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Monitoring of Sangiovese Red Wine Chemical and Sensory Parameters along One-Year Aging in Different Tank Materials and Glass Bottle

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ABSTRACT: The aim of this research was to study how different tank materials affected the chemical composition and the sensory profile of a red wine during aging. For this purpose, a single varietal Sangiovese wine was aged at the same time by using different tank materials including stainless steel, epoxy-coated concrete, uncoated concrete, earthenware raw amphorae, and new and used oak barrels. Phenolic and volatile compounds, elemental content, tartaric stability, and sensory discriminant attributes of Sangiovese wine from the 2018 harvest were measured after 6 and 12 months of aging in tanks and 6 months in glass bottle (after the aging of 6 months carried out in each relevant container). The results showed that the different tanks significantly differentiated the wines on the base of all the chemical and sensory parameters considered. In particular, wines aged in earthenware raw amphorae and uncoated concrete registered a high content of polymeric pigments as the wine aged in the new oak barrel, resulting in materials that better promote the wine color stabilization. The same wines also showed the highest pH and tartaric stability, mostly likely related to the observed release of inorganic compounds from the tank material. Moreover, bottle aging enhanced the chemical and sensory differences between all the wines: they were characterized by a higher content of varietal volatiles such as norisoprenoids and terpenes, probably due to the reductive conditions in the bottle. The bottle also affected the perceived quality of the wines aged in concrete (uncoated and epoxy-coated) associated to the floral flavor, floral odor, sweetness attributes, and, to a lesser extent, acidity, while the ones aged in stainless steel and amphorae is associated to the berry jam odor.

KEYWORDS: *amphorae, tank material, volatile profile, phenolic compounds, sensory profile, elemental analysis, Sangiovese wine*

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1. INTRODUCTION

Wine aging is a fundamental phase for obtaining a stable product. Many physical−chemical reactions take place during this phase that changes the wine chemical structure and sensory profile. During red wine aging, several factors, such as kind of tank, dissolved oxygen, and phenolic composition, are involved in the evolution and stabilization of wine. In particular, the choice of the aging tank affects the final wine characteristics since it modulates the oxygen permeation and the release of compounds such as tannins or elementals.[1−3] Nowadays, winemakers have a wide range of different kinds of tanks available for the wine aging phase. Traditionally, the oak barrel is considered one of the best tanks to improve wine sensory complexity and stability of color[4] but wine, beyond wood and stainless steel, can be aged also in other materials such as concrete or amphorae according to the need of market differentiation and distinction.[3,5] The aging tank choice, however, should be made with awareness of the specific influence of the tank material on the physical−chemical characteristics of wine, according to varietal characteristics and oenological goal, in order to achieve a defined sensory profile and wine style. It is known, for example, that every kind of tank material is characterized by a specific oxygen permeability[6] and this affects the formation/degradation of compounds with important consequences on wine aging. Recently, some authors[6,7] characterized the tank materials in order to test their permeability to oxygen by measuring the diffusion and permeability coefficients and the oxygen transmission rate (OTR). The materials involved in this study were different types of concretes (uncoated and epoxy-coated), earthenware, claystone, and woods classified by botanical species and staves grain. Results showed a clear permeation of all materials to oxygen with the exception of epoxy-coated concrete that does not afford any exchanges. In particular, the concrete samples reached mean values of OTR between 1.22×10^{-8} and 87.54 cm^3/m^2 day, the earthenware samples from 0.12 to 14.65 × 104 cm^3/m^2 day, and the wood samples between 8.27 and 12.24 mg/L day. The OTR values obtained were very different between each materials, and, thanks to this intrinsic characteristics, they could afford a specific amount of oxygen to wine.

The contact of wine during aging with the raw surface of the tanks can determine the release of compounds such as ellagitannins, in the case of oak barrel, or elementals, in the

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case of concrete and amphorae.[2,3] All these compounds might interact with the wine matrix with consequences on its final properties. Indeed, the dissolved oxygen in wine and the presence of ellagitannins and/or elementals induce a series of redox reactions involving the polyphenol compounds of wine that enhance the color stability.[7,8] For instance, Castellari *et al.*,[9] measuring the dissolved oxygen in 561 wines, which are sampled in different wine cellars and aged in concrete and stainless steel tanks, and in wood barrels, highlighted that micro-oxygenation in stainless steel was effective in increasing the dissolved oxygen up to levels comparable to those in small wooden barrels. However, they found that the storage temperature had to be taken into account to avoid oxygen accumulation.

