Influence of different types of LEDs lights on the formation of volatile sulfur compounds in white and rosé wines

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Abstract

The effect of LEDs light on the formation of volatile sulfur compounds (VSCs) and the final sensory quality of white and rosé wines was evaluated. Thus, different commercial wines were exposed for ten days to three types of lights. All wine samples were analyzed throughout the exposure period to determine the usual oenological parameters together with some other chemical characteristics (color evolution; riboflavin, cysteine and methionine photodegradation), VSC amounts and sensory characteristics. The results showed that the wines exposed to ultraviolet light suffered greater degradation of the aromatic precursors, mainly riboflavin, and had higher concentrations of VSCs. Regarding LED lights, these produced minimal degradative effects. So that we can consider this type of light as an alternative to reduce the economic impact that currently occurs due to the photodegradation of bottled wines.

Keywords: amino acids, wine, riboflavin, aroma, LED ligths, sensory analysis

1. Introduction

Sustainable development is currently one of the main goals of the European Union Commission as well power consumption has become one of the most considerable environmental issues. Light-Emitting Diodes (LED), ubiquitous in modern electronic devices and lighting, offer a high series of advantages, especially from a sustainability point of view. From an oenological standpoint, the recent emergence of high-power LEDs brings new opportunities to modernize wineries as this type of lighting offers an exceptional flux range, better light distribution efficiency, versatility, longer shelf life, and best power conversion, among others (Mills, 2004). Thus, the replacement of existing lighting in wineries with LED technology can generate significant savings of up 60 % when an optimal control and automation system is used (Vela, 2017).

On the other hand, the effect of light radiation on the quality of wine is a recurring theme. There are studies from the 70s in which already it was observed that the quality of Champagnes sold in supermarkets was lower than those sold in specialized stores and that this was due to UV-visible radiation exposure (A. Maujean, Haye, M., Feuillat, M., 1978). Later it was found that was happening was a photochemical transformation that promoted an unwanted change in the wine properties which was called Goût de Lumière (D'Auria, Emanuele, Mauriello, & Racioppi, 2003) and it has been suggested that the most damaging wavelengths in bottled wines are those below 520 nm (Clark, Dias, Smith, Ghiggino, & Scollary, 2011; A. Maujean, Haye, M., Feuillat, M., 1978). This change occurs in color, odor, and flavor and depends on several factors. The most important ones are; i) the chemical composition of wines, ii) the irradiation conditions, and iii) the exposure time (Grant-Preece, Barril, Schmidtke,

48 Scollary, & Clark, 2017). Among the different compounds degradable by light, one of
49 the most studied is riboflavin, which is generated in significant quantities during
50 alcoholic fermentation (Mattivi, Monetti, Vrhovsek, Tonon, & Andrés-Lacueva, 2000;
51 Santos, García-Ramírez, & Revuelta, 1995). This molecule has a chemical structure that
52 absorbs radiation between 300 and 510 nm with maximum absorbance at 370 and 442
53 nm. Therefore, if wine is irradiated with fluorescent lamps that provide mercury
54 emissions with maxima around 313, 365, 405, 436, 546, and 578 nm, and phosphor
55 emissions with maxima around 480 and 580 nm (Spikes, 1981), this molecule will be
56 irretrievably affected. As for LED lamps, they emit light in wavelength ranges from 350
57 nm to 750 nm and when dealing with cool white LEDs (commonly used in the wine
58 industry) they show a maximum emission at 450 nm. However, this technology allows
59 designing lights that minimize or even remove the emission of some wavelengths so it
60 could minimize the risk of wine degradation.

61 Apart from riboflavin, many other molecules can be degraded due to light exposure.
62 Some of them have been related to the Fenton reaction which consumes free SO_2 and
63 promotes the oxidation of some compounds such as tartaric acid to glyoxylic acid, a
64 known precursor of the xanthylium cation pigments. The formation of this compound
65 has been correlated with an increased level of browning, so these chemical
66 degradations, induced by UV-visible radiation, usually imply loss of wine quality (Clark,
67 2008; Clark, Prenzler, & Scollary, 2007; George, Clark, Prenzler, & Scollary, 2006;
68 Maury, Clark, & Scollary, 2010). In addition to these color changes, also UV-visible light
69 exposure has been found to accelerate oxygen consumption which promotes obtaining
70 an increasingly reducing atmosphere. These conditions directly affect the aromatic
71 composition of wine since they favor the appearance of new compounds, among

which volatile sulfur compounds (VSCs) stand out (Grant-Preece, Barril, Schmidtke, Scollary, & Clark, 2017; Haye, 1977). In fact, although VSCs can be formed during the fermentation process, the photosensitivity of some sulfur-amino acids found in bottled wine can also lead to their formation. These photo-oxidation reactions also involve significant amounts (> 50 µg/L) of the riboflavin molecule in its triplet excited state. As this is a strong oxidant, it can easily react with reductant molecules such as methionine or cysteine, giving rise to other unstable and photosensitive chemical species, which, in turn, decompose, into more stable compounds such as sulfides, disulfides and some thiols (Daniela Fracassetti, Tirelli, Limbo, Mastro, Pellegrino, & Ragg, 2020; Kinzurik, Herbst-Johnstone, Gardner, & Fedrizzi, 2016). These VSCs have a significant impact on the wine aroma, as they are the key contributors to some undesirable wine flavors described as rotten eggs, cabbage, or cooked onions.

Currently, the photo-oxidation of wine is in the framework for wine researchers (D. Fracassetti, Di Canito, Bodon, Messina, Vigentini, Foschino, et al., 2021; Daniela Fracassetti, Tirelli, Limbo, Mastro, Pellegrino, & Ragg, 2020; Lan, Li, Yang, Li, Yuan, & Guo, 2021). However, little information regarding the influence of the currently used LEDs on the quality of the wine has been reported. This research aims to evaluate the use of new LED lights to avoid bottled wines spoilage by determining the photo-degradation of riboflavin, cysteine, and methionine, the formation of VSCs, and changes in color throughout the time of light exposure.

2. Material and Methods

2.1. Chemicals and reagents

Thiophene, 2-propanethiol and methyl ethyl sulfide were used as internal standards for the analysis of aromas. Hydrogen sulfide, methanol, ethanol, dimethyl sulfide, diethyl sulfide, dimethyl disulfide, and diethyl disulfide were used as sulfur volatile standards. The other standards used were riboflavin, cysteine, and methionine. All of them were supplied by Sigma-Aldrich (Darmstadt, Germany) with a purity ≥ of 90 %. HCl and HNO_3 solvents were of high quality and were supplied by Panreac (AppliChem, Barcelona, Spain).

2.2. Samples and experimental design

Six commercial white wines representative from Albariño variety (Rias Baixas Appellation of Origin) and three rosé wines from Garnacha variety (Rioja Appellation of Origin) from 2017 and 2018 chosen randomly were evaluated. All bottles of wine were subjected to direct light incidence by using three different types of lamps. Light A (LA) was achieved by using an ultraviolet light lamp like the current one used in wineries, warehouses, and supermarkets. Light B (LB) is a type of LED that minimized the 400-450 nm radiation and light C (LC) as an LED lamp that eliminated the radiation emitted into the 400-450nm region. To carry out the experiment, a black wooden box was designed into which the bottles were introduced in a horizontal position and the tested lamps were in the upper part (Figure S1A and B). A box for each type of light was built and, during the experiment, the three boxes containing the wine samples were kept in darkness in a controlled temperature room (20 ± 2 °C). All controls were stored in darkness also in a controlled temperature room (20 ± 2 °C). The exposure was carried out for 10 days. Samples were taken at different analysis times (3, 6, 24, 48, 120, and 240 hours). All treatments were performed in duplicate.

2.3. Oenological parameters

Titratable acidity and pH were potentiometrically measured with an automatic titrator (TitroMatic Hach from Crison®) and turbidity with a HACH TL2310 turbidimeter. Free and total sulfur content, alcoholic degree and volatile acidity were determined by using an infrared spectroscopy (FTIR) system (WineScanTM by FOSS, Hilleroed, Denmark), internally calibrated according to OIV reference methods.

Colorimetric measurements were performed by using a Helios-α spectrophotometer (Thermo Fisher Scientific, Waltham, MA USA). CIELAB color parameters and color differences between samples in darkness and samples exposed to light (ΔE * ab = $((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$) were calculated.

