

# A Review of Sulfite Management Protocols Based on SO<sub>2</sub> Levels and Type of Wine

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**Abstract:** Free sulfur dioxide (SO<sub>2</sub>) is a key parameter monitored throughout the winemaking process to ensure wine is adequately protected from oxidative effects and microbial spoilage. Regular monitoring is necessary as some free SO<sub>2</sub> is lost due to its volatility and reaction chemistry. Free SO<sub>2</sub> must therefore be adjusted on a periodic basis. Several de facto sulfiting protocols are used by winemakers to compensate for free SO<sub>2</sub> losses based on the type of wine and the amount of total SO<sub>2</sub> present using a threshold of 50 mg/L. The aim of this study was to examine free SO<sub>2</sub> losses in four types of wines—white, rosé, and two reds with one having higher total phenol content—and each with total SO<sub>2</sub> levels below and above 50 mg/L. This study confirms the strong correlation between free SO<sub>2</sub> losses and binding with total phenol content, the need to adjust SO<sub>2</sub> level additions at the start of the sulfiting regimen, and the need to monitor and adjust free SO<sub>2</sub> levels on a periodic basis, typically every 30–90 days. The level of adjustment at the initial addition depends on total SO<sub>2</sub> for white and rosé wines; for reds, an adjustment is required independently of total SO<sub>2</sub> levels, but smaller adjustments are required as total phenolic content increases.

**Key words:** sulfur dioxide, SO<sub>2</sub>, sulfite, color density, tint, hue, phenol content

**Introduction.** Sulfur dioxide has long been used in winemaking to protect wine from enzymatic and chemical oxidative effects and microbial spoilage.

In aqueous solutions, molecular sulfur dioxide (SO<sub>2</sub>), bisulfite (HSO<sub>3</sub><sup>-</sup>) and sulfite (SO<sub>3</sub><sup>2-</sup>) ions exist in equilibrium as per the equation:



The sum of SO<sub>2</sub>, HSO<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup> concentrations is referred to as free SO<sub>2</sub> (FSO<sub>2</sub>) and is the active form that affords protection in wine. The recommended nominal level of FSO<sub>2</sub> depends on the pH of wine and is calculated according to the formula:

$$[\text{SO}_2]_{\text{free}} = [\text{SO}_2]_{\text{molecular}} \times [1 + 10^{(\text{pH}-1.81)}]$$

A molecular SO<sub>2</sub> level of 0.5 mg/L and 0.8 mg/L are recommended for red and white wines, respectively.

At wine pH, usually in the range 3–4, HSO<sub>3</sub><sup>-</sup> is the most abundant form representing about 94–99% of the total free form, the rest being SO<sub>2</sub>; SO<sub>3</sub><sup>2-</sup> is negligible.

FSO<sub>2</sub> diminishes over time as 1) SO<sub>2</sub> is lost to the atmosphere via tank or barrel headspace and during processing activities, as 2) HSO<sub>3</sub><sup>-</sup> binds with carbonyl compounds (e.g.

acetaldehyde and ketone acids) and phenolic compounds (e.g. anthocyanins and tannins) to form bound SO<sub>2</sub> (BSO<sub>2</sub>), as 3) HSO<sub>3</sub><sup>-</sup> reduces brown-colored *o*-quinones back to their phenol forms, and as 4) HSO<sub>3</sub><sup>-</sup> is oxidized to sulfates (SO<sub>4</sub><sup>2-</sup>) by oxygen radicals, such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). HSO<sub>3</sub><sup>-</sup> binding reactions can change based on changes in wine chemistry; for example, HSO<sub>3</sub><sup>-</sup> could be released from anthocyanins if the free acetaldehyde level were to increase from oxidation (Ribéreau-Gayon et al. 2012a; Schmidtke et al. 2011). Acetaldehyde is a stronger binder and HSO<sub>3</sub><sup>-</sup> would preferentially bind to those molecules.

At any point in time, total SO<sub>2</sub> (TSO<sub>2</sub>) in wine is the sum of free (FSO<sub>2</sub>) and bound SO<sub>2</sub> (BSO<sub>2</sub>) concentrations, all expressed in mg/L. TSO<sub>2</sub> is expected to drop over time given the greater losses in FSO<sub>2</sub> compared to gains in BSO<sub>2</sub>.

But SO<sub>2</sub> dynamics make it very challenging to predict the extent of FSO<sub>2</sub> changes. Winemakers add more sulfite to maintain a nominal FSO<sub>2</sub> level based on the expected drop in FSO<sub>2</sub> while ensuring that TSO<sub>2</sub> never exceeds the maximum set by regulatory agencies.

FSO<sub>2</sub> and TSO<sub>2</sub> can be measured analytically using aeration-oxidation or Ripper titration techniques; BSO<sub>2</sub> is then calculated accordingly. A method for estimating the impact of binding compounds involves measuring and calculating an index, TL35, determined by adding known quantities of SO<sub>2</sub> to wine and measuring free and total SO<sub>2</sub> to establish the linear relationship, and then calculating the amount of total SO<sub>2</sub> to achieve a desired free SO<sub>2</sub> of 35 mg/L (Barbe 2000; Ribéreau-Gayon et al. 2012; Coulon et al. 2014).

The amount of sulfite needed to re-establish a desired FSO<sub>2</sub> level in wine is posited to depend largely on whether the amount of TSO<sub>2</sub> is below or above 50 mg/L. Several de facto protocols are commonly used to determine the amount of sulfite to add based on this working assumption.

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One such protocol assumes that 50% of FSO<sub>2</sub> added becomes bound when TSO<sub>2</sub> is below 50 mg/L, and so, sulfite additions are increased by 50%. Above 50 mg/L TSO<sub>2</sub> it is assumed that sulfite additions result in 100% FSO<sub>2</sub> though some winemakers make a 10% adjustment to compensate for some binding that may still occur (Margalit 1990; Rotter 2011) while others use a straight rule that one third of FSO<sub>2</sub> always becomes bound (Ribéreau-Gayon et al. 2012), and so, sulfite additions are increased by 33%.

The purpose of this study was to examine SO<sub>2</sub> dynamics in four types of wines over a 90-day period to validate de facto sulfiting protocols. The four wines included a white, a rosé, and two reds with different total phenol contents, and each with TSO<sub>2</sub> levels below and above 50 mg/L.

Color intensity, tint and total phenol content were also measured to establish any causal relationships with SO<sub>2</sub> changes.

Color intensity (IC) or density of a specific color is a measure of the spectral absorbance ( $A_\lambda$ ), also known as optical density (OD), of a substance and is defined as the fraction of radiation absorbed at a specific wavelength  $\lambda$ : The greater the absorbance of a wavelength of an absorbed color, the less intense the complementary (visible) color. Anthocyanins in red wine have absorbance peaks at  $\lambda_{\min}=420$  nm (yellow) and  $\lambda_{\max}=520$  nm (red); IC is the sum of  $A_{420}$  and  $A_{520}$ . Pure water is used as a reference with  $IC_{\text{water}}=0$ . Wines have IC values in the range 0–15 with reds at the high end and whites usually less than 1.000.

As the color of white wine cannot be characterized by a specific wavelength, IC is measured at 420 nm (Blouin and Cruège 2003). The absorbance curve for whites is characteristically smooth throughout the visible spectrum. The absorbance at 420 nm, i.e.,  $A_{420}$ , is used to assess oxidative damage in white wines based on the extent of browning.

Hue (H), or tint, describes variations of a color produced by adding white to it and characterized by a low saturation with relatively high lightness. Saturation describes chromatic purity or vividness of a color. Mathematically, hue is the ratio of spectral absorbances at two wavelengths, or  $A_{420}$  and  $A_{520}$  in red wine. And therefore, H is a ratio of yellow color concentration to that of red and is indicative of the degree of color evolution. H values are in the range 0–10 with red wines typically ranging from 0.50 for those expressing more of a purple color to 1.00–1.50 for reds that have evolved to an orange or brick-red color.