Moreover, the elementals released into the wine from the container can act as reaction catalysts as well as influence the equilibrium between tartaric acid and hydrogen tartrate forms in dissolution leading to alteration of the pH, titratable acidity, and tartaric stability.[3]

Up to date, various studies have been carried out on the relation between winemaking and tank materials. Some authors,[10] evaluating the polyphenolic and volatile characteristics of Minutolo white wines during aging, highlighted that wine aged in amphorae was characterized by a higher dry extract and content of caftaric and ferulic acids as compared to the same wine aged in a stainless steel tank. Moreover, as compared to the wine aged in stainless steel, the one aged in amphorae had a more intense minerality and varietal flavor. According to other authors,[11] Chardonnay wine appeared to have less sensory characters typical of those grape when fermented in amphorae tank. On the other hand, a panel of experts appreciated more the tannin content of the amphorae wine as compared to the same oak-wine. Always regarding Chardonnay wine, the same authors[12] detected negligible differences from the sensory point of view in the wines induced by in-amphorae and in-wood vinification (solvent and acetone odor, astringency, and fruity and color intensity). Moreover, they highlighted a higher content of free phenolic acids and higher volatile alcohols in the amphorae wine. The effect of different types of amphorae (raw, glazed, engobe) as compared to stainless steel, on the physical−chemical properties and antioxidant capacity of the Falanghina wines, was studied by Baiano *et al.*[13] According to the authors, engobe amphorae and stainless steel tanks allowed better retention of phenolic compounds reactive with vanillin throughout the aging time. The wines aged in the other types of amphorae (raw and glazed) suffered a strong decrease in the concentration of phenols reactive with vanillin, but they better maintained their antioxidant capacity after 1 year.

Recently, some authors[3] studied the effect of different sizes and tank materials, including alternative ones such as ceramic and uncoated concrete, on a Sauvignon Blanc wine after fermentation and decanting on lees. Their results already showed significant differences between wines for the phenolic composition, elemental content, and volatiles after 6 months aging. In particular, the wines elaborated in concrete vessels showed the highest pH and the lowest titratable acidity, most likely related to the release of inorganic compounds from the concrete walls.

A period of bottle aging is normally foreseen before the wine is ready to be commercialized and consumed. During this period, a series of reactions, depending on the aging treatments of wine before bottling and involving the polyphenol and volatile compounds, occur in wine.[14,15] These reactions affect the sensory properties and the shelf life of wine, and, for this reason, in certain wine regions, a minimum period of bottle aging is prescribed by the regulation of specific appellations (*e.g.*, the regulation of DOCG Chianti Classico Riserva provides 3 months of bottle aging before commercialization).

To our knowledge, a simultaneous comparison during wine aging of different types of containers, using the same type of wine, has not previously been done. Here, the impact on the chemical and sensory characteristics of a Sangiovese wine through the use of different aging tank materials such as concrete, wooden, stainless steel, and amphorae has been evaluated. In particular, an experimental aging test, at the industrial scale, of a single varietal wine was set up in an underground cellar. The wine was aged for 12 months in different tanks. Moreover, the same wine was bottled in glass bottles at the beginning of the experiment and used as a reference. In order to study their evolution, a small volume of wines from each tank was bottled at 6 months of aging. The wines were analyzed for chemical and sensory parameters, after 6 and 12 months of aging in tanks, and 6 months in glass bottle, after the aging of 6 months carried out in each relevant container. The reference wine aged in the glass bottle was also analyzed at 6 and 12 months.

2. MATERIALS AND METHODS

2.1. Wine and Tank Materials. The red wine used for the experiment was a Sangiovese from the 2018 harvest. After completing the malolactic fermentation, it was centrifuged (0 NTU was set on the nephelometer installed on the centrifuge GEA Westfalia Separator Group GmbH, GSC 60-03-077) and sulfites were adjusted at 50 mg/L of total SO_2 before the racking in the aging tanks. Stainless steel (SS), epoxy-coated concrete (CC), uncoated concrete (CR), earthenware raw amphorae (AM), new oak barrel (TN), used oak barrel (TO), and glass bottle (GB) were the materials used for the experimental. All the tanks were 5 hL of volume, and every treatment was set up in triplicate. All tanks, except for TO and SS, were brand new and were filled for the first time with wine for this experiment. The AM, CR, and TN tanks were treated before filling according to the company protocols for first-time use. The TN and TO barrels were made in medium toasted French oak. The TO was 5 years old, and the wine was aged inside the barrel for 5 times.

The GB wine was used as references and bottled in 1 L glass bottles for the entire 1 year aging, using a crown cap closure. The main chemical parameters of the Sangiovese wine are reported in Table S1 as the Supporting Information.

All different tanks (including the glass bottles) were stored in an underground cellar at Valvirginio cooperative winery (Montespertoli, Firenze, Tuscany, Italy), in order to simulate the real wine-aging operating conditions. The cellar temperature ranged between 15 and 22 °C, and the relative humidity was approx. 80% over the year.

Wines were kept to age for 12 months in the different tanks, with no oxygen exposure except for the wine in SS. In fact, the SS wine was submitted to a pumping over with air exposure at 6 months aging, since it was in a very reductive state perceivable by the sensory analysis.

Physical, chemical, and sensory analyses were carried out at 6 and at 12 months aging on wines sampled from each different tank. At 6 months aging, 24 glass bottles (0.75 L Bordelaise, crown cap closures), equal to 3.6% of total tank volume (5 hL), were filled with wine from each different tank and aged till the end of the experiment. Each tank was than filled up with the same wine volume (about 18 liters corresponding to 24 bottles) sampled from a 50 hL stainless steel tank containing the same Sangiovese wine. Wine samples were coded with the name of the tank material and the sampling time (_6: 6 months aging; _12: 12 months aging; _6 + 6: 6 months tank aging plus 6 months glass bottle aging).