2.4. Analysis of aromatic precursors by UPLC

2.4.1. Riboflavin

For the determination and quantification of riboflavin (vitamin B12) the method described by (Andrés-Lacueva, Mattivi, & Tonon, 1998) was followed with slight modifications. Thus, all wine samples were passed through a 0.2 µm syringe filter (Millipore Corporation, Bedford, MA, USA) and directly injected into the ultra-performance liquid chromatograph (UPLC 1260 Series, Agilent, Palo Alto, USA) with a fluorescence detector. The solvents used were solvent A, 0.05 M NaH_2PO_4 buffer at pH 3.0 with H_3PO_4, and solvent B, acetonitrile. The calibration lines used for quantitation were carried out by preparing standard solutions under dim light, amber glass bottles, and vials. The concentration range was from 5 to 200 µg/L. The different riboflavin standard solutions were prepared by diluting a concentrated solution (10.000 µg/L) with suitable amounts of a mixture of 20 % solvent B and 80 % solvent A. Then each

one was filtered and injected into the UPLC. Both the standard and samples were analyzed in duplicate.

2.4.2. Amino Acids

Methionine and cysteine were determined following a procedure previously optimized and validated (Roda, Martín, Mislata, Castaño, Puxeu, & Ferrer-Gallego, 2019). Wine samples were filtered using a 0.2 µm Millex syringe filter (Millipore Corporation, Bedford, MA, USA) and subjected to automatic pre-column derivatization with *o*-phthaldialdehyde (OPA Reagent, Agilent) before the injection to the UPLC (Agilent UPLC 1260 Series (Palo Alto, USA) equipped with DAD detector and autosampler. The solvents used were, solvent A: 40 mM Na_2HPO_4 at pH 7.8, and solvent B: ACN: MeOH: water (45:45:10, v/v/v). Detection was performed at λ = 338 nm. The identification of the amino acids was carried out by comparing their retention times with those of the pure reference standards. Standard calibration curves were used to quantify amino acids, whose concentration ranges were from 0.1 to 5 mg/L for cysteine and from 1 to 50 mg/L for methionine. The different standard amino acid solutions were prepared by diluting a concentrated solution (1000 mg/L) in a synthetic wine solution (130 mL of pure ethanol with 5.5 g of tartaric acid in one liter of Milli-Q water). Then each was filtered and injected into the UPLC. Both the standard and the samples were run in duplicate. All samples for analysis were injected in duplicate (n = 2).

2.5. Analysis of aromatic sulfur compounds by GC-FPD

The analysis of aromas was carried out according to the method developed by M. Mestres et al. 1999 (Mestres, Martí, Busto, & Guasch, 1999), with some minor modifications. To avoid loss of volatile compounds during sample handling, the wines

were refrigerated at -4 ºC for 24 hours in a cold room. Once a wine bottle was opened, the sample to be analyzed was prepared by using a dry ice bath under a stream of nitrogen gas to provide an inert atmosphere. Specifically, 10 mL of wine together with, 100 µL of 2-propanal to eliminate interference caused by the sulfur content of wine, and 100 µL of a mixture composed of 1000 µg/L of each internal standard were placed into a 20 mL glass vial which contained 2.7 g of NaCl and 0.15 g of ethylenediaminetetraacetic acid (EDTA).

The volatile sulfur compounds were extracted and concentrated using the headspace-solid phase microextraction (HS-SPME) technique with Carboxen/PDMS fibers of 85 µm. The samples were equilibrated for 20 min at 35 ºC with shaking and, afterwards, the fiber was exposed to the headspace for 30 minutes at the same temperature in the GC auto sampler. The fiber desorption was carried out into a TDU-thermal desorption unit coupled to a cold equipment, making a temperature ramp from -60 ºC to 260 ºC, which allowed the retention of extremely volatile sulfur compounds. After 120 seconds, the unit was heated up to 260 ºC and the sample was injected into a GC 7890A gas chromatograph (Agilent Technologies) equipped with a flame photometric detector (FPD) (G3348B, Agilent Technologies). The separation was carried out using an HP-1 column (30 m x 0.320 mm x 4.00 µm, Agilent), with helium as carrier gas at a flow rate of 2.09 mL/min. The oven temperature ramp was: 35 ºC to 260 ºC in 8 min. The detector temperature was 200 ºC and it was fed with 75 mL/min of hydrogen, and 86 mL/min of synthetic air.

The quantification was carried out by means of calibration curves of standards. With the use of the standards, the retention times of each of the compounds were

identified and determined. The results of the volatile compounds were expressed as quantitative data expressed in μg/L as a response in consideration to the internal standard. All analyzes were done in duplicate.

2.6. Sensory analysis

The quantitative descriptive analysis (QDA) was performed by a tasting panel accredited by ISO 8586: 2010, and in a sensory standardization room (ISO 8589: 2007). Due to the pandemic situation arising from COVID 2019, the sensory panel was limited to four expert tasters.

The sensory analysis was carried out in 9 sessions of 3 blocks made up of 7 wines each session, where the panelists did not know the identification of the sample in each of the glasses, nor the type of light, nor the exposure time of the same.

Therefore, a total of 189 wines were tasted, grouped into 9 references by type of wine, and in turn by type of light and by the time they were exposed. The analysis was based on the olfactory phase. The aromatic descriptors considered were fresh fruit, candied/dried fruit, spicy, floral, pastry, evolution, reduction and 'light taste'. All the data obtained were processed with the FIZZ software (Biosystems, V.2.47B). And a specific tasting sheet was designed according to the aforementioned olfactory descriptors.

2.7. Statistical analysis

A simple analysis of variance (ANOVA) was carried out and the data were presented as the mean ± standard deviation. The Tukey procedure was used and differences in p

values <0.05 were considered significant. StatGraphics Centurion XVI (Manugistics Inc., Pockville, MD, USA) was the program used.

3. Results

3.1. Oenological analysis

The oenological parameters of the different samples were determined in duplicate after 0, 3, 6, 24, 48, 120, and 240 hours of light exposure. Table 1 shows the mean values obtained for each sample at the beginning of the experiment (samples in darkness or 0 hours of exposure), and after 240 hours (10 days) exposed to the three types of light. As can be seen, the values found at the beginning of the experiment are comparable to those found after 10 days to light exposure, except when dealing with SO_2 and color. Wines presented values of total SO_2 lower than 100 mg/L avoiding problems related to greater wine reduction when working at high SO_2 amounts (Lopes, Silva, Pons, Tominaga, Lavigne, Saucier, et al., 2009; Ugliano, 2013). Some changes on the free and total SO_2 were found in samples exposed to lights. In general, free sulfur was more affected in samples exposed to LB after 10 days of exposure. According to other authors (Lan, Li, Yang, Li, Yuan, & Guo, 2021), the exposure to light accelerated the consumption of free SO_2 compared to controls (in darkness). Furthermore, UV irradiation resulted in a greater decrease in free SO_2 than white light after 160 days of storage. This fact raises the possibility of thinking that although after 10 days LB was the light that most affected free SO_2, it could be that if we increased this exposure time it was LA (UV light) that increased the loss of free sulfur in the wines.

Regarding color, in general the absorbance of the wines at 420 nm remained stable in the wines exposed to lights for 10 days compared to 0h. As Diaz et al 2021 (Díaz,

Castro, Ubeda, Loyola, & Laurie, 2021) observed until the concentration of free SO_2 was not remarkably low, the absorbance at 420 nm of the wines remained without differences between the wines kept in the light and those kept in the dark. In the Cielab coordinates, it was mainly the *b** coordinate that presented the most significant differences in the wines exposed to LA after 10 days compared to 0h. Table 1 shows how the *b** values are lower in the wines exposed to LA (UV light), which indicates a greater loss of yellow color or a greater browning of the wines. As observed by Lan et al 2021 (Lan, Li, Yang, Li, Yuan, & Guo, 2021), the exposure to ultraviolet light affected the color parameters more compared to the control (in the dark). However, when calculating AE**ab*, all the results obtained were less than 1.0 CIELAB unit (table 1). However, the wines exposed to LA return values very close to 1 so that, if we consider the dispersion, they will exceed it, although not in all cases Therefore, it is probable that if the experiment was extended along time, color differences will be appeared and detected with the naked eye by the human eye in LA samples (Gonnet, 1998).