Total phenol content (TPC) is a measurement of the concentration of phenolic compounds including anthocyanins and tannins, and is expressed in g/L as gallic acid equivalent (GAE).

IC, H and TPC can be measured analytically using a spectrophotometer, and can provide valuable data on SO<sub>2</sub> dynamics as HSO<sub>3</sub><sup>-</sup> binds to carbonyls and phenolics or oxidizes.

## Materials and Methods

**Test Equipment.** Vinmetrica SC-300 SO<sub>2</sub> & pH/TA Analyzer Kit purchased from MoreWine! Concord, CA.; Hanna HI 83742 Photometer for the Determination of Color and Total Phenols in Wine purchased from Hanna Instruments, Laval, Québec, Canada (via Prolab Scientific, Laval, Québec).

**Instrumentation.** Syringes and other volumetric apparatus supplied with the instruments were substituted for a higher-accuracy 25-mL pipette to minimize sample errors and a self-zeroing burette for SO<sub>2</sub> titrations.

Test equipment was calibrated prior to testing. Reagents were purchased or prepared fresh. Potassium metabisulfite (KMS) was purchased fresh. Accuracy and resolution were recorded for all instrumentation.

**Wine Samples.** Wine samples were prepared from bottled commercial wines purchased from the SAQ, Montréal, Québec: a 2013 Chardonnay from Pays d’Oc, France; a 2013 Syrah from Pays d’Oc, France; a 2013 Cabernet Sauvignon from Mendoza, Argentina. These wines were specifically selected for their low sulfite content, which would allow adjustments required for this study. The rosé was prepared by adding approximately 5% Syrah to the Chardonnay.

A slightly fuller-bodied style with 0.5 g/L of Laffort’s Biotan grape tannins, purchased from Vines to Vintage, Niagara, Ontario, was added to the Cabernet Sauvignon.

The pH, FSO<sub>2</sub>, TSO<sub>2</sub>, IC, H and TPC were measured and recorded for each sample, as per Table 1. These are measurements at the start (S) of the study, just prior to taking measurements on day 0.

The wines were divided into two batches each. KMS was added to the first batch (low-sulfite wines) to achieve a FSO<sub>2</sub> level of around 35 mg/L but keeping TSO<sub>2</sub> below 50 mg/L. 100 mg/L KMS was added to the second batch (high-sulfite wines) to achieve a TSO<sub>2</sub> level above 50 mg/L followed by a second addition of 30–35 mg/L.

For the purpose of reporting results, the low- and high-sulfite samples for each wine are referred to as Chard<50, Chard>50, Rose<50, Rose>50, Syrah<50, Syrah>50, CabSauv<50 and CabSauv>50.

Samples were then transferred to 60-mL air-tight bottles and coded according to the day each sample would be tested, i.e., day 0, 1, 2, 3, 4, 5, 7, 30, 60 and 90. All samples were held at ambient room temperature of approximately 20°C (68°F).

Parameter	pH	FSO <sub>2</sub> (mg/L)	TSO <sub>2</sub> (mg/L)	Color Intensity	Tint	TPC (mg/L GAE)
Chardonnay	3.61	2.0	4.0	0.113	1.07	0.174
Rosé	3.64	2.0	4.0	0.27	1.48	0.49
Syrah	3.76	10.0	12.0	11.57	0.66	2.29
CabSauv	3.84	16.0	44.0	11.09	0.80	3.22

**Table 1:** Initial wine parameters measured at the start (S) of the study

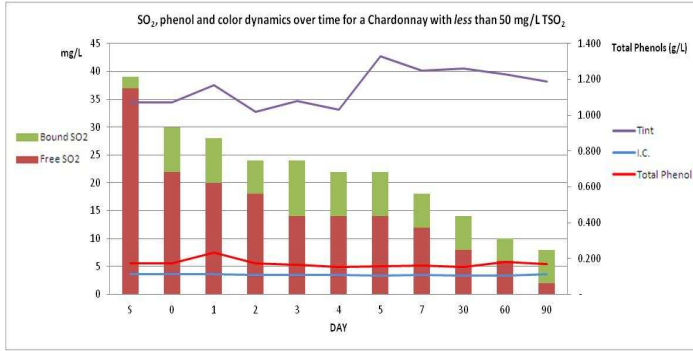
**Test Procedure.** Each sample was tested and measured once only for FSO<sub>2</sub>, TSO<sub>2</sub>, IC, H and TPC each day. BSO<sub>2</sub> was calculated from TSO<sub>2</sub> and FSO<sub>2</sub>. All measurements with the HI 83742 photometer were taken by first calibrating the unit for each test type using distilled H<sub>2</sub>O as reference.

Test results for the same type of wine were compared for analytical purposes. Comparisons between types of wines cannot be made because the wines are different.

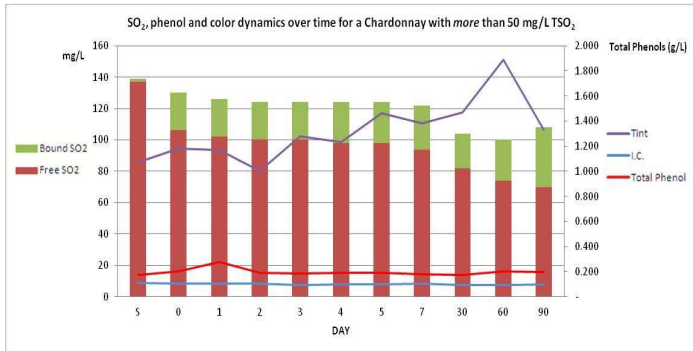
**Test Errors.** Errors on all instrumentation were recorded and factored into test results where possible.

## Results and Discussion

**Chardonnay.** Test results data are presented in Tables 2 and 3 and Figures 1 and 2.



**Figure 1:** SO<sub>2</sub>, phenol and color dynamics over time for a Chardonnay with less than 50 mg/L total SO<sub>2</sub>



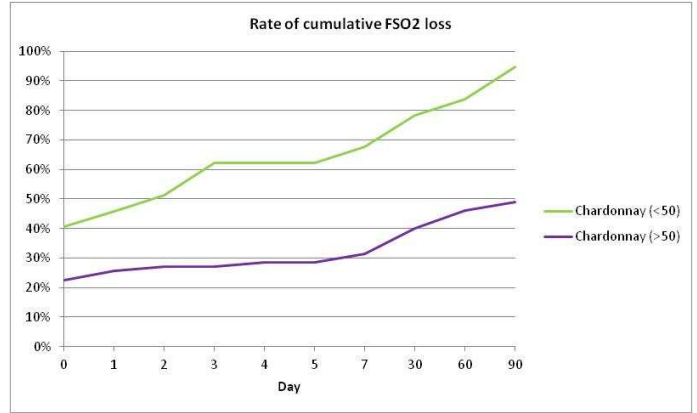
**Figure 2:** SO<sub>2</sub>, phenol and color dynamics over time for a Chardonnay with more than 50 mg/L total SO<sub>2</sub>

The analysis of cumulative FSO<sub>2</sub> loss shown in Figure 3 demonstrates an immediate 41% loss of the initial 35 mg/L SO<sub>2</sub> addition and existing FSO<sub>2</sub> in the Chard<50 sample and an almost complete loss after 90 days, compared to a 23% and 49% loss in the Chard>50 sample. FSO<sub>2</sub> loss in Chard<50 continued to grow quickly in the first week but was relatively flat in Chard>50. The rate of loss was also steeper in Chard<50 during the 30-to-90-day period. FSO<sub>2</sub> losses may be attributed to volatility during sample storage, handling and analysis, and possibly some binding to any small level of phenols present and oxidation to SO<sub>4</sub><sup>2-</sup>.