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2.2. Chemical Standard Parameters. The standard parameters (pH, titratable acidity, volatile acidity, alcohol content, and residual sugars) were measured through FT-IR analyses and carried out by means of a FOSS WineScan (FT 120 Reference Manual, Foss, Hamburg, Germany). SO_2 content was measured according to the official EU methods (Official Methods of Wine Analysis, Reg. 440/2003).

2.3. Elemental Analysis by ICP-OES. Seventeen elements were quantitated in each wine using 5 g of wine sample digested with 10 mL of HNO_3 (67% v/v), in Teflon reaction vessels, to perform the mineralization in a microwave oven (Mars 5, CEM Corp., Matthews, NC, USA), using the program 1600 W, 100% power, at 200 °C for 20 min. At the end of the mineralization, the final volume of 25 mL was reached by adding ultra-pure water. The concentrations of B, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, and Pb were determined using an inductively coupled argon plasma optical emission spectrometer (ICP−OES iCAP series 7000 Plus Thermo Scientific). A standard method for the 17 different elements was applied, using the Qtegra Intelligent Scientific Data Solution (ISDS), and the wavelengths selected were 209.0 nm for B, 589.6 for Na, 285.2 nm for Mg, 394.4 nm for Al, 766.5 nm for K, 315.9 nm for Ca, 205.6 for Cr, 257.6 nm for Mn, 259.9 for Fe, 228.6 for Co, 231.6 nm for Ni, 327.4 nm for Cu, 202.5 nm for Zn, 193.8 nm for As, 226.5 for Cd, and 220.4 nm for Pb quantification. The calibration was performed with several dilutions of the multi-element standard Astasol-Mix (ANALYTIKA, spol. s.r.o., Prague, Czech Republic) in 1% HNO_3 (v/v) at different concentrations (0.1, 1, and 10 mg/L). All analyses were carried out in triplicate.

2.4. Measure of Wine Tartaric Stability. The tartaric stability of the wines was evaluated by a conductivity test. The conductivity test (mini-contact test) was performed by measuring the drop in electric conductivity ($\Delta\sigma$, expressed as μS/cm) of 100 mL of wine at 0 °C that was stirred for 12 min after the addition of 20 g/L of finely micronized potassium bitartrate as a precipitating agent. The evaluation was performed with a Check Stab α-2016 Millennium instrument (Delta Acque, Firenze, Italy). Measurements were taken with a probe consisting of two electrodes of platinized platinum and calibrated with a 0.01 N KCl solution. The drop in conductivity indicated that the level of stability $\Delta\sigma$ <30 was considered very stable; 30 to 50 was stable; 50 to 70 was warning level; and >70 was not stable.[16]