3.2. Analysis of aromatic precursors by UPLC

3.2.1. Riboflavin

The mean riboflavin values of the samples that remained in the dark (time 0h) presented concentrations between 138-182 µg/L in white wines, and between 152-178 µg/L in rosé wines (table S1). These values indicate that the studied wines presented high concentrations of riboflavin, since in all cases they exceeded 100 µg/L. Although the concentration values agree with others found in literature, these are above 100 µg/L so, according to previous studies, the sample wines are at risk of triggering the appearance of volatile sulfur compounds in wine (D. Fracassetti, Limbo, Pellegrino, &

253 Tirelli, 2019; Mattivi, Monetti, Vrhovsek, Tonon, & Andrés-Lacueva, 2000). In general,
254 rosé wines presented more abrupt degradation of riboflavin than white wines
255 throughout the time of exposure to the lights. Furthermore, this greater degradation
256 of riboflavin was observed in all the wines exposed mainly to light LA followed by LB
257 (figure 1). However, it is worth noting the behavior of the wines with exposure to LC,
258 because the riboflavin concentrations practically did not vary throughout the exposure
259 time. This behavior is probably due to wavelengths in the 370 to 450 nm range.
260 Wavelengths at which LA light emits and LC light completely removes, can probably
261 excite riboflavin to the short-lived singlet state and then to the triplet state, which
262 then participates in photo-oxidation reactions through various mechanisms (Grant-
263 Preece, Barril, Schmidtke, Scollary, & Clark, 2017).

264 In general, as figure 1 shows, white wines (W1-W6) presented different degrees of
265 affectation. After the last exposure time (240 hours) with LA, riboflavin losses of up to
266 44 % (W1 and W6) were observed. This decrease in riboflavin concentration occurred
267 progressively over time of exposure. Even after only 24 hours of exposure, the wines
268 showed losses of 17 and 13 % (W1 and W6, respectively). Regarding the values
269 obtained in the samples exposed with LB light, in general, the wines showed a trend
270 like that observed with LA light but with less degradation of riboflavin in all cases. With
271 this light (LB), after 48 hours of exposure, the wines presented losses between 11 and
272 16 % and these degradation values increased up to 35-38 % after the last exposure
273 time (240h) (W1 and W6, respectively). In general, both lights, LA and LB, behaved
274 similarly in the degradation of riboflavin in white wines with the exception of W4 and
275 W5 wines in which there was hardly any degradation with LB (and LC) but where the
276 degradation of riboflavin reached values up to 20 % after 240 h of exposure to LA. The

277 green color of the bottle of these two samples, which unlike the rest of the wines had
278 bottles of clear color, could be a crucial factor in the lowest photodegradation showed.
279 Different wavelengths of light will be transmitted depending on the glass color, and
280 exposing wine to light at wavelengths close to 370 or 442 nm is particularly effective in
281 inducing riboflavin degradation and the formation of volatile sulfur compounds,
282 especially when using transparent glass bottles (Dias, Smith, Ghiggino, & Scollary,
283 2012; D. Fracassetti, Gabrielli, Encinas, Manara, Pellegrino, & Tirelli, 2017).

284 In the case of rosé wines, as shown in figure 1, the pronounced degradations produced
285 with exposure to light LA over the time in all wines (W7-W9) stand out, reaching losses
286 of up to 85 % (W8) after 10 days of exposure. Even after 24 hours of exposure, this
287 decrease was already around 30 % of degradation. And only after 6 hours a loss of 10
288 % of riboflavin was produced. As for rosé wines exposed to LB light, they showed a
289 similar trend to that observed with LA light, but with less degradation of riboflavin over
290 time. After the last time of exposure, they showed degradation of around 45 %, half of
291 the degradation produced with LA.

292 Finally, it should be emphasized again that in general none of the white and rosé wines
293 exposed to LC light showed riboflavin degradation over time.

294 3.2.2. Methionine and Cysteine

295 Amino acids such as cysteine and methionine represent the most important form of
296 total nitrogen in musts and wines. In addition to being the most important precursors
297 of certain volatile sulfur compounds (Bekker, Wilkes, & Smith, 2018), due to their
298 polyfunctional character, amino acids have great chemical reactivity compared to
299 carbonyl compounds, in particular with sugars, according to the Maillard reaction

(Marchand, De Revel, & Bertrand, 2000). This Strecker degradation of methionine and cysteine to aldehydes by α-dicarbonyl compounds formed during fermentation or oxidation contributes to the evolution of aroma in bottled wine (Ugliano, 2013).

The initial content of cysteine ranged between 0.35 and 1.79 mg/L in white wines and between 0.56 and 0.86 mg/L in rosé wines (table S2), values that are within the usual ones (Bekker, Wilkes, & Smith, 2018). As can be seen in figure 2, on the whole, the wines suffered decreases in cysteine after exposure to light, mainly with LA light, reaching decreases of around 30-45 % in white wines, and even up to 55 % in rosé wines (W9). In the case of exposure to LB light, these decreases in cysteine were slightly less than those produced with LA, reaching values of around 20-35% in white wines and up to 50 % in rosé wines (W9). However, the cysteine decreases of the samples with exposure to LC light were between 10-35 %, up to three times less than the losses obtained with LA.

This degradation of the amino acid cysteine observed in all the wines studied may have as a consequence the formation of VSCs through Strecker degradation of sulfur amino acids, as already observed by Pripis et al 2000 (Pripi-Nicolau, De Revel, Bertrand, & Maujean, 2000). Cysteine can react with the α-dicarbonyl compound in wine to form hydrogen sulfide, methanethiol, and other volatile compounds (Marchand, De Revel, & Bertrand, 2000)

The initial concentrations of methionine in the wines ranged between 3.6 and 6.0 mg/L in white wines and between 4.8 and 8.1 mg/L in rosé wines (table S2), values similar to those found in literature (D. Fracassetti, Limbo, Pellegrino, & Tirelli, 2019; Grant-Preece, Barril, Schmidtke, Scollary, & Clark, 2017). Furthermore, the range of

concentrations in wine was around between 1 and 37 mg/L (Bekker, Wilkes, & Smith, 2018). Figure 2 shows how in general, after 10 days of exposure, the wines exposed to LA light presented further degradation of methionine, reaching losses of around 10-30 % in white wines and up to 40 % in rosé wines. (W9). In the case of samples exposed to LB light, generally this decrease in methionine was slightly less than with LA, but decreases in methionine were achieved in the same range (around 10-30 %). However, it should be noted that W1, W4, W5, W6, and W7 wines exposed to LC light, did not exceed 10 % loss of methionine in the last exposure time.

These decreases in methionine may be due to the presence of riboflavin, which acts as a photosensitizer in its degradation. Fracassetti et al 2019 (D. Fracassetti, Limbo, Pellegrino, & Tirelli, 2019) observed that methionine proved to be stable in a hydroalcoholic acid solution without riboflavin since no degradation occurred in the model wine enriched with methionine (3 mg/L) and exposed to light for two hours. In contrast, the presence of riboflavin caused methionine degradation of up to 27 %, depending on the initial concentrations of the two compounds. Furthermore, when riboflavin and methionine concentrations were high, then the amounts of degraded methionine increased as well, which demonstrated the influence of the methionine concentration on its own degradation.

3.3. Analysis of volatile sulfur composition

The analysis of volatile sulfur compounds (VSCs) was carried out as these can be generated by the degradation of riboflavin and the amino acids, methionine, and cysteine, later in post-bottling (Bekker, Day, Holt, Wilkes, & Smith, 2016; D. Fracassetti, Limbo, Pellegrino, & Tirelli, 2019). In total six compounds were detected and

quantified, which were grouped in three aromatic families based on their chemical structures: thiols, sulfides and disulfides.

The thiol family consisted of hydrogen sulfide (H_2S), methanethiol (MeSH), and ethanethiol (EtSH). Although, as in other studies (Bekker, Day, Holt, Wilkes, & Smith, 2016; Siebert, Solomon, Pollnitz, & Jeffery, 2010), EtSH was not detected in any of the samples analyzed. Regarding H_2S and MeSH, these are the main compounds responsible for the formation of "reducing" aromas after bottling (Ugliano, 2013; Ugliano, Dieval, Siebert, Kwiatkowski, Aagaard, Vidal, et al., 2012; Ugliano, Kolouchova, & Henschke, 2011). As shown in figure 3, in general both compounds, increased their concentrations throughout the light exposure time but this increase was much higher when dealing with the exposure to light A, followed by light B, and to a lesser extent, light C.