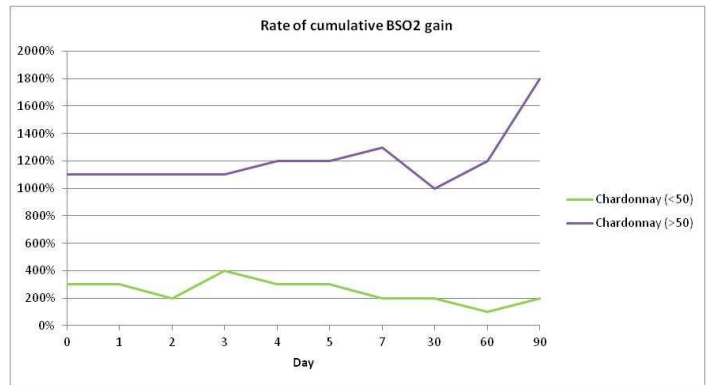
These results suggest that FSO<sub>2</sub> decline is highly correlated to TSO<sub>2</sub> levels, and that the initial SO<sub>2</sub> dose should be increased in the order of 50% in the Chardonnay when TSO<sub>2</sub> is less than 50 mg/L and in the order of 25% in the Chardonnay when TSO<sub>2</sub> is more than 50 mg/L. Chard<50 will benefit from an adjustment after one week and should be adjusted every month. Chard>50 too may benefit from similar adjustments although adjustments every 90 days is acceptable.

Both samples displayed a surge in BSO<sub>2</sub> (Figure 4) upon the initial SO<sub>2</sub> addition, suggesting quick binding of HSO<sub>3</sub><sup>-</sup> to carbonyls and phenolics, particularly in Chard>50. Binding behavior in both samples exhibited sawtooth patterns with BSO<sub>2</sub> increasing sharply in Chard>50 in the last month. BSO<sub>2</sub> in Chard<50 was much flatter throughout the duration of the study.

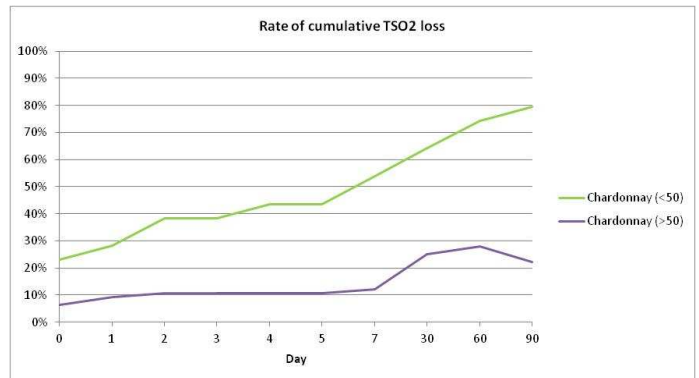
TSO<sub>2</sub> decline (Figure 5) in both samples mirrored FSO<sub>2</sub> decline except in Chard>50 in the last month due to the sharp rise in BSO<sub>2</sub>.



**Figure 3:** Rate of cumulative FSO<sub>2</sub> loss in Chardonnay as a percentage of the initial value at time S



**Figure 4:** Rate of cumulative BSO<sub>2</sub> gain in Chardonnay as a percentage of the initial value at time S



**Figure 5:** Rate of cumulative TSO<sub>2</sub> loss in Chardonnay as a percentage of the initial value at time S

Parameter	DAY										
	S	0	1	2	3	4	5	7	30	60	90
FSO2 (mg/L)	37	22	20	18	14	14	14	12	8	6	2
TSO2 (mg/L)	39	30	28	24	24	22	22	18	14	10	8
Color density	0.113	0.113	0.114	0.108	0.107	0.108	0.106	0.108	0.103	0.106	0.113
Tint	1.07	1.07	1.17	1.02	1.08	1.03	1.33	1.25	1.26	1.23	1.19
TPC (mg/L GAE)	0.174	0.174	0.234	0.172	0.166	0.153	0.157	0.161	0.153	0.181	0.167

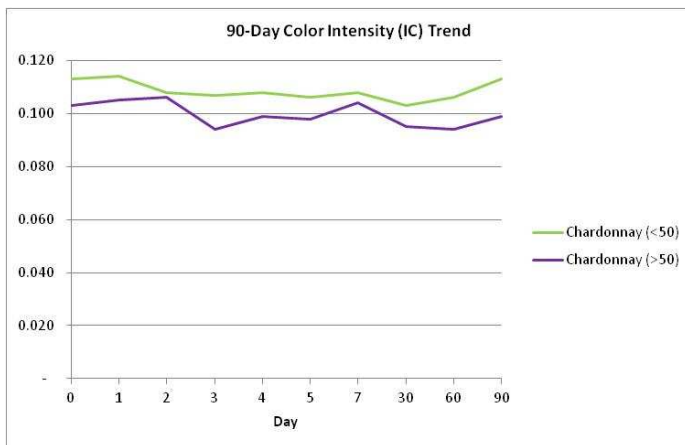
**Table 2:** Test measurements for low-sulfite Chardonnay (Chard<50)

Parameter	DAY										
	S	0	1	2	3	4	5	7	30	60	90
FSO2 (mg/L)	137	106	102	100	100	98	98	94	82	74	70
TSO2 (mg/L)	139	130	126	124	124	124	124	122	104	100	108
Color density	0.113	0.103	0.105	0.106	0.094	0.099	0.098	0.104	0.095	0.094	0.099
Tint	1.07	29.45	29.15	24.95	32.00	30.85	36.40	34.45	36.75	47.25	33.30
TPC (mg/L GAE)	0.174	0.204	0.275	0.191	0.187	0.191	0.189	0.178	0.173	0.205	0.198

**Table 3:** Test measurements for high-sulfite Chardonnay (Chard>50)

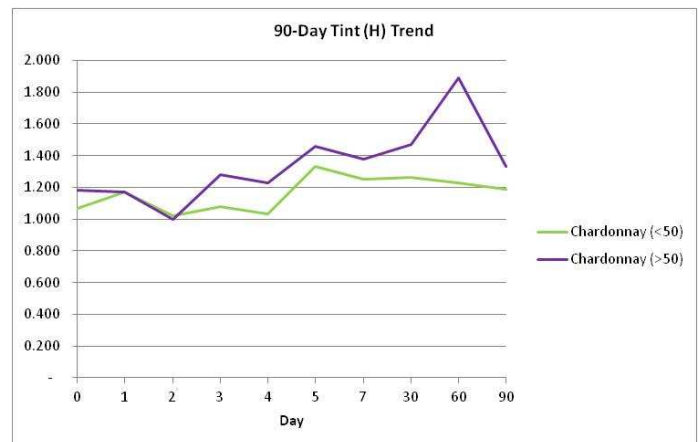
IC (Figure 6) was only negligibly affected by SO<sub>2</sub> and remained relatively flat for both samples. IC for Chard>50 was marginally lower but within error margins.

H (Figure 7) for both samples was higher at the end of the study, but no correlation or clear pattern emerged except that both samples displayed sawtooth behaviors. Chard>50 also increased sharply between the first and second months, then decreased sharply between the second and third months.