2.5. Volatiles Profile by Headspace SPME GC−MS. Free volatile profile of wines was determined according to a method developed previously.[17] Thirty-five compounds were identified in wines (Table S2) and verified by analyzing reference compounds, except for ethyl 3-methylbutanoate, octan-2-one, eptan-1-ol, 4-methyl-1-propan-2-ylcyclohex-3-en-1-ol (4-terpineol), (2*R*,5*R*)-2,6,6-trimethyl-10-methylidene-1-oxaspiro[4.5]dec-8-ene (vitispirane I), (2*S*,5*R*)-2,6,6-trimethyl-10-methylidene-1-oxaspiro[4.5]dec-8-ene (vitispirane II), ethyl nonanoate, 2,2,6,8-tetramethyl-7,11-dioxatricyclo(6.2.1.0)-1,6-undec-4-ene (riesling acetal), 1,1,6-tri-methyl-1,2-dihydronaphthalene (TDN), *n*-pentadecanoic acid, 5-butyl-4-methyloxolan-2-one (whiskey lactone), 5-butyl-4-methyloxolan-2-one (*cis*-oak lactone), octanoic acid, 4-allyl-2-methoxyphenol (eugenol), and nonanoic acid. Volatile standards ethyl butanoate 99%, 3-methylbutyl acetate ≥95%, ethyl hexanoate 98%, hexyl acetate 99%, octan-2-ol 99%, ethyl octanoate ≥98%, and 2-phenylethyl acetate 99%, were purchased from Aldrich (Milwaukee, WI, USA). 2-Phenylethanol 99% was purchased from Sigma-Aldrich (St. Louis, MO, USA). Hexan-1-ol, 99.9%, 3,7-dimethylocta-1,6-dien-3-ol (β-linalol), and 3,7-dimethyloct-6-en-1-ol (β-citronellol) 95%, were purchased from Fluka (Sigma-Aldrich, St. Louis, MO, USA). Diethyl butanedioate (diethyl succinate) 99%, and phenylmethanol (benzyl alcohol) ≥99%, were purchased from SAFC Supply Solution (Sigma Aldrich, St. Louis, MO, USA). The analytical system for the determination of the volatile compounds comprised an AutoSystem XL gas chromatograph (Perkin Elmer, Shelton, CT, USA) paired with a Turbomass Gold mass selective detector (Perkin Elmer). The software used was Turbomass v.5.1.0. An HP-Innowax column (30 m × 0.25 mm o.d., 0.25 μm film thickness, Agilent Technology, Little Falls, DE, USA) was used for all analyses. The retention times of the authentic standards were matched to the compounds measured. The compounds were also verified using quantifier/qualifier ion ratios and published retention indices reported for a HP-Innowax column. Chemical volatiles standard mixtures were prepared in a model wine solution consisting of 5 g/L of tartaric acid 99% (Sigma-Aldrich, St. Louis, MO, USA) dissolved in purified water, pH adjusted to 3.5 with NaOH (Sigma-Aldrich) and 12% v/v absolute ethanol. Water was purified through an Elix 5 System (Millipore, Billerica, MA, USA) prior to use. Ethanol absolute anhydrous was purchased from Carlo Erba (Cornaredo, Milano, Italy). Standard concentrations were selected to bracket the concentrations of each individual compound in the wine samples. All standards were analyzed in triplicate. The peak area of each standard (calculated as total ion), relative to the peak area of the octan-2-ol internal standard, were plotted against the standard concentration to create a standard curve. The linear regression equations obtained were used to calculate the concentration (mg/L−μg/L) of each compound in the wine samples. Samples were prepared by transferring 8 mL aliquot of wine to a 20 mL amber glass headspace sample vial containing 3 g of NaCl (Fisher Scientific, Fair Lawn, NJ, USA) and then adding 5 μL of the octan-2-ol internal standard solution (82 mg/L in ethanol solution) for a final concentration of 5.1×10^{-2} mg/L. The mixture was carefully shaken to dissolve the NaCl and then left for 1 h in the dark at room temperature (22 ± 1 °C) to equilibrate before analysis. The SPME fiber used for extraction was polydimethylsiloxane (PDMS), 100 μm thickness, 23 gauge. The fiber was purchased from Supelco (Sigma Aldrich, St. Louis, MO, USA) and thermally conditioned before the first use in accordance with the manufacturer's recommendations. The prepared wine samples were warmed up to 40 °C for 10 min before exposing the SPME fiber to the sample headspace. Headspace extraction times of 30 min, at a temperature of 40 °C, were performed with continuous stirring (500 rpm). Thermal desorption of analytes from the SPME fiber occurred during splitless injection of the fiber (straight glass liner, 0.8 mm i.d.) at 240 °C for 1 min. Following the SPME desorption, the inlet was switched to purge on for the remainder of the GC−MS run, and the SPME fiber was conditioned for 10 min more before it was removed from the injector. Helium carrier gas was used with a total flow of 2.33 mL/ min (constant pressure). The oven parameters were as follows: initial temperature of 40 °C held for 4.0 min followed by an increase to 80 °C at a rate of 2.5 °C/min, a second increase to 110 °C at a rate of 5 °C/min, and a final increase to 220 °C at a rate of 10 °C/min. The oven was then held at 220 °C for 5 min before returning to the initial temperature (40 °C). The total cycle time, including oven cool down, was 50 min. The MS detector was operated in scan mode (mass range 50−200 *m*/*z*), and the transfer line to the MS system was maintained at 230 °C.

2.6. Ethanal and Higher Alcohols Analysis by GC−FID. Ethanal and higher alcohols were determined with a method previously developed[18] and using an AutoSystem XL gas chromatograph equipped with a flame ionization detector (FID) (Perkin Elmer). Volatile standards ethanal ≥99.5%, propan-1-ol ≥99.5%, ethyl acetate ≥99%, 2-methylpropan-1-ol 99%, 3-hydroxy-2-butanone≥95%, 3-methylbutan-2-ol ≥99%, 2-methylbutan-1-ol ≥99%, and 3-methylbutan-1-ol ≥99%, ethyl 2-hydroxypropanoate (ethyl lactate) ≥99% were purchased from Sigma-Aldrich. A packed column (2 m × 2 mm o.d. tubing) tubing packed with 80/100 mesh Carbopack C coated with 0.2% (*w/w*) Carbowax 1500, a product of Supelco was used for all analyses. Chromatography operating conditions were as follows: 2 min at 35 °C and then increased to 165 °C with a slope of 4 °C/min. The carrier gas flow (He) was set to 20 mL/min. The injector and detector were set at 250 °C. Wine samples were added 3-methyl-2-butanol as an internal standard (final concentration of 163.4 mg/L) and injected. The injection volume was of 1 μL, and data were processed using Total Chrome Navigator software (Perkin Elmer). The total cycle time, including oven cool down, was 50 min. All samples were analyzed in triplicate. The retention times of the authentic standards were matched to the compounds measured. Chemical volatile standard mixtures were prepared in a model wine solution consisting of 5 g/L of tartaric acid

(99%, Sigma-Aldrich) dissolved in Elix 5 System water, and pH was adjusted to 3.5 with NaOH (Sigma-Aldrich) and 12% v/v absolute ethanol. Water was purified through an Elix 5 System (Millipore, Billerica, MA, USA) prior to use. Ethanol absolute anhydrous was purchased from Carlo Erba (Cornaredo, Milano, Italy).