Hydrogen sulfide is a characteristic compound for providing wines with unpleasant aromas of rotten eggs, decomposing algae, or wastewater when its concentration is higher than its odor threshold (OT) of 1.6 µg/L in vinica matrix (Siebert, Solomon, Pollnitz, & Jeffery, 2010). As can be seen in figure 3a, all the wines except for W4 exceeded the OT concentration of H_2S just after 6 hours of exposure with both LA and LB light. In the case of exposure to LC light, this sensory limit was not or slightly exceeded. In general, it should be noted that rosé wines (W7-W9) presented the highest concentrations of this compound after exposure to all lights. In general, the highest concentrations of H_2S were obtained in the wines exposed to LA. In some cases, these wines exposed to LA came to present twice the concentration of H_2S than

368 that obtained with LB light, and even three times higher than that obtained with LC
369 light.

370 After the last exposure time (240 hours) with light LA, in general, the samples
371 continued to show an increase in the concentration of H_2S compared to the 6 hours of
372 exposure. However, after 10 days (240 hours) of exposure to LB light, only rosé wines
373 were affected. The same happened with LC light, which mainly affected rosé wines but
374 to a lesser extent than with previous lights, being half the concentration obtained with
375 LB.

376 Another of the thiols studied was methanethiol (MeSH). This compound is
377 characteristic for providing wines with aromas related to descriptors such as
378 putrefaction and cooked cabbage. In addition, it should be noted that this compound
379 presents very low OT values (0.3 µg/L) which makes it play an important role in the
380 perception of 'reducing' aromas in wine (D. Fracassetti & Vigentini, 2018; Nguyen
381 Dang-Dung, 2012). As can be seen in figure 3.b, only after 6 hours of exposure to LA
382 light, all wines (except W4 and W6) exceeded the OT concentration of MeSH.
383 However, only two white wines (W3 and W5) and two rosés (W8 and W9) exceeded
384 the OT with exposure to LB light. And in the case of exposing the samples in LC, only
385 two wines (W3 and W9) slightly exceeded the sensory limit. After the last analysis time
386 (240 hours), the samples exposed to LA light increased their MeSH concentrations
387 concerning the previous time, mainly highlighting the large increase produced in W9
388 (5.5 µg / L), since it was practically the double that obtained after 6 hours. In the case
389 of exposure to LB light, generally, the wines that were already affected after 6 hours,
390 followed an increase in concentration. And finally, in general, the wines exposed to LC

391 light did not show great changes in the concentrations of MeSH throughout the
392 exposure time.

393 As seen in other studies, cysteine and methionine are the main sources of H_2S and
394 MeSH formation (Bekker, Wilkes, & Smith, 2018; Perpète, Duthoit, De Maeyer, Imray,
395 Lawton, Stavropoulos, et al., 2006). But in addition, riboflavin plays a key role in the
396 induction of methionine degradation (D. Fracassetti, Limbo, Pellegrino, & Tirelli, 2019).
397 This fact could explain the relationship observed between the higher degradations of
398 these amino acids (figure 2) and the higher concentrations of these aromatic
399 compounds (figure 3) obtained in the studied wines and exposed to LA light, mainly in
400 the case observed in W9.

401 Therefore, exposure to LA light favored the appearance of thiols in the samples, mainly
402 in rosé wines. The LB light affected to a lesser extent than the LA, but emphasizing the
403 increase of H_2S mainly in rosé wines. And especially, it should be noted that the LC
404 light hardly affected the samples in the formation of thiols, except in rosé wines where
405 the concentration of H_2S increased, although to a lesser extent compared to the other
406 lights.

407 The next family studied was the sulfides. This family consisted of dimethyl sulfide
408 (Me_2S) and diethyl sulfide (Et_2S) (figure 4). As shown in figure 4, and as was the case in
409 the thiol family, in general, both compounds, Me_2S and Et_2S, increased their
410 concentrations throughout the exposure time, in all wines. In general, this increase
411 was much greater with the exposure of light LA, followed by light LB and to a lesser
412 extent with light LC.

413 Dimethyl sulfide (Me_2S) is a compound that is associated with cabbage, asparagus,
414 corn, or vegetable flavors when present in high concentrations, since it has an odor
415 threshold of 25 μg/L (Mestres, Busto, & Guasch, 2000; Siebert, Solomon, Pollnitz, &
416 Jeffery, 2010; Ullrich, Neef, & Schmarr, 2018). Factors that influence Me_2S formation in
417 wines after bottling include grape variety, viticulture and winemaking processes, and
418 wine pH value. These factors likely affect the Me_2S precursor compounds (Bekker, Day,
419 Holt, Wilkes, & Smith, 2016; Escudero, Campo, Fariña, Cacho, & Ferreira, 2007;
420 Ugliano, 2013). As shown in figure 4a, in general rosé wines and some white wines (W4
421 and W6) presented the highest concentrations of the compound Me_2S under the
422 exposure of all the lights, presenting very high values after 6 hours of exposure to the
423 light LA. Also, it should be noted that W9 was the only wine that exceeded the OT of
424 this compound. However, in the particular case of the wines exposed to both LB and LC
425 light, none of them exceeded the OT, at this time. After 10 days of exposure with LA
426 light, all rosé wines exceeded the OT, in addition to white wine W6. In the case of
427 exposure to LB light, on the whole, the wines behaved similarly to those exposed to LA
428 light. However, it should be noted that none of the samples exposed to LC light
429 presented values higher than OT for Me_2S.

430 As is already known, riboflavin and methionine can be precursors of Me_2S (D'Auria,
431 Emanuele, Mauriello, & Racioppi, 2003; A. Maujean, Haye, Feuillat, Thomas, & Petit,
432 1978). Therefore, when observing figures 1 and 2, the highest degradations of
433 riboflavin and methionine are obtained in samples from W6 to W9, which also coincide
434 with the highest concentrations of Me_2S obtained (Figure 4a).

435 The second compound analyzed within the sulfide family was **diethyl sulfide**. This
436 compound is characteristic because it has garlic as the main aromatic descriptor. In
437 addition, it has a great reducing influence on wines since it has a very low sensory
438 limit, OT 0.93 µg/L (Mestres, Busto, & Guasch, 2000; Siebert, Solomon, Pollnitz, &
439 Jeffery, 2010; Ullrich, Neef, & Schmarr, 2018). In figure 4.b it can be seen how the
440 white wine W2, and all the rosés (W7-W9), in general, presented the highest
441 concentrations of Et_2S after being exposed to all the lights. After the 6-hour exposure
442 time to LA light, three of the study wines (W2, W7 and W9) presented Et_2S values
443 higher than their OT. In the case of exposure with the LB and LC lights, only two wines
444 (W2 and W9) exceeded the OT value. After 10 days of exposure to LA light, in general,
445 all the wines exceeded the OT of Et_2S. In the case of the exposure with the LB and LC
446 lights, it was the rosé wines (W7-W9) and the W2 white wine, which exceeded the OT
447 of Et_2S (with the exception of the W8 with LC). However, it should be noted that
448 exposure of the wines to LC light over time did not dramatically increase the
449 concentrations of the Et_2S compound.

450 Therefore, exposure to LA light favored the appearance of sulfides in the samples,
451 mainly in rosé wines. The LB light affected less than the LA light. And the LC light, in
452 general, did not favor the formation of sulfides in the wines over time.

453 And finally, there is the family of disulfides, in which the compounds dimethyl disulfide
454 (Me_2S_2) and diethyl disulfide (Et_2S_2) were evaluated. As in the previous families (thiols
455 and sulfides), both compounds were increasing their concentrations throughout the
456 exposure time to the lights. In addition, generally this increase was greater with the
457 exposure of light LA, followed by light LB and to a lesser extent with light LC.