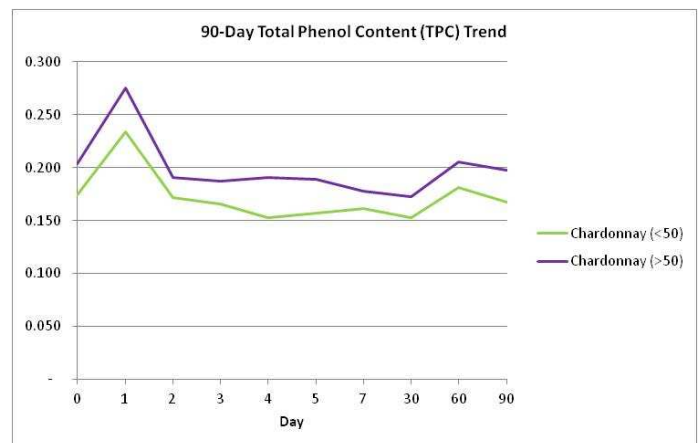


**Figure 6:** 90-day color intensity (IC) trend in Chardonnay

TPC (Figure 8) for both samples displayed the same behavior with the Chard>50 only marginally higher. Both samples displayed a steep increase on the first day followed by a similar decline the second day. This behavior was repeated between the first and third months although the changes were not as pronounced.



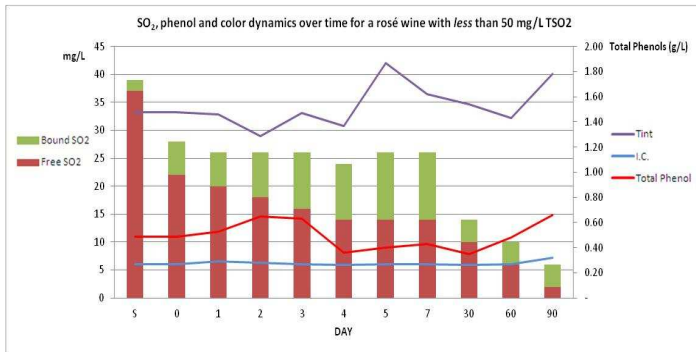
**Figure 7:** 90-day hue (H) trend in Chardonnay



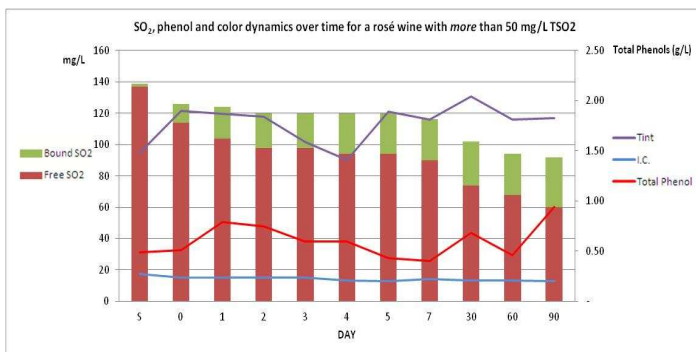
**Figure 8:** 90-day total phenol content (TPC) trend in Chardonnay

The day 1 surge in TPC may be indicative of  $\text{HSO}_3^-$  reducing *o*-quinones back to their phenol forms, resulting in a decrease in FSO<sub>2</sub> while the day 2 drop may represent re-oxidation of phenols to *o*-quinones, which then bind to  $\text{HSO}_3^-$  to form bisulfite addition products and increase BSO<sub>2</sub>. These behaviors seem to repeat themselves in the last two months, but then, there are possibly much less *o*-quinones available for reduction and  $\text{HSO}_3^-$  now binding to carbonyls and phenolics.

**Rosé.** Test results data are presented in Tables 4 and 5 and Figures 9 and 10.



**Figure 9:** SO<sub>2</sub>, phenol and color dynamics over time for a rosé with less than 50 mg/L total SO<sub>2</sub>



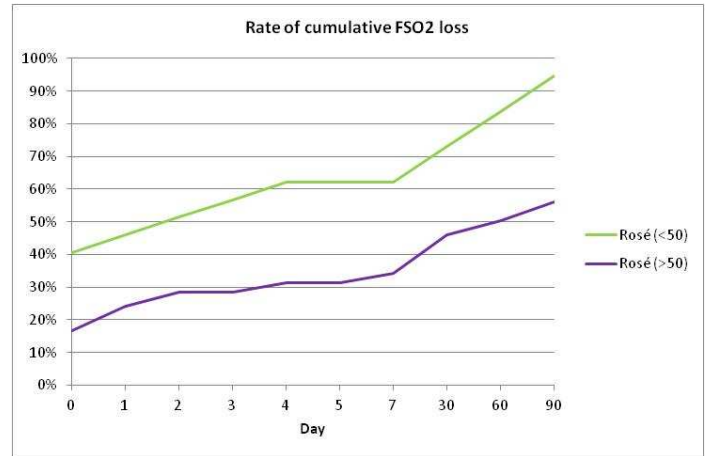
**Figure 10:** SO<sub>2</sub>, phenol and color dynamics over time for a rosé with more than 50 mg/L total SO<sub>2</sub>

Both samples exhibited similar FSO<sub>2</sub> (Figure 11) decline patterns as the Chardonnay samples, but with the Rose>50 sample exhibiting a higher rate of decline in the first 2 days and again at the end of each month compared to the Chard>50 behavior.

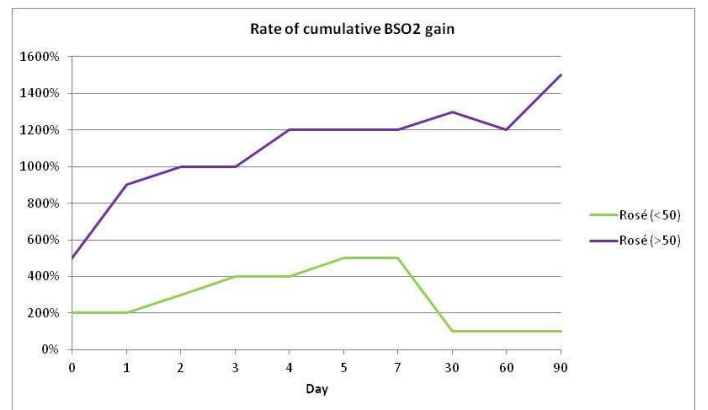
These results suggest that FSO<sub>2</sub> decline is highly correlated to the TSO<sub>2</sub> level, and a similar SO<sub>2</sub> protocol as with Chardonnay is recommended.

There was significant binding (Figure 12) in both samples in the first week, suggesting quick binding of  $\text{HSO}_3^-$  to carbonyls and phenolics, particularly in Rose>50. Rose>50 continued binding and peaked at day 90. This binding may be due to  $\text{HSO}_3^-$  quickly binding to the small amount of anthocyanins. There was a sharp decrease thereafter until day 30 in Rose<50.

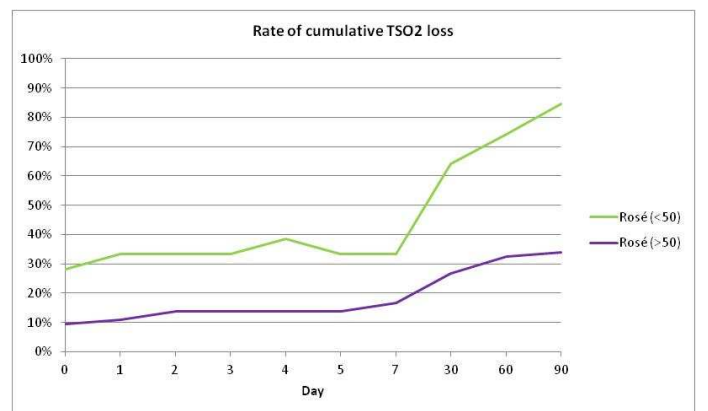
TSO<sub>2</sub> decline (Figure 13) in both samples mirrored FSO<sub>2</sub> decline except in Rose<50 between days 7 and 30 due to the sharp decline in BSO<sub>2</sub>.