Standard concentrations were selected to bracket the concentrations of each individual compound in the wine samples. All standards were analyzed in triplicate.

2.7. Phenolic Profile by RP-HPLC DAD. Monomeric anthocyanins (delphinidin-3-*O*-glucoside, cyanidin-3-*O*-glucoside, peonidin-3-*O*-glucoside, petunidin-3-*O*-glucoside, malvidin-3-*O*-glucoside) and polymeric pigments (colored polymeric pigments resistant to sulfite bleaching) were quantitated by HPLC,[19] and the analysis was carried out on a Perkin Elmer Series 200 LC equipped with an autosampler and a diode-array detector (DAD series 200) (Perkin Elmer). Chromatograms were acquired at 520 nm, recorded, and processed using Total Chrome Navigator software (Perkin Elmer). A polystyrene divinylbenzene column (250 mm × 4.6 mm PLRP-S 100A 5 μm, Polymer Laboratories) was used with a guard cartridge (10 × 4.6 mm) packed with the same material and both purchased from Lab Service Analytica Srl (Bologna, Italy). Both columns were held at 28 °C. Wine samples, before the analysis, were previously centrifuged at 12,000 rpm for 10 min in a Mikro 12-24 centrifuge (Hettich, Tuttlingen, Germany) and filtered with 0.22 μm syringe filter (Minisart RC 4, Sartorius, Germany). A total of 1 mL of sample was collected in 2 mL HPLC vials with an addiction of 10 μL of formic acid. The volume injected was 20 μL with the binary pump flow set on 1 mL/min. The A eluent was a water solution of 1.5% (*w/w*) of *ortho*-phosphoric acid (85%), and B eluent was prepared with 20% of A eluent in acetonitrile. The eluent gradient were set as follows: for the first 55 min, from 92 to 73% of A eluent, maintaining the isocratic conditions of 73% from minute 55 to 59, reduction from 73 to 30% between 59 and 64 min, maintaining at 30% from minute 64 to 69 and increasing to 92% from 70 to 76 min. Acetonitrile of HPLC grade was from Panreac (Barcelona, Spain). Orthophosphoric acid and ethanol of analytical reagent grade were from Sigma-Aldrich (Steinheim, Germany). The identity of monomeric anthocyanins and polymeric pigments by HPLC-DAD was achieved by comparing the retention times and UV spectra with reference standards previously injected. In order to convert the peak area into mg/L, a calibration curve was performed with four solutions of malvidin-3-*O*-glucoside at four different concentrations (25, 50, 100, 200 mg/L), acquiring chromatograms at 520 nm. All solutions were prepared using an acidic hydroalcoholic medium (12% v/v ethanol, 5 g/L tartaric acid, pH 3.5). Malvidin-3-*O*-glucoside ≥99% was purchased from Sigma Aldrich.

2.8. Color Indices. Color intensity (CI) and hue (Hue) were measured according to the method of Glories[20] and the total phenols index (TPI) as described by Ribereau-Gayon.[21] CI was measured using a 1 mm path length quartz cell and expressed as the sum of absorbances at 420 (A420), 520 (A520), and 620 nm (A620) and referred to a 10 mm path lengh (× 10). Wine hue was measured using a 1 mm path length quartz cell and expressed as the ratio between absorbance at 420 (A420) and 520 nm (A520). TPI was measured as absorbance at 280 nm using a 10 mm path length quartz cell, and samples were diluted 1:100 with an Elix 5 System (Millipore, Billerica, MA, USA). The ultraviolet−visible (UV−vis) absorbance of the samples was measured on a Lambda 35 (Perkin Elmer) UV−visible spectrophotometer, and UV WinLab Software was used to record the spectra (version 2.85.04, Perkin Elmer). Elix 5 System water was used as a reference. Wine samples were centrifuged before analysis (10,000 rpm × 10 min). All of the analyses were performed in triplicate.

2.9. CIELab Coordinates. CIE (Commission Internationale de l'Eclairage) L^*, a^*, and b^* color coordinates were measured according to OIV (Resolution 1/2006). Visible spectra were recorded in trasmittance at 400−700 nm using a 1 mm path length quartz cell and the Lambda 35 UV−visible spectrophotometer (Perkin Elmer) equipped with the RSA-PE-20 Integrating Sphere accessory assembly (Labsphere, North Sutton, NH). Elix 5 System water was used as a reference. UV WinLab Software was used to record the spectra (version 2.85.04, Perkin Elmer) and CIELab color coordinates were calculated using Color software (version 3.00, 2001, Perkin Elmer). Color differences between wines were determined during aging using the ΔE value of the CIELab diagram, according to the following equation (eq 1):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

When $\Delta E > 3$, the differences between wines are perceivable by human sight.[22]

