provided excellent protection against oxygen ingress in the control wine but that the Coravin Wine System had an impact on wine parameters after 30 days and getting very close to threshold levels after 6 months and then the wine dropping in quality within one year. As the needle was not sanitized prior to use, it is quite conceivable that it contributed to an infection by acetic acid bacteria.

Microagglomerate stopper. Refer to Figures 7 and 13 to 17.

Wines under microagglomerate stoppers exhibited similar behaviors as with the wines under natural cork and twin-disc stoppers in all parameters measured. But both the control and test wines measured higher TPO on DAY -5 (Figure 13), 0.284 and 0.361 mg/L, compared to the wines under natural cork stoppers, which measured 0.281 and 0.177 mg/L (Figure 2).

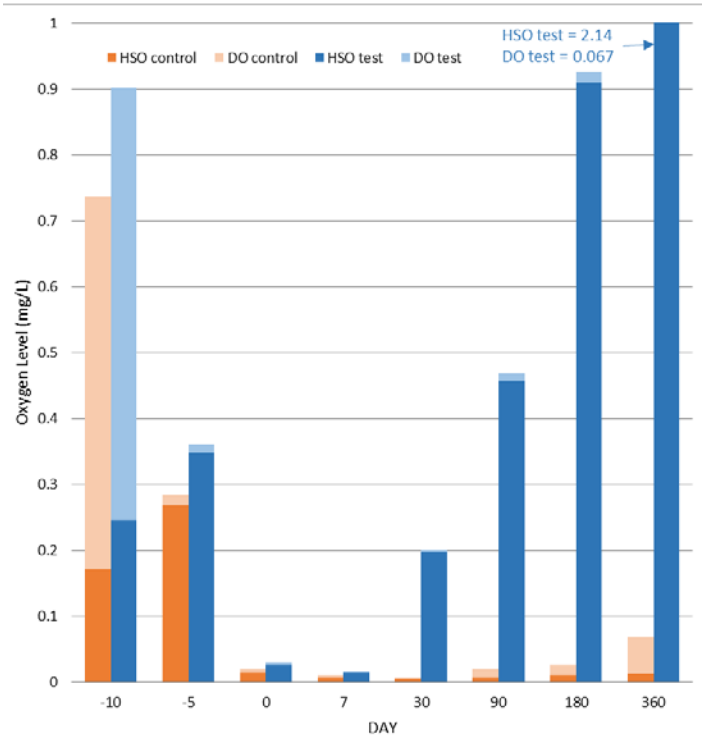

Figure 13: Oxygen evolution in wine under a microagglomerate stopper.

The test wine behaved similarly with respect to decreasing HSO and DO levels (Figure 13), both dropping significantly from DAY -5 levels until DAY 30. There was a gradual drop in FSO2 (Figure 14) until DAY 30 from 50.3 mg/L to 38.7 mg/L, a drop of approximately 23% of its initial level. The small loss of FSO2 measured on DAY 7 was likely due to a combination of H_2O_2 binding, carbonyl binding, regeneration of *o*-quinones into their *o*-diphenols, dissipation at bottling owing to the drop in TSO2, and dissipation from pouring wine into the graduated cylinder. TSO2 then remained relatively constant until DAY 30 with a constant BSO2. TA and VA (Figure 15) remained constant within the error range of instrumentation. IC and H (Figure 16) remained constant while TPC (Figure 17) dropped but only slightly, suggesting oxidation of phenolic substances in line with observations on oxygen and SO_2 consumption.

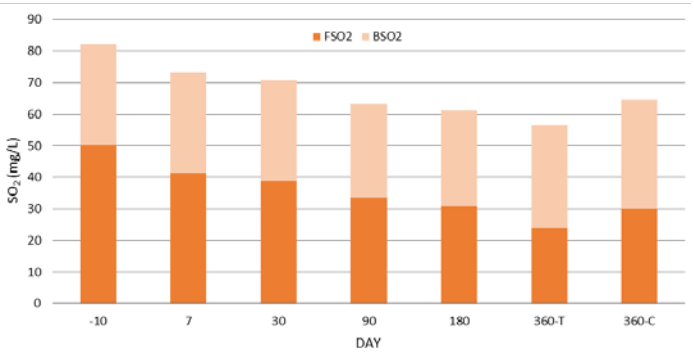

Figure 14: FSO2, BSO2 and TSO2 evolution in wine under a microagglomerate stopper.