458 Dimethyl disulfide is a characteristic compound for providing aromas related to cooked
459 cabbage, sulfurous or onion, and for having a high odor threshold (29 μg/L) (Siebert et
460 al 2010; Ullrich et al 2017). As shown in figure 5a, in general all wines (except W5)
461 were affected by LA light, followed by LB, over time. After 6 hours of exposure to LA
462 light, all wines exceeded the OT of Me_2S_2 (except W4 and W5). This could be because
463 the W4 and W5 wines had the green bottle color, which can act as a protector in the
464 formation of the Me_2S_2 compound. However, with LB light exposure, only rosé wines
465 (W7 and W8) exceeded OT. It should be noted that exposure to LC light, in general, did
466 not affect the increase in the concentration of Me_2S_2, since none of the wines
467 exceeded the OT. After the last analysis time (240 hours), all samples exceeded the
468 sensory limit of Me_2S_2 with exposure to LA light. In the case of exposure to LB, the
469 highest increases in Me_2S_2 occurred in the same wines as with exposure to LA, but with
470 lower concentrations. And in the case of exposure with LC light, it should be noted that
471 in general none of the wines exceeded the OT of Me_2S_2 (except W7, which slightly
472 exceeded it).

473 Maujean and Seguin, 1983a, b (A. Maujean, Haye, Feuillat, Thomas, & Petit, 1978),
474 observed that two MeSH molecules could produce dimethyl disulfide. This mechanism
475 has been investigated in white wines that are responsible for an unpleasant aroma,
476 generally called 'lumière'. In this study, when comparing the values obtained from the
477 degradation of riboflavin (figure 1) and those obtained from the compound of Me_2S_2
478 (figure 5a), it can be observed that the wines with the highest degradation of riboflavin
479 were those with the highest concentration of Me_2S_2, in whites wines W1, W3, W6 and
480 in all rosé wines (W7-W9).

The second disulfide analyzed was diethyl disulfide (Et_2S_2). This compound gives wines aromas associated with bad smells or onion notes when concentrations are higher than 4.3 µg/L (OT) (Mestres, Busto, & Guasch, 2000; Siebert, Solomon, Pollnitz, & Jeffery, 2010; Ullrich, Neef, & Schmarr, 2018). As can be seen in figure 5.b, in general, the samples that presented higher concentrations were rosé wines and W2 white wine, with exposure to LA and followed by exposure to LB. However, it should be noted that exposure of the samples to LC light did not affect the increase in Et_2S_2. After 6 hours of exposure with LA, almost all wines (except W1, W4, and W5) exceeded the OT. In the case of exposure to LB, it was the same wines as those with LA that exceeded the OT of Et_2S_2, presenting similar concentrations. However, with exposure to LC none of the samples presented concentrations higher than OT. After 10 days of exposure to LA, all the wines presented values higher than OT (except W1). The same happened with the exposure to LB, where most of the wines exceeded the OT (except W1 and W3). However, it should be noted that in exposure to LC, none of the wines presented higher OT values (except W7).

Therefore, both exposures to LA light and LB light favored the appearance of disulfides in the samples, mainly after 10 exposure times. However, it should be noted that the LC light hardly affected the samples in the formation of both disulfides.

3.4. Sensory analysis

Finally, the chemical analysis of the volatile composition of the wines was completed by sensory analysis. The results of the sensory analysis seem to confirm the patterns observed in the chemical analysis of aromatic compounds (figure S2). In general, the

wines showed a greater appearance of reduction and 'lumiere' aromas after the longest exposure time, mainly with exposure to LA light and LB light, although less intense with the latter (LB). However, the wines exposed to LC light showed hardly any reduction or ‘lumiere’ notes. In addition, in the analysis, it was observed how throughout the exposure time the fresh fruit and the floral notes, are decreasing, presenting a greater intensity of the same all the controls in general.

4. Conclusions

Our findings highlighted that both the degradation of methionine and to a greater extent the degradation of riboflavin resulted in the formation of high levels of VSCs. As expected, the photodegradation of riboflavin was greatly affected by the light emitted in the region of 400-450 nm (LA), reaching losses of up to 80 % after 10 days of exposure. However, it should be noted that wines exposed to new LEDs, eliminated by this wavelength region (LC), showed conservation of riboflavin concentration throughout the exposure time. Consequently, the wines exposed to LA presented higher concentrations of thiols, sulfides, and disulfides, exceeding the sensory limits in most cases. Wines with LB behaved similarly but presenting less intense riboflavin degradation than with LA, and the formation of VSCs but in lower concentrations than with LA. However, LC was the light with which the wines were preserved over time without presenting high concentrations of VSCs. Demonstrating that simply by eliminating this wavelength range (400-450), new LEDs sources ca completely avoid the appearance of unpleasant aromas in wines related to VSCs. Further research

526 should be done to evaluate the effect of different factors such as glass color, bottle
527 thickness or type of wines.

528

529 **Figure captions**

530 Figure 1. Riboflavin degradation in % of all wines (W1-W9) throughout the time of
531 exposure (0-240 hours) to the different study lights (LA, LB and LC).

532 Figure 2. Degradation of methionine and cysteine in percentage of all wines (W1-W9)
533 throughout the exposure time (0-6-240 hours) at different LEDs lights (LA, LB and LC).

534 Figure 3. Aromatic family of thiols, hydrogen sulfide (a) and methanethiol (b)
535 concentrations (µg/L) obtained in all wines (W1-W9) throughout the exposure time (0-
536 6-240 hours) with each of the study lights (LA, LB and LC). Samples (n = 2).

537 Figure 4. Aromatic family of sulfides, dimethyl sulfide (a) and diethyl sulfide (b)
538 concentrations (µg/L) obtained in all wines (W1-W9) throughout the exposure time (0-
539 6-240 hours) with each of the study lights (LA, LB and LC). Samples (n = 2).

540 Figure 5. Aromatic family of disulfides, dimethyl disulfide (a) and diethyl disulfide (b)
541 concentrations (µg/L) obtained in all wines (W1-W9) throughout the exposure time (0-
542 6-240 hours) with each of the study lights (LA, LB and LC). Samples (n = 2).

543 Figure S1. a) Experimental design of the black wooden box where the wines were
544 exposed to the three study lights. b) Spotlights which were located in the upper part of
545 the black box. c) Wine bottles exposed to light, and protected with aluminum foil for
546 protection until analysis.

Figure S2. Aromatic profiles of W1-W9 wines obtained with exposure to the three types of lights (LA, LB and LC) throughout the exposure time (0 - 240 hours). Results obtained by the mean of the scores given by the tasters.

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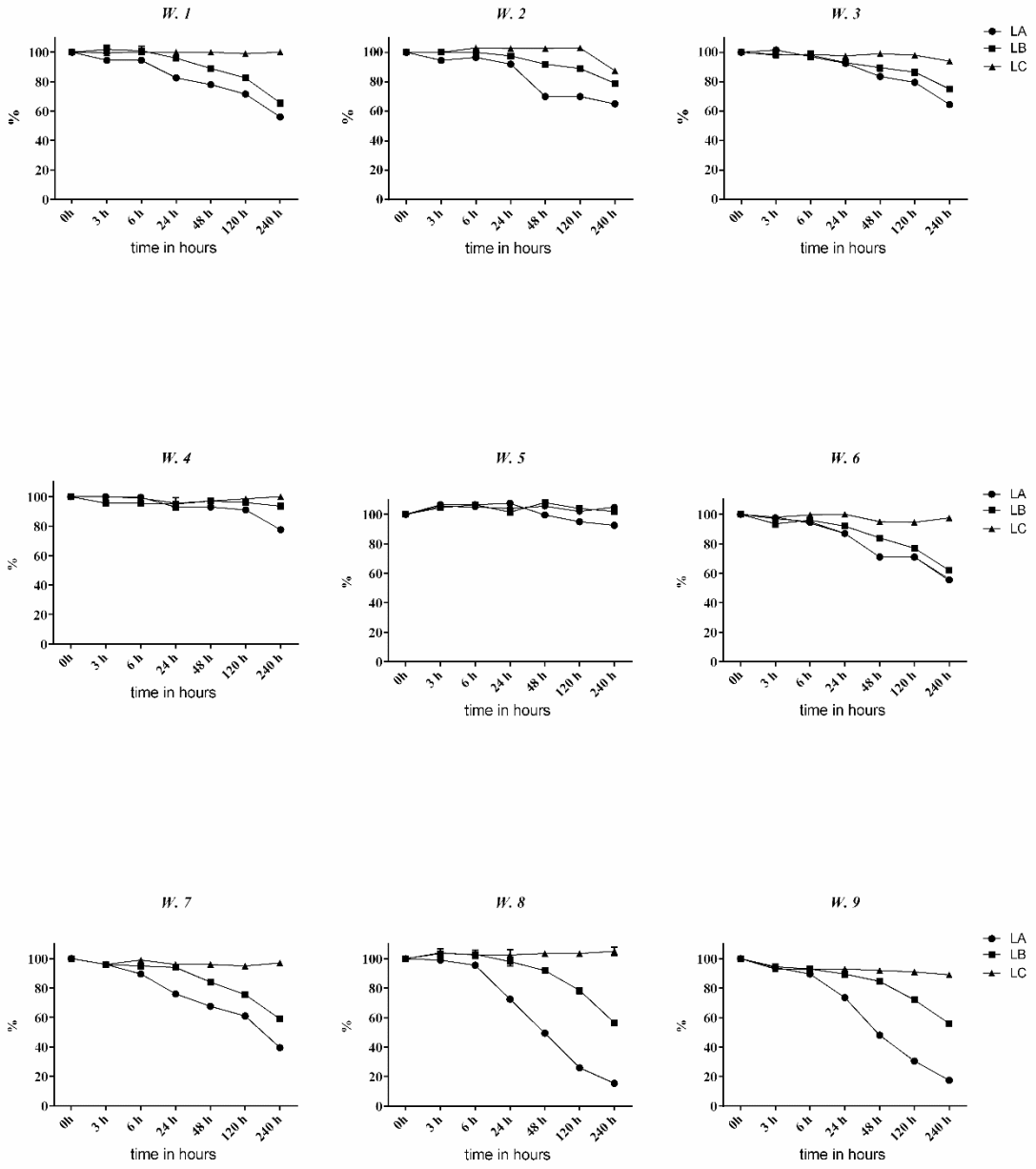
Table 1. Basic analysis of all wines (W1-W9), without exposure to light (time 0 hours) and after the last exposure time (240 hours) with each of the study lights (LA, LB and LC). The asterisk (*) indicates significant differences in the samples with exposure to each of the lights (240 hours) compared to the samples in darkness (0 hours). Free sulfur (SO_2 F, mg/L), total sulfur (SO_2 T, mg/L), total acidity (TA, g/L expressed as tartaric acidity), alcoholic strength (AG, %vol), and volatile acidity (VA, g/L). Luminosity *(L)*, *a* and *b* coordinates CIELAB. Samples (n = 2).