**Figure 11:** Rate of cumulative FSO<sub>2</sub> loss in rosé as a percentage of the initial value at time S



**Figure 12:** Rate of cumulative BSO<sub>2</sub> gain in rosé as a percentage of the initial value at time S



**Figure 13:** Rate of cumulative TSO<sub>2</sub> loss in rosé as a percentage of the initial value at time S

IC (Figure 14) in Rose<50 was relatively flat for the first 60 days and then jumped in the last month. IC Rose>50 decreased only marginally over the course of the study but displayed a dull, “tired” color after 30 days.

H (Figure 15) for both samples exhibited haphazard sawtooth behaviors but no correlation or clear pattern emerged. Rose>50

measured higher H values suggesting greater spectral absorbances at  $\lambda_{420}$  than Rose<50 and therefore a shift to a more of a yellow color; however, H for Rose>50 was similar at day 90 as it was at the start of the study whereas Rose<50 ended up higher and close to the Rose>50 value.

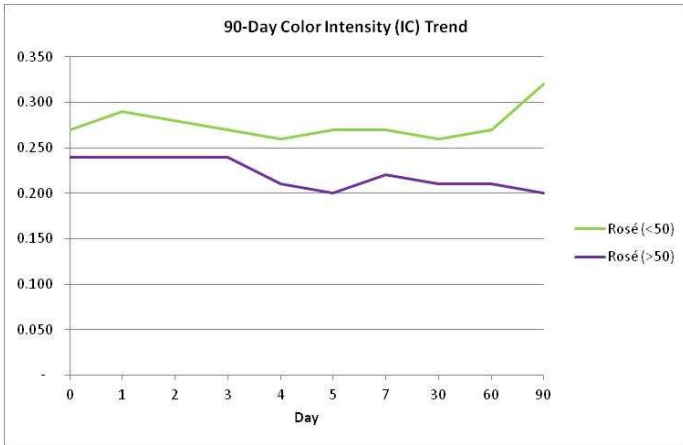


Figure 14: 90-day color intensity (IC) trend in rosé

TPC (Figure 16) for both samples displayed similar sawtooth behaviors with Rose>50 showing higher content than Rose<50 at the end of the study.

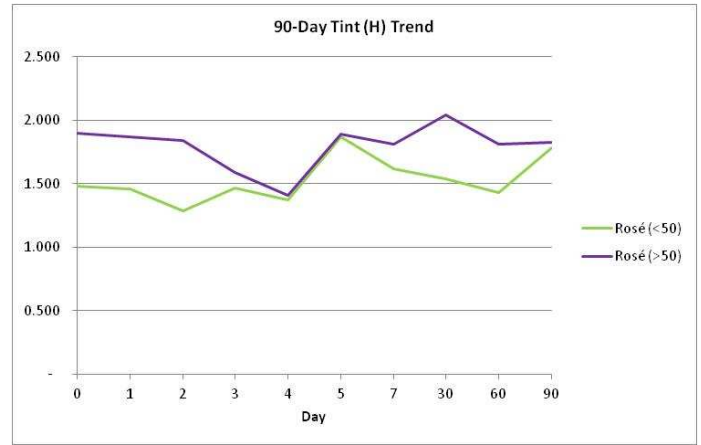


Figure 15: 90-day hue (H) trend in rosé

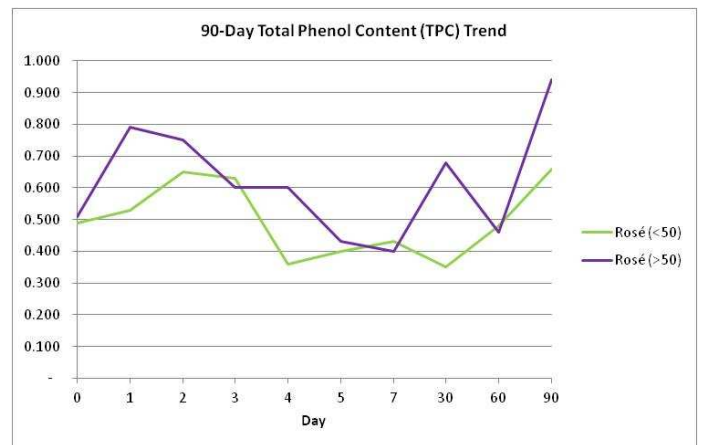


Figure 16: 90-day total phenol content (TPC) trend in rosé

Parameter	DAY										
	S	0	1	2	3	4	5	7	30	60	90
FSO2 (mg/L)	37	22	20	18	16	14	14	14	10	6	2
TSO2 (mg/L)	39	28	26	26	26	24	26	26	14	10	6
Color density	0.27	0.27	0.29	0.28	0.27	0.26	0.27	0.27	0.26	0.27	0.32
Tint	1.48	1.48	1.46	1.29	1.47	1.37	1.87	1.62	1.54	1.43	1.78
TPC (mg/L GAE)	0.49	0.49	0.53	0.65	0.63	0.36	0.40	0.43	0.35	0.48	0.66

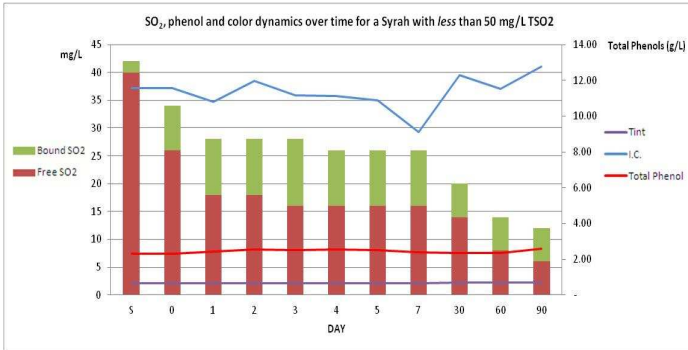
Table 4: Test measurements for low-sulfite rosé (Rose<50)

Parameter	DAY										
	S	0	1	2	3	4	5	7	30	60	90
FSO2 (mg/L)	137	114	104	98	98	94	94	90	74	68	60
TSO2 (mg/L)	139	126	124	120	120	120	120	116	102	94	92
Color density	0.27	0.24	0.24	0.24	0.24	0.21	0.20	0.22	0.21	0.21	0.20
Tint	1.48	1.90	1.87	1.84	1.59	1.41	1.89	1.81	2.04	1.81	1.83
TPC (mg/L GAE)	0.49	0.51	0.79	0.75	0.60	0.60	0.43	0.40	0.68	0.46	0.94

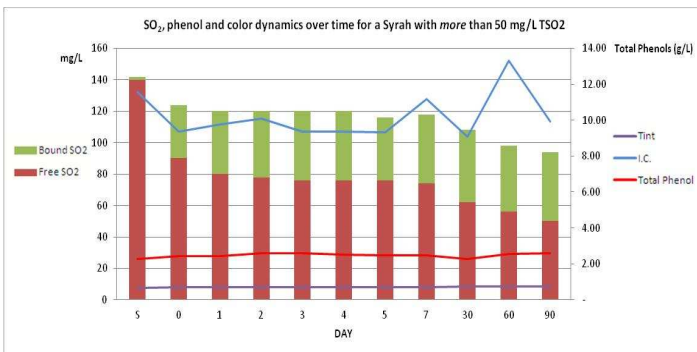
Table 5: Test measurements for high-sulfite rosé (Rose>50)



**Syrah.** Test results data are presented in Tables 6 and 7 and Figures 17 and 18.



**Figure 17:** SO<sub>2</sub>, phenol and color dynamics over time for a Syrah with less than 50 mg/L total SO<sub>2</sub>



**Figure 18:** SO<sub>2</sub>, phenol and color dynamics over time for a Syrah with more than 50 mg/L total SO<sub>2</sub>