2.10. Gelatin Index. The gelatin index of wines was measured by using the methodology described by Glories.[20] Briefly, 4 mL of wine were placed in two centrifuge tubes. Tube A (sample) received an addition of 0.4 mL of aqueous BSA (Bovine serum albumin, Sigma Aldrich) solution (7% w/v). Tube B (control) was prepared similarly, but the added BSA solution was replaced with water. After 24 h at room temperature, the two tubes were centrifuged (10,000 rpm for 10 min), and the supernatants were diluted 1:100 with water and read at 280 nm in a 1 cm quartz cell, obtaining the absorbance values (A0 for tube B diluted solution, A for tube A diluted solution). Elix 5 System water was used as a reference. The gelatin index was calculated according to the following equation (eq 2):

$$\text{gelatin index} = ((A0 - \text{A})/A0) \times 100 \quad (2)$$

This index gives information concerning the reactivity of polyphenols: the higher the value, the higher the reactivity of the wine tannins toward proteins. The ultraviolet absorbance of the samples was measured on a Lambda 35 (Perkin Elmer) UV−visible spectrophotometer, and UV WinLab Software was used to record the spectra (version 2.85.04, Perkin Elmer). All of the analyses were performed in triplicate.

2.11. Descriptive Sensory Analysis. Sensory analyses were carried out following the quantitative descriptive analysis method (QDA)[23] by a panel of 13 trained judges (8 males and 5 females) after 6 months of aging and 9 trained judges (3 males and 6 females) after 12 months, recruited from students, staff, and friends of DAGRI Department in Firenze. Both panels were composed by the same judges but one subject that entered in the second evaluation, given that five judges of the first panel did not participate to the evaluation of the 12 months wine samples. The panel was already trained for the evaluation of the red wine and was submitted to a further training for the set of Sangiovese in two slightly different ways.

The panel that evaluated the wines after 6 months first tasted and described the taste and tactile descriptors of the samples while in three subsequent sessions described and discussed the volatile profile. In every session, the panel was provided with a set of referenced standards, prepared as illustrated in Table S3. At the end of the training sequel, two sessions of trial evaluation were performed in order to check the consensus and select the significative attributes.

Given that the second evaluation after 12 months had to be performed using the same attributes, the second panel was presented with the ballot used in the first evaluation and the relative standard attributes. In order to verify the consensus and calibrate the use of the descriptors, a subset of the wines was submitted to the evaluation in two sessions of two replicates until the panel reached the consensus.

The samples, after the malolactic fermentation were evaluated globally (*i.e.,* orthonasal aroma after swirling, plus retronasal aroma, taste, and mouthfeel after sipping), and then expectorated. After each one, the judges had to wait 30 s and to rinse the mouth with water. The standard of references for every attribute were provided before every session, and judges had to test and recognize them before the evaluation. The reference standards submitted to the judges (Table S3) corresponded to 6 on the intensity scale (medium intensity).

The presentation was monadic with a balanced presentation order for the carry-over effect, according to a complete block design,[24] in three replicates. The evaluation of the 6 months aged wines was performed in the Sensory laboratory of DAGRI Department in Firenze. The samples (30 mL) were poured at room temperature (around 19 °C) and presented under red light to mask little color differences, in standard tasting glasses (ISO-3591, 1977) covered with

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Table 1. List of Polyphenol Compounds, Color Indices, and Gelatin Index Measured in Sangiovese Red Wine during Aging (_6, _12, and _6 + 6 Months) in Different Tanks (LSD, Least Significant Difference Test; 95% Significance Level; Different Letters in the Same Column Indicate Statistical Significances)

code[a,b]	total phenols index (TPI)	color intensity (CI)	hue	gelatin index	monomeric anthocyanins[c]	polymeric pigments[c]
TO_6	56.60 b	8.56 a	0.76 a	35.03 a	44.72 a	65.90 c
TN_6	58.56 c	9.30 d	0.81 b	43.12 d	65.01 d	72.08 d
CR_6	55.42 a	8.90 b	0.83 c	40.00 c	55.77 c	55.97 b
CC_6	55.54 a	8.90 b	0.81 b	44.11 e	43.73 a	46.04 a
SS_6	55.64 a	8.91 b	0.81 b	44.16 e	45.09 a	61.76 b
AM_6	55.55 a	9.11 c	0.86 d	44.29 f	47.11 b	62.48 b
GB_6	55.99 ab	9.10 c	0.81 b	39.62 b	56.94 c	43.32 a
p value	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
TO_12	53.33 d	8.65 a	0.81 a	47.39 a	29.21 e	84.55 f
TN_12	51.85 c	9.05 d	0.84 b	49.95 d	20.01 b	74.34 d
CR_12	51.29 b	8.74 b	0.88 d	49.23 c	30.33 f	81.89 e
CC_12	51.64 ab	8.89 c	0.86 c	48.00 b	16.76 a	63.89 b
SS_12	51.38 b	8.65a	0.86 c	47.25 a	25.70 c	79.74 e
AM_12	51.50 ab	8.90 d	0.90 d	49.68 d	25.96 d	73.56 c
GB_12	50.72 a	8.75 b	0.84 a	50.39 c	30.92 g	58.92 a
p value	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
TO_6 + 6	52.15 a	8.57 c	0.81 a	50.25 c	20.66 b	66.47 ab
TN_6 + 6	51.34 a	8.61 cd	0.86 bc	51.78 f	17.43 a	74.17 c
CR_6 + 6	51.16 a	8.45 b	0.88 d	50.51 d	25.60 c	89.66 d
CC_6 + 6	51.32 a	8.43 b	0.87c	50.02 b	23.38 bc	65.14 ab
SS_6 + 6	51.54 a	8.36 a	0.85 b	49.15 a	23.90 bc	70.67 b
AM_6 + 6	48.43 a	8.43 ab	0.89 e	50.71 c	29.20 d	67.62 ab
GB_6 + 6	52.90 a	8.68 d	0.85 b	50.48 d	30.92 e	58.92 a
p value	0.7975 ns	<0.05	<0.05	<0.05	<0.05	<0.05