	SO2 F	**SO2 T**	**pH**	**TA**	**AG**	**VA**	**420nm**	***L***	***a***	***b***	***AE ab***
W1 0h	18 ± 0.0	95 ± 0.7	3.31 ± 0.0	6.3 ± 0.1	12.6 ± 0.0	0.4 ± 0.0	0.085 ± 0.0	99.1 ± 0.1	(-1.1) ± 0.0	6.6 ± 0.0	-
W2 0h	16 ± 0.7	96 ± 0.7	3.25 ± 0.0	6.3 ± 0.0	12.5 ± 0.0	0.4 ± 0.0	0.101 ± 0.0	98.2 ± 0.1	(-0.5) ± 0.1	6.7 ± 0.1	-
W3 0h	11 ± 0.0	82 ± 0.7	3.28 ± 0.0	6.1 ± 0.1	12.8 ± 0.0	0.5 ± 0.0	0.086 ± 0.0	98.7 ± 0.1	(-0.9) ± 0.0	5.7 ± 0.3	-
W4 0h	15 ± 0.7	89 ± 0.7	3.25 ± 0.0	6.5 ± 0.0	12.4 ± 0.0	0.4 ± 0.0	0.106 ± 0.0	98.2 ± 0.1	(-1.2) ± 0.0	7.5 ± 0.1	-
W5 0h	17 ± 0.0	91 ± 0.7	3.30 ± 0.0	5.9 ± 0.1	12.6 ± 0.0	0.4 ± 0.0	0.085 ± 0.0	98.7 ± 0.1	(-0.8) ± 0.0	6.1 ± 0.1	-
W6 0h	18 ± 0.0	79 ± 0.7	3.08 ± 0.0	6.1 ± 0.0	12.6 ± 0.0	0.4 ± 0.0	0.112 ± 0.0	97.0 ± 0.1	0.9 ± 0.0	6.9 ± 0.0	-
W7 0h	11 ± 0.7	60 ± 0.0	3.11 ± 0.0	5.5 ± 0.1	12.4 ± 0.0	0.3 ± 0.0	0.117 ± 0.0	96.7 ± 0.1	1.0 ± 0.0	7.9 ± 0.1	-
W8 0h	19 ± 1.4	81 ± 0.7	3.10 ± 0.0	5.9 ± 0.1	12.6 ± 0.0	0.3 ± 0.0	0.111 ± 0.0	96.9 ± 0.1	1.8 ± 0.0	7.5 ± 0.1	-
W9 0h	20 ± 1.4	87 ± 0.0	3.10 ± 0.0	6.0 ± 0.1	12.8 ± 0.0	0.3 ± 0.0	0.111 ± 0.0	97.0 ± 0.1	1.6 ± 0.0	7.4 ± 0.1	-
W1 LA 240h	18 ± 1.4	96 ± 4.2	3.31 ± 0.0	6.4 ± 0.0	12.6 ± 0.0	0.4 ± 0.0	0.082 ± 0.0	99.0 ± 0.2	(-1.1) ± 0.1	6.0 ± 0.3	0.6 ± 0.3
W2 LA 240h	20 ± 0.0	100 ± 0.7	3.25 ± 0.0	6.4 ± 0.1	12.5 ± 0.0	0.4 ± 0.0	0.090 ± 0.0	98.6 ± 0.1	(-1.1) ± 0.1 *	6.0 ± 0.1 *	1.0 ± 0.3
W3 LA 240h	12 ± 2.1	86 ± 2.1	3.29 ± 0.0	6.1 ± 0.0	12.8 ± 0.0	0.4 ± 0.0	0.079 ± 0.0 *	98.6 ± 0.2	(-1.0) ± 0.3	5.6 ± 0.1	0.2 ± 0.2
W4 LA 240h	14 ± 0.0 *	86 ± 1.4	3.25 ± 0.0	6.5 ± 0.1	12.4 ± 0.0	0.4 ± 0.0	0.103 ± 0.0	98.4 ± 0.1	(-1.1) ± 0.0	7.2 ± 0.0	0.4 ± 0.2
W5 LA 240h	18 ± 0.7	93 ± 0.7	3.29 ± 0.0	5.8 ± 0.0	12.6 ± 0.0	0.4 ± 0.0	0.084 ± 0.0	98.5 ± 0.1	(-1.0) ± 0.1	5.8 ± 0.0 *	0.4 ± 0.3
W6 LA 240h	18 ± 0.0	77 ± 1.4	3.08 ± 0.0	6.1 ± 0.0	12.6 ± 0.0	0.4 ± 0.0	0.103 ± 0.0	97.6 ± 0.2	0.9 ± 0.1	6.6 ± 0.4	0.7 ± 0.2
W7 LA 240h	11 ± 0.0	60 ± 0.7	3.09 ± 0.0	5.5 ± 0.0	12.4 ± 0.0	0.3 ± 0.0	0.106 ± 0.0	97.0 ± 0.0	0.9 ± 0.0	7.2 ± 0.0	0.8 ± 0.4
W8 LA 240h	21 ± 0.7	82 ± 1.4	3.10 ± 0.0	5.9 ± 0.0	12.6 ± 0.0	0.3 ± 0.0	0.106 ± 0.0	96.9 ± 0.1	2.0 ± 0.1	6.6 ± 0.1 *	0.9 ± 0.4
W9 LA 240h	20 ± 0.7	82 ± 1.4	3.09 ± 0.0	6.0 ± 0.0	12.8 ± 0.0	0.3 ± 0.0	0.103 ± 0.0 *	97.0 ± 0.1	1.9 ± 0.0	6.5 ± 0.2 *	0.9 ± 0.3
W1 LB 240h	18 ± 0.0	94 ± 0.7	3.30 ± 0.0	6.4 ± 0.1	12.6 ± 0.0	0.4 ± 0.0	0.083 ± 0.0	99.2 ± 0.0	(-1.0) ± 0.0	6.2 ± 0.0	0.2 ± 0.0
W2 LB 240h	17 ± 3.5	95 ± 7.1	3.28 ± 0.0	6.3 ± 0.1	12.6 ± 0.0	0.4 ± 0.0	0.092 ± 0.0	98.6 ± 0.1	(-0.9) ± 0.1	6.2 ± 0.1	0.3 ± 0.2
W3 LB 240h	12 ± 2.1	87 ± 2.1	3.29 ± 0.0	6.1 ± 0.0	12.7 ± 0.0	0.4 ± 0.0	0.082 ± 0.0	98.8 ± 0.0	(-0.9) ± 0.2	5.8 ± 0.1	0.3 ± 0.1
W4 LB 240h	14 ± 0.0 *	88 ± 1.4	3.25 ± 0.0	6.5 ± 0.0	12.4 ± 0.0	0.4 ± 0.0	0.106 ± 0.0	98.3 ± 0.1	(-0.9) ± 0.3	7.4 ± 0.1	0.2 ± 0.2