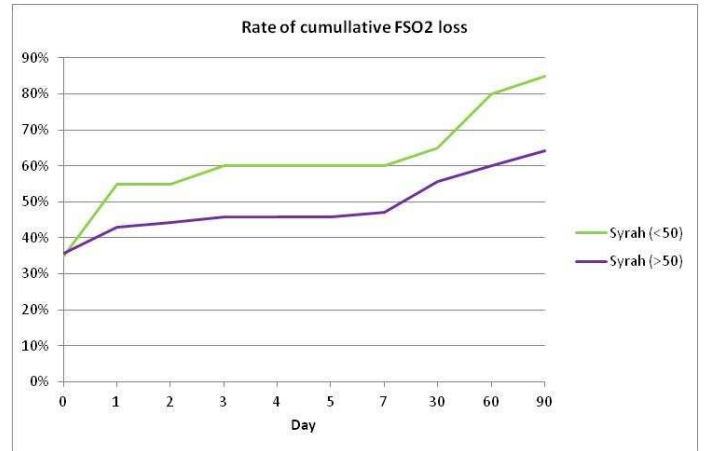
The rate of cumulative FSO<sub>2</sub> loss (Figure 19) for both samples displayed similar patterns, and with behaviors similar to the Chardonnay and rosé samples. The main difference with the Syrah samples were that the majority of week 1 FSO<sub>2</sub> losses were on the first day, and the rate of FSO<sub>2</sub> loss curves for the Syrah sample were closer, suggesting more binding in the Syrah>50.

FSO<sub>2</sub> loss analysis demonstrates an immediate loss in the order of 35% of the initial 30 mg/L SO<sub>2</sub> addition and existing FSO<sub>2</sub> in both samples and cumulative losses of 85% and 64% after 90 days.

These results suggest that FSO<sub>2</sub> decline is highly correlated to the TSO<sub>2</sub> level but that the gap is now narrower, and that the initial SO<sub>2</sub> dose should be increased in the order of 35%, irrespective of TSO<sub>2</sub> levels. Both wines will benefit from monthly adjustments.

Binding (Figure 20) in Syrah<50 occurred quickly at the start of the study and remained flat for the rest of the first week, and then dropped between the first week and the end of the first month. Syrah>50 displayed extensive binding at the start and increased for several days, and then exhibited a sawtooth behavior for the rest of the study although the pattern was relatively flat.

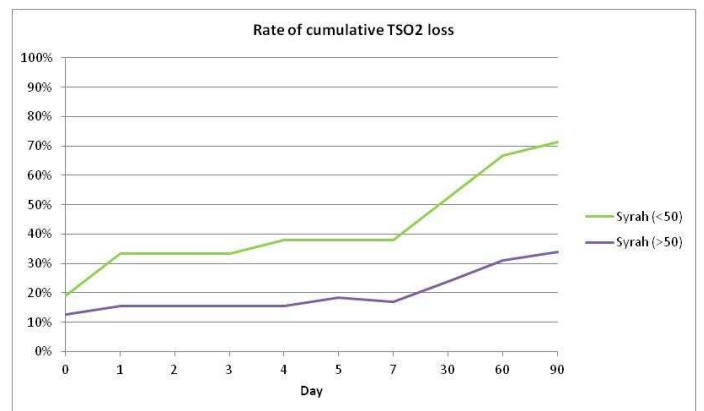
TSO<sub>2</sub> (Figure 21) patterns in both samples closely mirrored FSO<sub>2</sub> loss behaviors.



**Figure 19:** Rate of cumulative FSO<sub>2</sub> loss in Syrah as a percentage of the initial value at time S



**Figure 20:** Rate of cumulative BSO<sub>2</sub> gain in Syrah as a percentage of the initial value at time S



**Figure 21:** Rate of cumulative TSO<sub>2</sub> loss in Syrah as a percentage of the initial value at time S

Both samples exhibited haphazard sawtooth patterns for color intensity (Figure 22) with the Syrah<50 sample measuring higher IC values in the first week suggesting a more intense color than Syrah>50, and similarly at day 90. However, the sawtooth pattern was most pronounced in the day 7–day 90 interval causing IC values to be greater in the Syrah>50 sample

on day 7 and day 60. In spite of the sawtooth effect, IC in Syrah<50 was higher at the end of the study and approximately the same in Syrah>50.

H (Figure 23) for both samples remained relatively flat in the first week and then increasing during the remainder of the study suggesting decreasing spectral absorbances at  $\lambda_{520}$  and therefore a greater loss of red color coupled with a shift to more of an orange color.

No color or color intensity changes were visible.

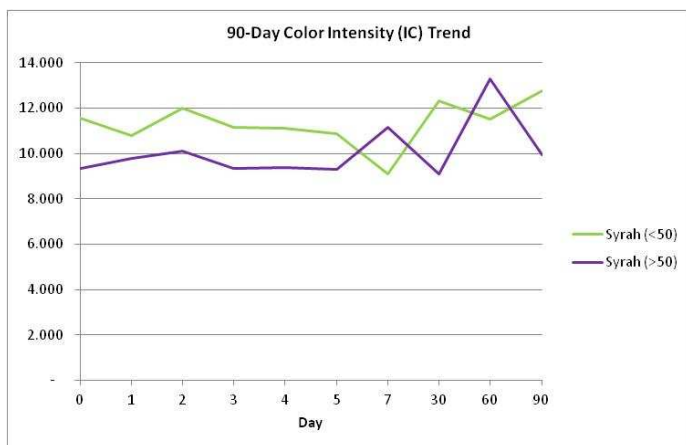


Figure 22: 90-day color intensity (IC) trend in Syrah

TPC (Figure 24) for both samples displayed similar sawtooth patterns, except for Syrah>50 measuring a significantly higher level on day 60, but then both ending at the same level on day 90.

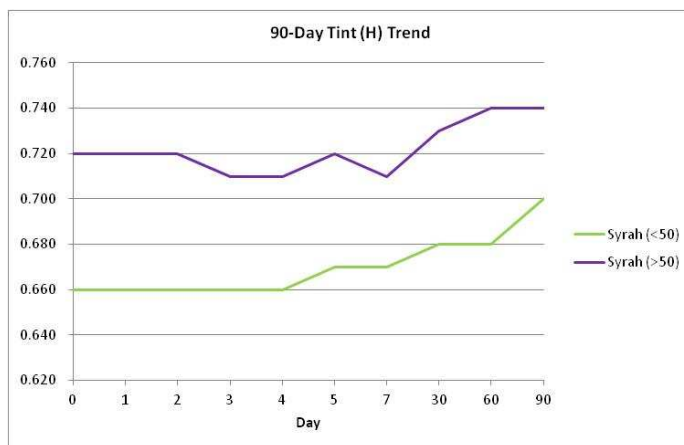


Figure 23: 90-day hue (H) trend in Syrah

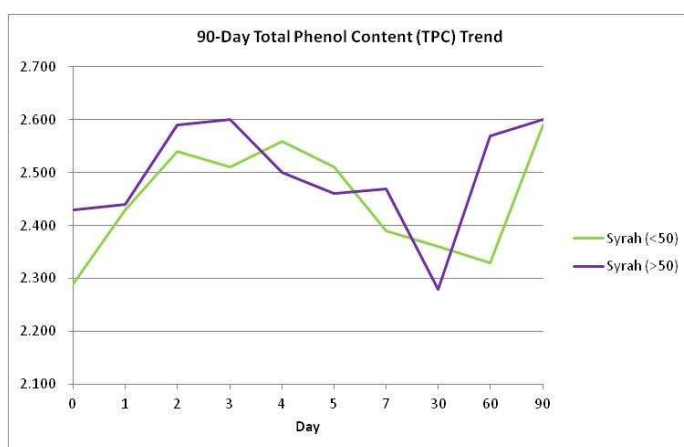


Figure 24: 90-day total phenol content (TPC) trend in Syrah

Parameter	DAY										
	S	0	1	2	3	4	5	7	30	60	90
FSO2 (mg/L)	40	26	18	18	16	16	16	16	14	8	6
TSO2 (mg/L)	42	34	28	28	28	26	26	26	20	14	12
Color density	11.57	11.57	10.80	11.99	11.17	11.11	10.88	9.11	12.31	11.51	12.76
Tint	0.66	0.66	0.66	0.66	0.66	0.66	0.67	0.67	0.68	0.68	0.70
TPC (mg/L GAE)	2.29	2.29	2.43	2.54	2.51	2.56	2.51	2.39	2.36	2.33	2.59