[a]TO: used oak barrel; TN: new oak barrel; CR: uncoated concrete; CC: epoxy coated concrete; SS: stainless steel; AM: raw earthenware amphorae; GB: glass bottle with wine bottled at the beginning of the experiment and used as a reference. [b]_6: 6 months aging in tank; _12: 12 months aging in tank; _6 + 6: 6 months aging in tank plus 6 months of bottle aging. [c]Expressed as mg/L of malvidin-3-*O*-glucoside.

plastic lids and identified by random three-digit codes. Given that the wines aged in the wood tanks had revealed already after 6 months a significative difference from all the others, for the evaluation at 12 months, it was considered that they could have acted as outliers, hiding any possible differences between the other kind of wines. For this reason, two sensory profiles were set up as follow: one for the SS, AM, CR, and CC and the other for the TO and TN wines. Both the evaluations were performed against the GB wine as reference. Given the limitation due to the COVID-19 pandemic, the QDA of the 12 months aged samples had to be set in a way that took into account the restrictions imposed by security protocols. Three calibration sessions and six evaluation sessions were for this reason carried out remotely. The judges were provided a suitable box with a set of eight samples (five samples, SS, AM, CR, CC, and GB, plus 3 samples, TO, TN, and GB) and nine standard references in amber glass bottles of 100 mL, with a plastic screwcap and coded with the three-digit numbers. This design was repeated three times for the _6 + 6 wines and three times for _12 months aging. The session was organized in such a way as to make the judges doing two distinct evaluations, with different master cards: first, the five no-wood tanks (SS, AM, CR, CC, and GB), and then the wood tanks (TO, TN, and GB). Judges were not aware of it. The cards with the list of the attributes were deployed to the judges by the Google Suite platform. They were trained to follow the instructions: "Please, before to start the testing session, taste the reference standards and then evaluate each sample as usual, respecting the interval of 30 seconds between them and rinsing the mouth with water".

The panelists answered on a 10-point category scale (one scale per sample), anchored with 1 (absent) on the left end and 10 on the right end (very strong).

2.12. Data Analysis. The chemical and sensory data of the wines were analyzed by multifactor analyses of variance (MANOVA) applying an LSD, least significant difference test, with 95% significance level, and frequency distribution, analyzed by the Chi-square test, was performed using Statgraphics Centurion (Ver.XV, StatPoint Technologies, Warrenton, VA). Tank material and replicates were considered as factors for both the chemical and the sensory analysis. Principal component analysis (PCA) was carried out using the software XLSTAT 2020.5.1.

3. RESULTS AND DISCUSSION

3.1. Chemical Characterization and Differentiation of Sangiovese Wines Aged in Different Tank Materials.

3.1.1. Phenolic Profile and Color Indices. Phenolic composition and color indices were determined in order to discriminate wines aged in different tank materials at different time of aging such as 6 months (_6), 12 months (_12), and 6 months in tank plus 6 months in glass bottle (_6 + 6) (Table 1).

All the variables were significantly different according to ANOVA except for TPI of _6 + 6 wines.

After 6 months aging, the _6 wines had a different composition according to all the determined parameters (Table 1). As expected, the highest values of TPI were evidenced in wines aged in oak barrels (TO_6 and TN_6) and significantly different from all the other wines, with TN_6 (the brand new barrel) higher than TO_6 (used barrel). In fact, it is known that oak staves release ellagitannins in wines during aging and the amount depends on the age of oak barrel, on the time of contact between wine and wood (time of aging), and on the botanical origin and staves toasting level. In particular, the ellagitannins release, and the relative increase in TPI in wines, is higher when barrels are brand new, from French oak and with a low-medium toasting level in comparison with the used oak barrel and American oak and high toasting level.[25]

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Table 2. CIELab Coordinates and ΔE Measured in Sangiovese Red Wine during Aging (_6, _12, and _6 + 6 Months) in Different Tanks (Complete Comparison between Tanks) (LSD, Least Significant Difference Test; 95% Significance Level; Different Letters in the Same Column Indicate Statistical Significances)