W5 LB 240h	15 ± 0.0 *	97 ± 1.4	3.30 ± 0.0	5.8 ± 0.0	12.3 ± 0.0	0.4 ± 0.0	0.088 ± 0.0	98.1 ± 0.1	(-1.2) ± 0.2	5.6 ± 0.0 *	0.4 ± 0.1
W6 LB 240h	19 ± 0.0	79 ± 0.7	3.08 ± 0.0	6.1 ± 0.0	12.6 ± 0.0	0.4 ± 0.0	0.097 ± 0.0	97.7 ± 0.1 *	0.7 ± 0.1	6.4 ± 0.1	0.4 ± 0.1
W7 LB 240h	11 ± 0.7	60 ± 2.1	3.10 ± 0.0	5.5 ± 0.0	12.4 ± 0.0	0.3 ± 0.0	0.117 ± 0.0	96.4 ± 0.4	1.0 ± 0.0	7.6 ± 0.2	0.7 ± 0.1
W8 LB 240h	21 ± 1.4	80 ± 0.7	3.09 ± 0.0	5.9 ± 0.0	12.6 ± 0.0	0.3 ± 0.0	0.113 ± 0.0	96.7 ± 0.1	1.8 ± 0.1	7.2 ± 0.1	0.7 ± 0.1
W9 LB 240h	14 ± 0.7 *	79 ± 0.0*	3.10 ± 0.0	6.0 ± 0.0	12.7 ± 0.2	0.3 ± 0.0	0.112 ± 0.0	96.7 ± 0.1	2.1 ± 0.2 *	7.2 ± 0.1	0.8 ± 0.2
W1 LC 240h	19 ± 0.0	98 ± 0.7	3.30 ± 0.0	6.4 ± 0.0	12.6 ± 0.0	0.4 ± 0.0	0.086 ± 0.0	99.0 ± 0.1	(-1.1) ± 0.1	6.4 ± 0.0	0.4 ± 0.1
W2 LC 240h	16 ± 0.7	98 ± 2.1	3.25 ± 0.0	6.3 ± 0.0	12.5 ± 0.0	0.4 ± 0.0	0.096 ± 0.0	98.4 ± 0.1	(-1.0) ± 0.2 *	6.4 ± 0.2	0.3 ± 0.2
W3 LC 240h	13 ± 1.4	85 ± 3.5	3.29 ± 0.0	6.1 ± 0.0	12.7 ± 0.0	0.4 ± 0.0	0.083 ± 0.0	98.7 ± 0.1	(-0.8) ± 0.0	5.8 ± 0.1	0.2 ± 0.2
W4 LC 240h	14 ± 0.0*	91 ± 1.4	3.24 ± 0.0	6.5 ± 0.0	12.4 ± 0.0	0.4 ± 0.0	0.103 ± 0.0	98.4 ± 0.1	(-1.0) ± 0.2	7.3 ± 0.1	0.2 ± 0.2
W5 LC 240h	16 ± 0.0	90 ± 2.8	3.30 ± 0.0	5.9 ± 0.1	12.6 ± 0.0	0.4 ± 0.0	0.086 ± 0.0	98.4 ± 0.1	(-1.0) ± 0.1	5.8 ± 0.0 *	0.4 ± 0.5
W6 LC 240h	18 ± 0.7	82 ± 0.7	3.08 ± 0.0	6.1 ± 0.1	12.6 ± 0.0	0.3 ± 0.0	0.102 ± 0.0	97.5 ± 0.1	0.6 ± 0.2	6.6 ± 0.1	0.3 ± 0.0
W7 LC 240h	12 ± 0.7	61 ± 2.1	3.09 ± 0.0	5.5 ± 0.0	12.4 ± 0.0	0.3 ± 0.0	0.115 ± 0.0	96.7 ± 0.1	0.9 ± 0.2	8.1 ± 0.3	0.6 ± 0.2
W8 LC 240h	18 ± 0.0	82 ± 0.0	3.10 ± 0.0	5.9 ± 0.0	12.6 ± 0.0	0.3 ± 0.0	0.113 ± 0.0	96.9 ± 0.1	1.6 ± 0.2	7.6 ± 0.1	0.4 ± 0.3
W9 LC 240h	20 ± 2.1	86 ± 2.1	3.09 ± 0.0	6.0 ± 0.0	12.8 ± 0.0	0.3 ± 0.0	0.113 ± 0.0	96.8 ± 0.1	1.7 ± 0.1	7.4 ± 0.1	0.5 ± 0.1

693 Figure 1.



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695 Figure 2.

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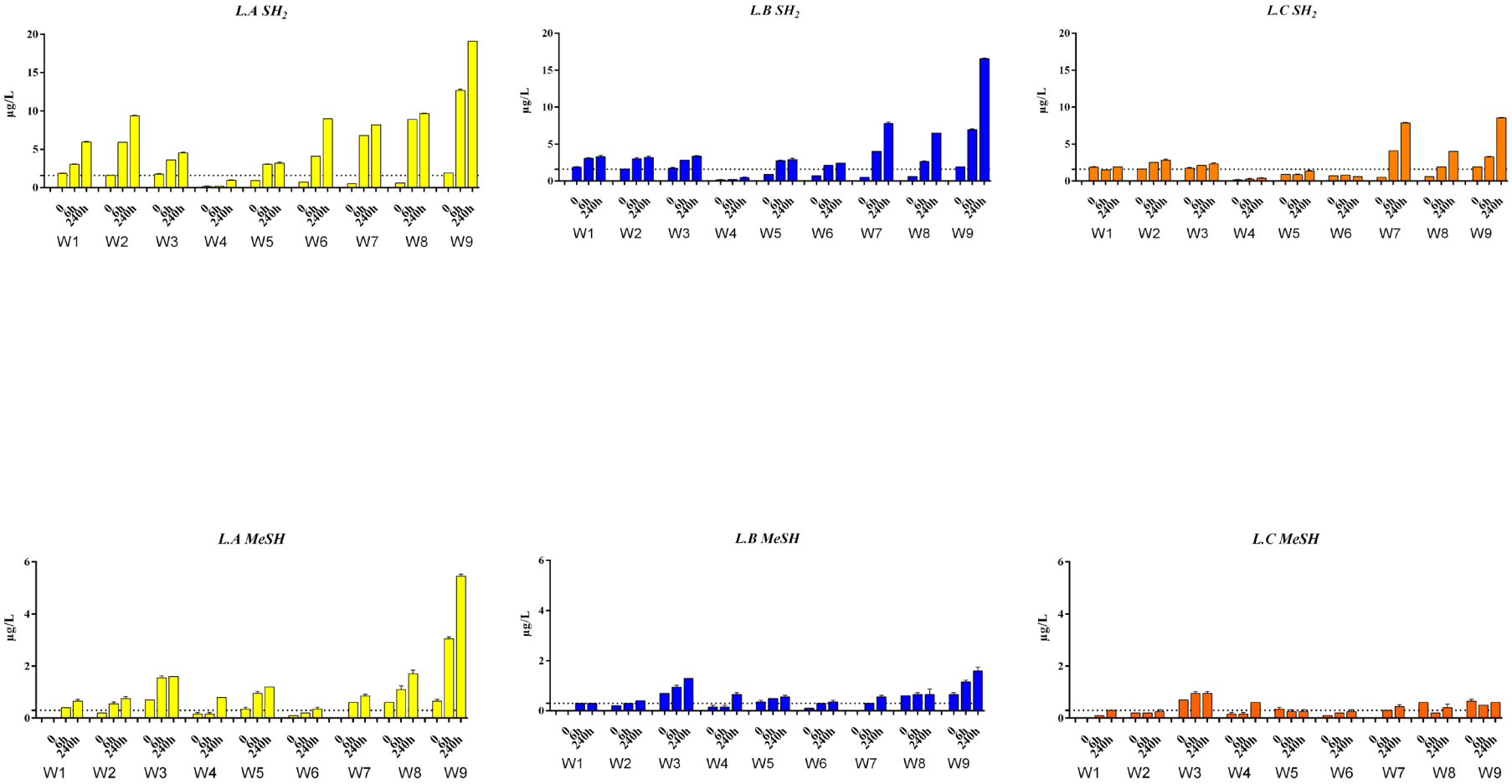
697 Figure 3.