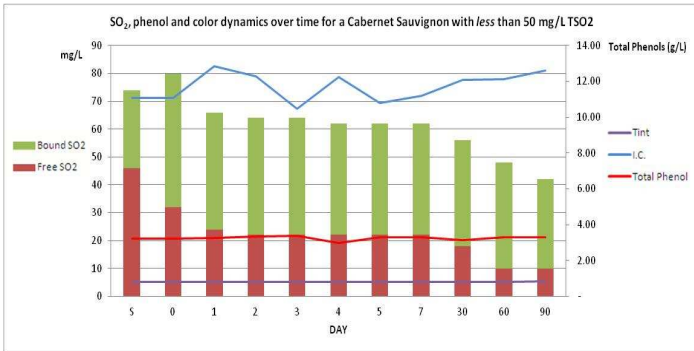
Table 6: Test measurements for low-sulfite Syrah (Syrah<50)

Parameter	DAY										
	S	0	1	2	3	4	5	7	30	60	90
FSO2 (mg/L)	140	90	80	78	76	76	76	74	62	56	50
TSO2 (mg/L)	142	124	120	120	120	120	116	118	108	98	94
Color density	11.57	9.36	9.77	10.10	9.35	9.37	9.31	11.16	9.09	13.31	9.93
Tint	0.66	0.72	0.72	0.72	0.71	0.71	0.72	0.71	0.73	0.74	0.74
TPC (mg/L GAE)	2.29	2.43	2.44	2.59	2.60	2.50	2.46	2.47	2.28	2.57	2.60

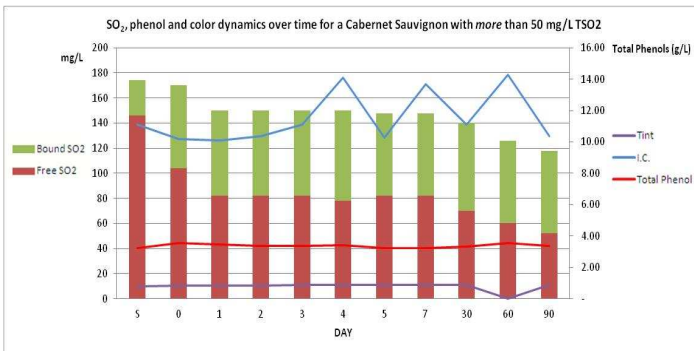
Table 7: Test measurements for high-sulfite Syrah (Syrah>50)



**Cabernet Sauvignon.** Test results data are presented in Tables 8 and 9 and Figures 25 and 26.



**Figure 25:** SO<sub>2</sub>, phenol and color dynamics over time for a Cabernet Sauvignon with less than 50 mg/L total SO<sub>2</sub>



**Figure 26:** SO<sub>2</sub>, phenol and color dynamics over time for a Cabernet Sauvignon with more than 50 mg/L total SO<sub>2</sub>

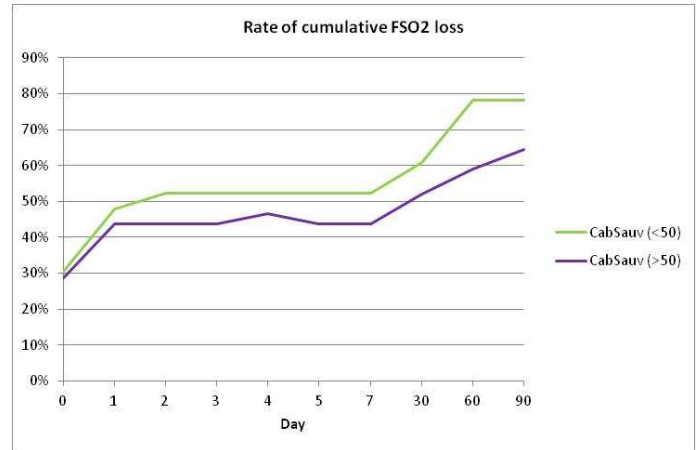
The rate of cumulative FSO<sub>2</sub> loss (Figure 27) for both samples displayed similar patterns, and with behaviors similar to the Syrah samples. The main difference with the Cabernet Sauvignon samples were that the majority of week 1 FSO<sub>2</sub> losses were on the first day with both samples exhibiting similar losses and rate of loss on the first day, and the rate of FSO<sub>2</sub> loss curves were again closer, suggesting even more binding in the CabSauv>50.

FSO<sub>2</sub> loss analysis demonstrates an immediate loss in the order of 30% of the initial 30 mg/L SO<sub>2</sub> addition and existing FSO<sub>2</sub> in both samples and cumulative losses of 78% and 64% after 90 days.

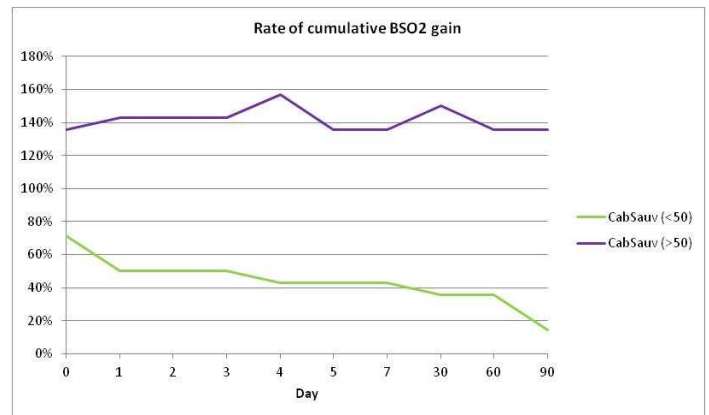
These results suggest that FSO<sub>2</sub> decline is highly correlated to the TSO<sub>2</sub> level but that the gap is now much narrower, and that the initial SO<sub>2</sub> dose should be increased in the order of 30%, irrespective of TSO<sub>2</sub> levels. Both wines will benefit from monthly adjustments.

Binding (Figure 28) in CabSauv<50 occurred quickly at the start of the study though considerably less than Syrah<50, dropped on day 1, remained relatively flat until day 60, and then dropped again. CabSauv>50 displayed more binding at the start of the study but, again, significantly less than that demonstrated by Syrah>50. BSO<sub>2</sub> for CabSauv>50 exhibited a sawtooth pattern although it remained relatively flat for the duration of the study.

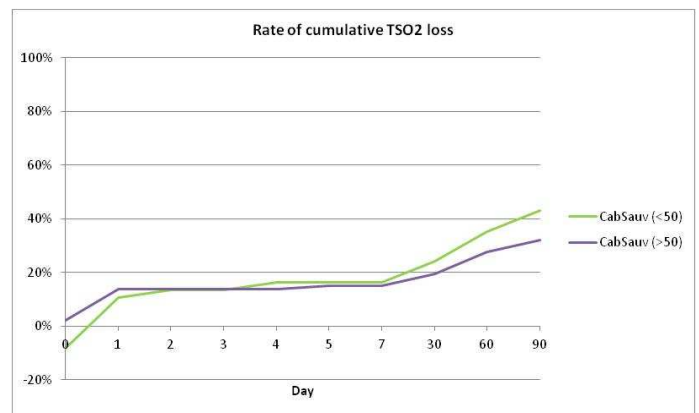
TSO<sub>2</sub> (Figure 29) patterns for both samples were very similar and mirrored FSO<sub>2</sub> loss behaviors.