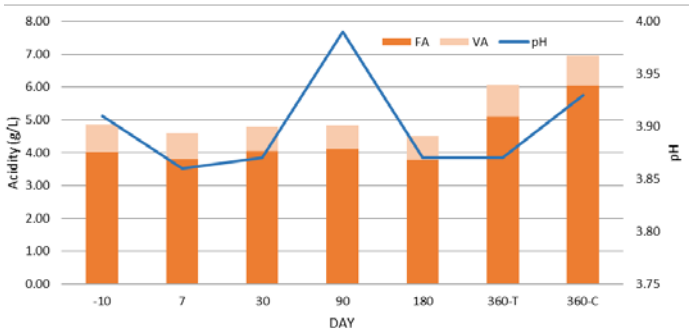

Figure 15: pH, TA and VA evolution in wine under a microagglomerate stopper.

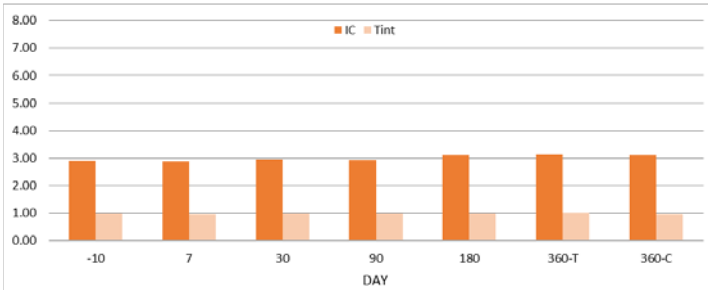

Figure 16: Color and hue evolution in wine under a microagglomerate stopper.

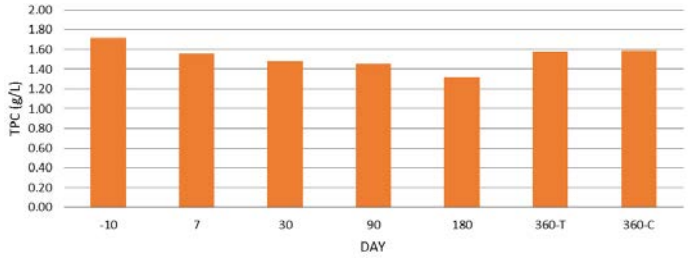

Figure 17: Total phenol content evolution in wine under a microagglomerate stopper.

On DAY 30 (Figure 13), there was a significant increase in HSO in the test wine but with TPO still well below acceptable levels, albeit significantly higher than in the control bottle, 0.200 vs. 0.006 mg/L; the latter was the lowest TPO level recorded in the control bottle during the study. The increase in HSO in the test wine under the microagglomerate stopper was slightly greater than that for the test wine under the natural cork stopper. The impacts on FSO2, TSO2, pH, TA, VA, IC, H and TPC (Figures 14, 15, 16 and 17) were limited as the headspace oxygen had likely not yet become dissolved in the wine. A small amount of leakage through the hole, where the needle pierced through, was observed. The top of the stopper was wiped with 90% v/v ethanol to remove wine likely due to removal of the needle.

However, on DAY 90, HSO (Figure 13) again increased substantially from 0.198 mg/L to 0.457 mg/L with an increase in DO from 0.002 mg/L to 0.011 mg/L, likely due to headspace oxygen becoming dissolved and oxygen being consumed. The increase in HSO in the test wine under the microagglomerate stopper was slightly greater than that for the test wine under the natural cork stopper. Both FSO2 and TSO2 (Figure 14) decreased with a small drop in BSO2, suggesting that FSO2 was likely being lost through the hole in the stopper. Some FSO2 loss may also be due to the same reasons stated above. FSO2 and TSO2 levels were down approximately 67% and 77% of their initial levels. Although there were no significant changes in TA and VA (Figure 15), pH increased by 0.12 but then dropped back down by a similar amount on DAY 180; this cannot be explained and is attributed to instrumentation or procedural error. IC and H (Figure 16) and TPC (Figure 17) remained constant. TPO in the control bottle increased from 0.006 mg/L to 0.020 mg/L. No further leakage was observed through the stopper continued.

On DAY 180 (Figure 13), there was another significant increase in HSO to 0.909 mg/L with TPO now at 0.926 mg/L and thus very close to the 1-mg/L threshold level. There were no significant changes in SO_2 levels (Figure 14), suggesting that headspace oxygen had not yet become dissolved in the wine. There were no significant changes in TA and VA (Figure 15), although, as reported above, pH dropped back down to its DAY 30 level. IC and H (Figure 16) and TPC (Figure 17) remained constant. No further leakage through the stopper was observed. TPO in the control bottle remained fairly unchanged.

On DAY 360 (Figure 13), HSO had increased to approximately 2.1 mg/L, just slightly beyond the critical maximum recommended level, and DO was at 0.067 mg/L. Compared to test wines under natural cork and twin-disc stoppers, FSO2 and TSO2 did not drop significantly; they dropped to 24.0 and 56.7 mg/L, respectively. Bound SO_2 increased slightly, and it can be concluded that, although FSO2 can be lost around the stopper, it is most probably completely through the stopper via the hole created by the needle. The control wine had the same FSO2 level as that on DAY 180 and a slightly higher TSO2. TA (Figure 15) increased from approximately 4.5 g/L to 6.1 g/L but with an increase in VA from 0.72 g/L to 0.98 g/L. IC and while H (Figure 16) remained constant. The color was visibly comparable to that of the control wine. TPC (Figure 17) increased from 1.32 to 1.58 g/L. There were no changes in ethanol levels (Figure 7). No further leakage through the stopper was observed.