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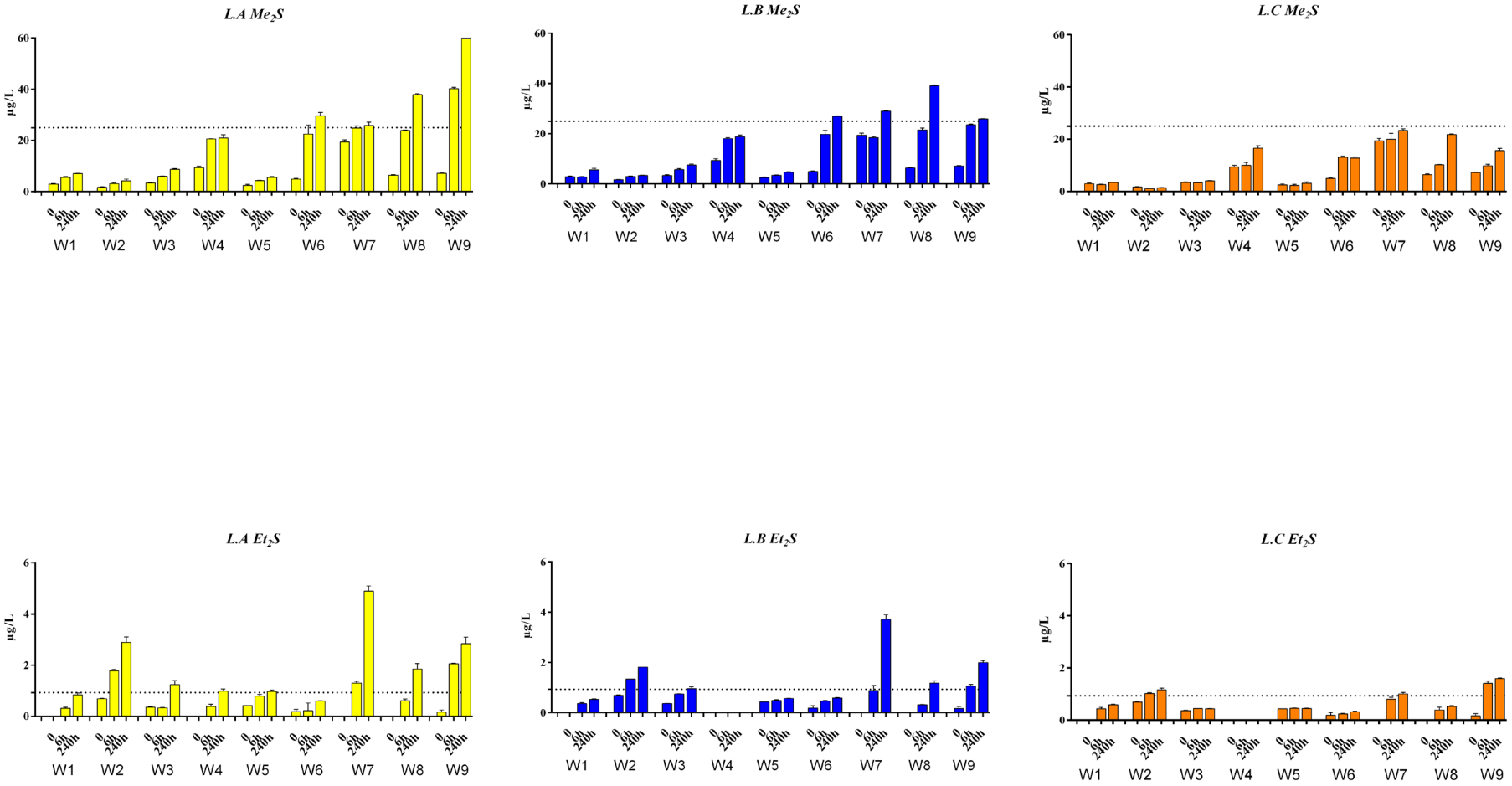
700 Figure 4.



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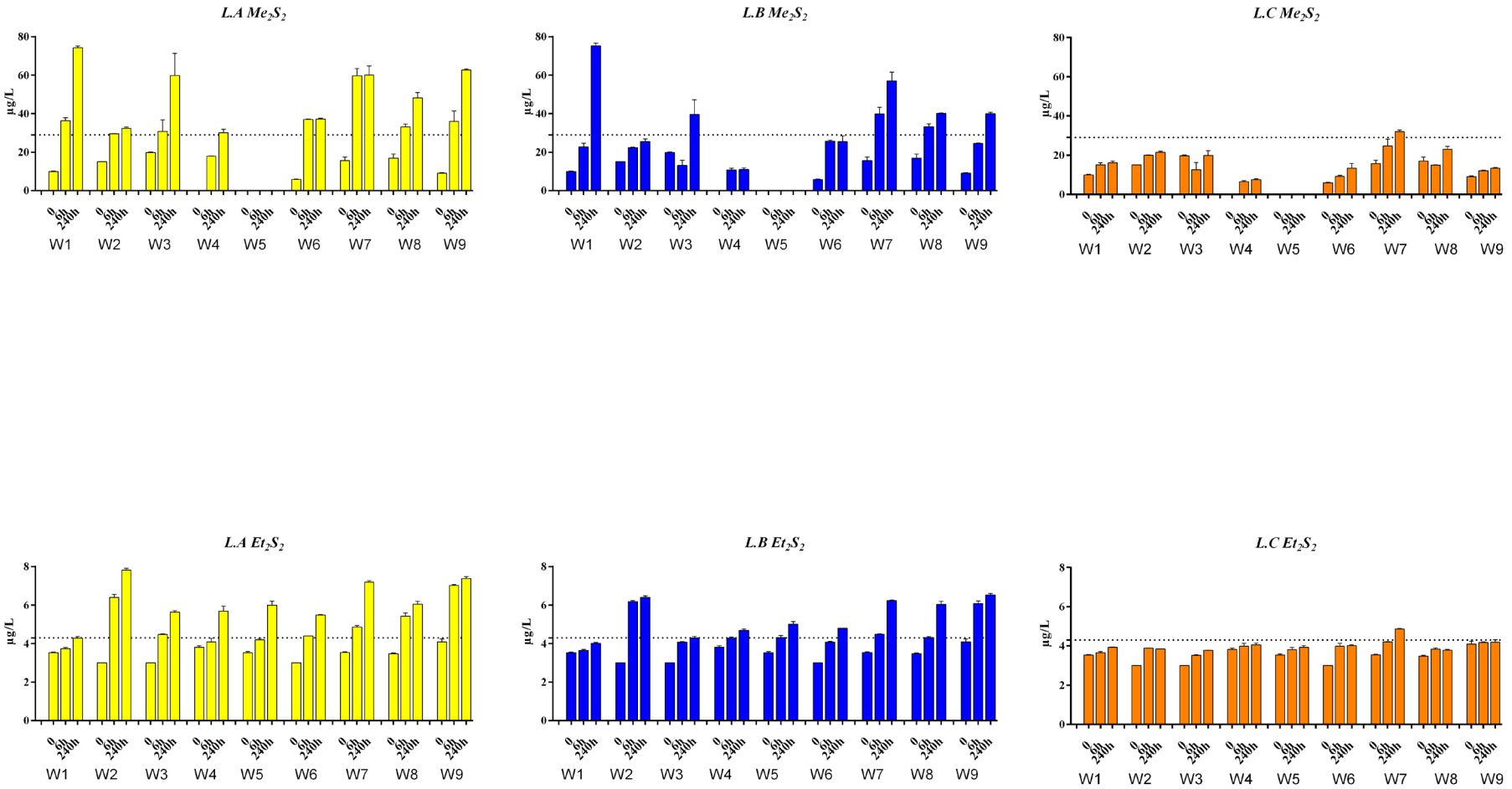
703 Figura 5.



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