**Figure 27:** Rate of cumulative FSO<sub>2</sub> loss in CabSauv as a percentage of the initial value at time S



**Figure 28:** Rate of cumulative BSO<sub>2</sub> gain in CabSauv as a percentage of the initial value at time S



**Figure 29:** Rate of cumulative TSO<sub>2</sub> loss in CabSauv as a percentage of the initial value at time S

Cabernet Sauvignon samples exhibited similar color intensity patterns (Figure 30) as the Syrah samples but with both Cabernet Sauvignon samples having coinciding peaks two days later than

the Syrah samples. In spite of the sawtooth effect, IC in CabSauv<50 was higher at the end of the study and approximately the same in CabSauv>50.

H (Figure 31) for both samples relatively remained flat with CabSauv>50 measuring only marginally higher values, suggesting greater spectral absorbances at  $\lambda_{420}$  than CabSauv<50 and therefore a shift to more of a yellow color and greater loss of red color. There is no result for CabSauv>50 on day 60 as the photometer was inexplicably reporting that the sample was absorbing less light than the distilled H<sub>2</sub>O sample; a value consistent with the trend was used for the purpose of this analysis. No color or color intensity changes were visible.

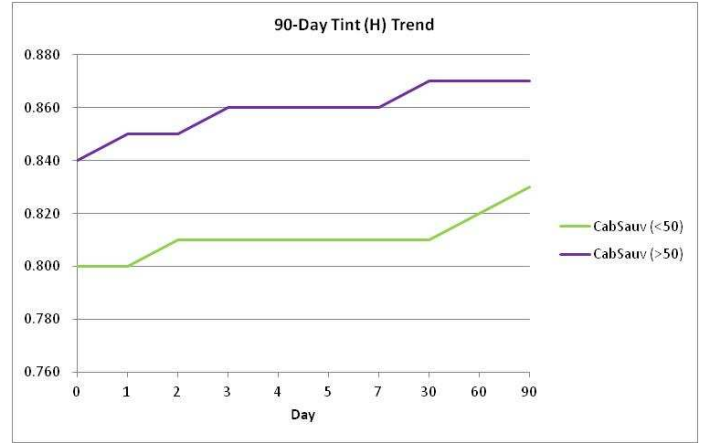


Figure 31: 90-day hue (H) trend in CabSauv (see the note in Table 9)

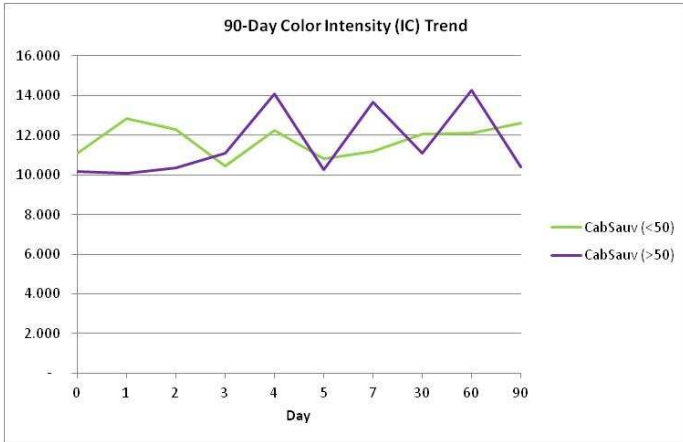


Figure 30: 90-day color intensity (IC) trend in CabSauv

TPC (Figure 32) for both samples remained relatively flat and unaffected by SO<sub>2</sub> and were very close on day 90 even though CabSauv>50 started at a higher level.

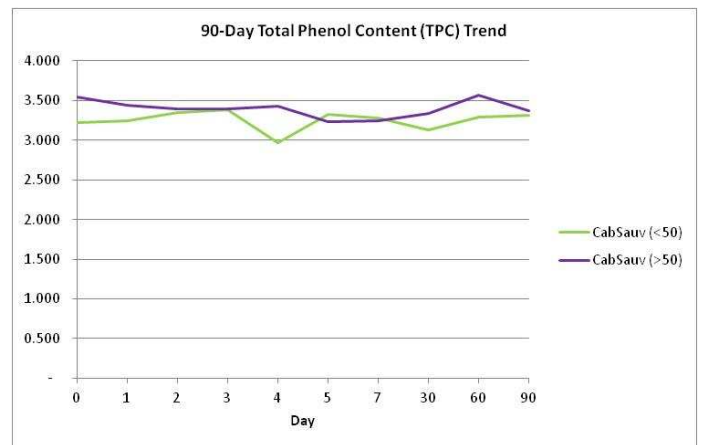


Figure 32: 90-day total phenol content (TPC) trend in CabSauv

Parameter	DAY										
	S	0	1	2	3	4	5	7	30	60	90
FSO2 (mg/L)	46	32	24	22	22	22	22	22	18	10	10
TSO2 (mg/L)	74	80	66	64	64	62	62	62	56	48	42
Color density	11.09	11.09	12.85	12.29	10.47	12.26	10.80	11.18	12.07	12.12	12.61
Tint	0.80	0.80	0.80	0.81	0.81	0.81	0.81	0.81	0.81	0.82	0.83
TPC (mg/L GAE)	3.22	3.22	3.24	3.35	3.38	2.97	3.32	3.28	3.13	3.29	3.31

Table 8: Test measurements for low-sulfite Cabernet Sauvignon (CabSauv<50)

Parameter	DAY										
	S	0	1	2	3	4	5	7	30	60	90
FSO2 (mg/L)	146	104	82	82	82	78	82	82	70	60	52
TSO2 (mg/L)	174	170	150	150	150	150	148	148	140	126	118
Color density	11.09	10.17	10.09	10.36	11.11	14.09	10.26	13.67	11.10	14.28	10.39
Tint	0.80	0.84	0.850	0.85	0.86	0.86	0.86	0.86	0.87	0.87*	0.87
TPC (mg/L GAE)	3.22	3.54	3.44	3.39	3.39	3.43	3.23	3.25	3.34	3.57	3.37

\*A valid reading could not be obtained for tint on day 60 with the unit reporting that the sample was absorbing less light than distilled water. A value of 0.87, consistent with the results, was used.

Table 9: Test measurements for high-sulfite Cabernet Sauvignon (CabSauv>50)

**Test Errors.** FSO<sub>2</sub> and TSO<sub>2</sub> errors for the SC-300 test unit is  $\pm 2$  mg/L. HI 83742 errors are:  $\pm 0.010$  for color density in white wine;  $\pm 0.20$  for color density in red wine;  $\pm 0.03$  for color hue;  $\pm 0.015$  mg/L for total phenols in white wine; and  $\pm 0.10$  mg/L for total phenols in red wine. The errors for the pipette and self-zeroing burette are  $\pm 0.03$  mL and  $\pm 0.1$  mL, respectively.

## Conclusions

This study confirms the strong correlation between FSO<sub>2</sub> losses and binding with total phenol content (TPC).

The results confirm the need to adjust sulfite level additions at the start of the sulfiting regimen and ideally checked and adjusted again after one week. The level of adjustment at the initial addition depends on total SO<sub>2</sub> for white and rosé wines;

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for reds, an adjustment is required independently of total SO<sub>2</sub> levels, but smaller adjustments are required as TPC increases. As is recommended by enologists, making small additions regularly is more effective than large infrequent additions.

The results also demonstrate that SO<sub>2</sub> levels be monitored and adjusted on a monthly basis or, at a minimum, every 3 months, as is the common practice.

Excessive use of SO<sub>2</sub> can also lead to color and color intensity changes.

This study should be repeated by analyzing wine samples at typical cellar temperatures, usually around 13°C (55°F), to assess SO<sub>2</sub> dynamics and validate SO<sub>2</sub> management protocols at colder temperatures.

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