TPO in the control wine on DAY 360 (Figure 13) increased to 0.069 mg/L but with HSO and DO still at very low levels, 0.013 and 0.056 mg/L, respectively. There was a small increase in DO from 0.015 mg/L and, although well below the critical maximum, it was still almost four times that than on DAY 180. It can be concluded that, between DAY 180 and DAY 360, there was oxygen ingress around (and possibly through) the stopper, and which became dissolved but not yet consumed by wine components. TA (Figure 15) increased substantially from 4.51 to 6.97 g/L, in contrast to 6.06 g/L in the test wine. This cannot be explained and is attributed to instrumentation or procedural error. IC, H and TPC (Figures 16 and 17) remained unchanged between the start and the end of the study.

Based on oxygen and SO_2 test results, it can be concluded that the microagglomerate stopper provided excellent protection against oxygen ingress in the control wine but that the Coravin Wine System had an impact on wine parameters after 30 days and getting very close to threshold levels after 6 months; TPO hovered around the 2-mg/L threshold after 12 months. As the needle was not sanitized prior to use, it is quite conceivable that it contributed to an infection by acetic acid bacteria.

Polymer stopper. Refer to Figures 7 and 18 to 22.

Wines under polymer stoppers exhibited similar behaviors as with the wines under natural cork, twin-disc and micro-agglomerate stoppers in all parameters measured until DAY 0. Both the control and test wines measured low TPO on DAY -5 (Figure 18), 0.202 and 0.306 mg/L, respectively.

Once the polymer stopper was pierced on DAY 0, it leaked excessively, as expected, and was therefore removed from the study.

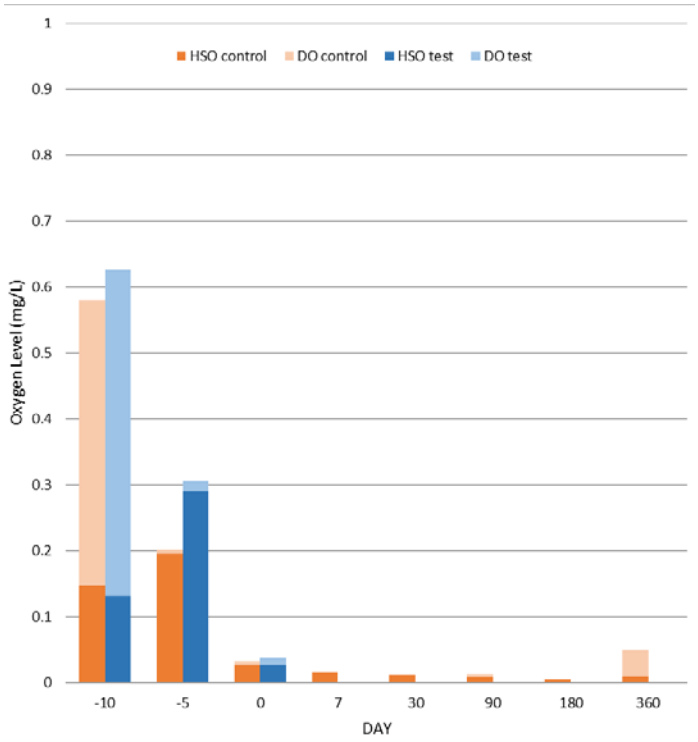

Figure 18: Oxygen evolution in wine under a polymer stopper.

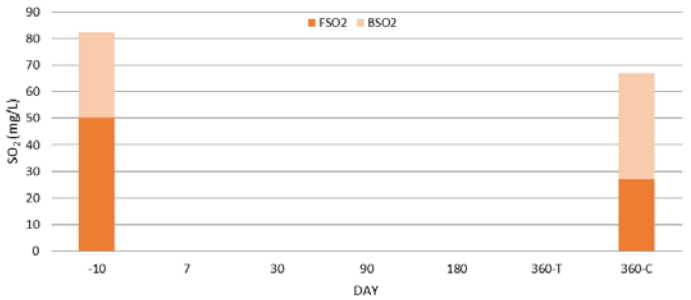

Figure 19: FSO2, BSO2 and TSO2 evolution in wine under a polymer stopper.

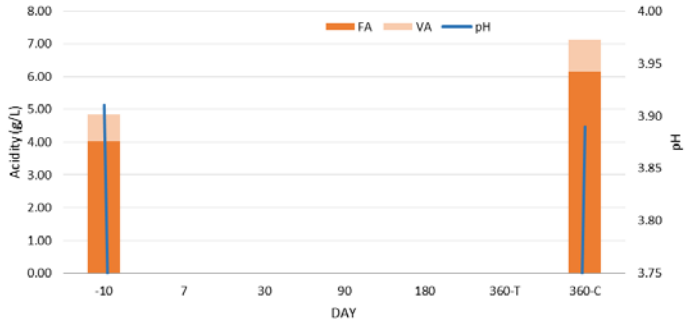

Figure 20: pH, TA and VA evolution in wine under a polymer stopper.

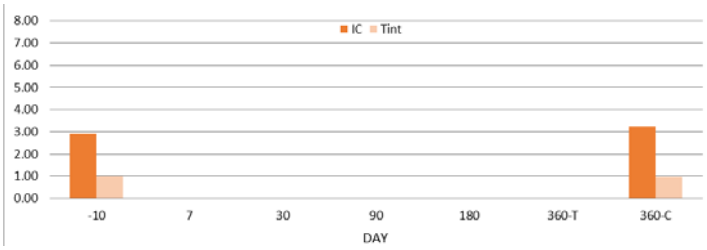

Figure 21: Color and hue evolution in wine under a polymer stopper.

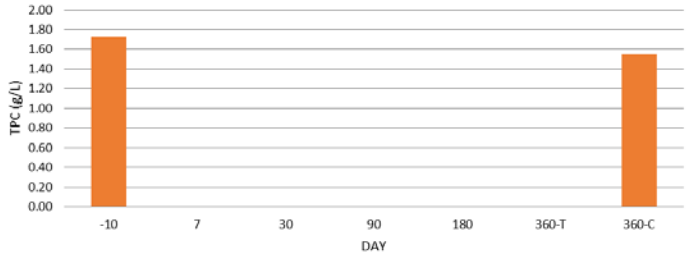

Figure 22: Total phenol content evolution in wine under a polymer stopper.

Unlike other stopper types, where TPO decreased until DAY 30 and then increased until DAY 360, TPO for the control wine under the polymer stopper decreased up to DAY 180 where it reached a level of 0.006 mg/L, and then increased to 0.049 mg/L on DAY 360, the lowest of all stopper types.

By DAY 360, FSO2 and TSO2 levels (Figure 19) in the control wine dropped to 54% and 81% of the initial levels on DAY -10. Within instrumentation errors, the polymer stopper performed as well as other stopper types based on SO_2 results.

As with other stopper types, TA (Figure 20) increased substantially from 4.85 to 7.13 g/L between DAY -10 and DAY 360 with no significant change in pH (3.91 vs. 3.89). This cannot be explained and is attributed to instrumentation or procedural error.

IC (Figure 21) increased slightly from 2.90 to 3.24 between the start and the end of the study while H remained unchanged; TPC (Figure 22) decreased from 1.72 to 1.55 g/L.

Based on oxygen and SO_2 test results, it can be concluded that the polymer stopper provided excellent protection against oxygen ingress in the control wine.

Conclusions

This study demonstrates that the Coravin Wine System can be used to pour wine out of a bottle, under the protection of argon gas, with no ill-effects to the wine in the first month. After the first month, there is conclusive evidence that, compared to control bottles, there is considerable oxygen ingress through the hole created by the Coravin Wine System needle, and that wines reach critical oxygen threshold levels within 6 months and exceed those within one year. Although cork is a natural material, it does not regenerate itself and, therefore, it cannot reseal the hole to its original condition. The best that the cork material can achieve is to "tighten" up the hole and impede the flow of wine out and flow of oxygen in.

By the end of the study duration, the test wine under the natural cork stopper had excessive ethyl acetate, a markedly deeper color compared to the control wine, and was completely depleted of free SO_2; it was spoiled. The test wine under the twin-disc stopper fared better but still had suffered in quality; it displayed a deeper color and was almost completely depleted of free SO_2. The test wine under the microagglomerate stopper performed best although oxygen levels also reached critical thresholds by the end of the study duration but considerably less than other stopper types, by one to two orders of magnitude. The test wine under the polymer stopper was removed from the study once the stopper was pierced with the Coravin Wine System as it leaked excessively; this stopper type is clearly stated as not supported by Coravin.

When using the Coravin Wine System it is highly recommended to sanitize the needle with a 70% v/v ethanol solution to minimize the risk of wine spoilage by acetic acid bacterial infection.

All stopper types in control bottles performed very well with very low TPO levels and normal SO_2 losses recorded at the end of the study duration; the control wine under the polymer stopper had the lowest TPO.

Future studies that measure acetaldehyde changes in addition to those measured in this study, and measured at more regular intervals, for example, at one-month intervals, may be able to further characterize the impacts to wines poured with the Coravin Wine System.

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