				ΔE						
code[a,b]	L*	a*	b*	TO_6	TN_6	CR_6	CC_6	SS_6	AM_6	GB_6
TO_6	75.90 d	24.91 d	3.52 abc		2.57	4.78	4.60	4.87	5.50	4.93
TN_6	73.52 c	24.80 d	2.55 a			3.05	2.60	3.04	4.17	2.61
CR_6	71.82 b	22.42 b	3.41 abc				1.12	1.02	1.40	1.43
CC_6	71.53 a	23.49 c	3.58 bc					0.51	1.98	0.97
SS_6	71.37 a	23.16 c	3.94 cd						1.52	1.34
AM_6	71.49 a	21.81 a	4.63 d							2.61
GB_6	71.26 a	23.49 c	2.65 ab							
p value	<0.05	<0.05	<0.05							

				ΔE						
code[a,b]	L*	a*	b*	TO_12	TN_12	CR_12	CC_12	SS_12	AM_12	GB_12
TO_12	77.63 b	24.86 d	5.30 a		2.83	3.22	3.30	3.23	4.50	3.56
TN_12	75.47 a	23.15 c	5.95 b			3.30	1.09	1.26	2.36	1.12
CR_12	77.14 b	21.97 b	6.63 d				1.28	1.07	1.63	1.56
CC_12	75.91 a	22.28 b	6.44 cd					0.35	1.38	0.34
SS_12	76.16 a	22.14 b	6.24 c						1.30	0.65
AM_12	75.90 a	20.91 a	6.57 d							1.34
GB_12	75.60 a	22.22 b	6.56 d							
p value	<0.05	<0.05	<0.05							

				ΔE						
code[a,b]	L*	a*	b*	TO_6 + 6	TN_6 + 6	CR_6 + 6	CC_6 + 6	SS_6 + 6	AM_6 + 6	GB_6 + 6
TO_6 + 6	75.73 a	23.29 c	6.31 b		1.87	2.80	2.07	2.90	3.13	1.44
TN_6 + 6	75.69 a	21.82 b	7.47 d			1.29	1.01	2.58	1.92	0.91
CR_6 + 6	76.40 b	20.76 ab	7.30 d				0.79	1.94	0.74	1.46
CC_6 + 6	76.35 b	21.39 ab	6.83 c					1.63	1.10	0.78
SS_6 + 6	76.81 c	20.76 ab	5.40 a						1.43	1.91
AM_6 + 6	76.72 c	20.36 a	6.77 c							1.78
GB_6 + 6	75.79 a	21.87	6.57 bc							
p value	<0.05	<0.05	<0.05							

[a]TO: used oak barrel; TN: new oak barrel; CR: uncoated concrete; CC: epoxy coated concrete; SS: stainless steel; AM: raw earthenware amphorae; GB: glass bottle with wine bottled at the beginning of experimental and used as a reference. [b]_6: 6 months aging in tank; _12: 12 months aging in tank; _6 + 6: 6 months aging in tank plus 6 months of bottle aging.

Concerning the wine color evolution and stabilization, as evidenced by the monomeric anthocyanins and polymeric pigments content, it is possible to state that TO and TN were the most evolved wines in terms of polymeric pigments formation. In particular, TN showed the highest content of monomeric anthocyanins that could be probably due to the high antioxidant capacity of ellagitannins released by the new oak that had a protective effect.[26,27] The TN_6, as well as AM_6, showed a higher value of CI while AM_6 had also the highest hue. The wines aged in the uncoated (CR_6) and coated (CC_6) concrete tanks appeared to be significantly different from each other. In fact, polymeric pigments and monomeric anthocyanins content were higher in the CR_6 wine compared to the CC_6 one. This last one had the lower amount of monomeric anthocyanins, like the wine aged in stainless steel (SS_6) and the lower amount of polymeric pigments, like the wine aged in the glass bottle (GB_6). Concerning the reactivity of the different wines with proteins (gelatin index) it was possible to highlight that the TO_6 wine had the lowest value, while AM_6, SS_6, and CC_6 wines the highest.

The estimation of wine color by the CIELab coordinates and the relative ΔE (Table 2) evidenced that the difference between TO_6 and all the other wines (except for TN_6) was perceivable by human sight ($\Delta E > 3$).[22] The TN_6 wine was instead different from CR_6, SS_6, and AM_6 wines but not from the CC_6 wine. The perceivable differences were probably related to the L* and a* coordinates that were highest in TO_6 and TN_6 wines. The AM_6 wine appeared to be different from both TO_6 and TN_6 and showed the highest value for b* coordinates, confirmed by the highest hue value.

After 12 months of wine aging in tanks and in the glass bottle, it was possible to observe an evolution of the wine polyphenol's profiles according to the different kinds of tank materials. In fact, in all the analyzed wines, the decrease in monomeric anthocyanins corresponded to the formation of polymeric pigments, thanks to the free anthocyanins condensation into polymeric pigments and phenols *via* the acetaldehyde-mediated reactions and non-oxidatively with tannins.[28,29] The increase in polymeric pigments across different periods suggested the polymerization reactions occurring in all the wines over time.[28,29] Moreover, while the TO_12 wine had the highest content of polymeric pigments, the TO_6 + 6 wine maintained a similar content of TO_6 wine. This evidence could be explained by the fact that in the TO tank, the release of ellagitannins and oxygen permeation through the oak staves were slower than in the case of a brand

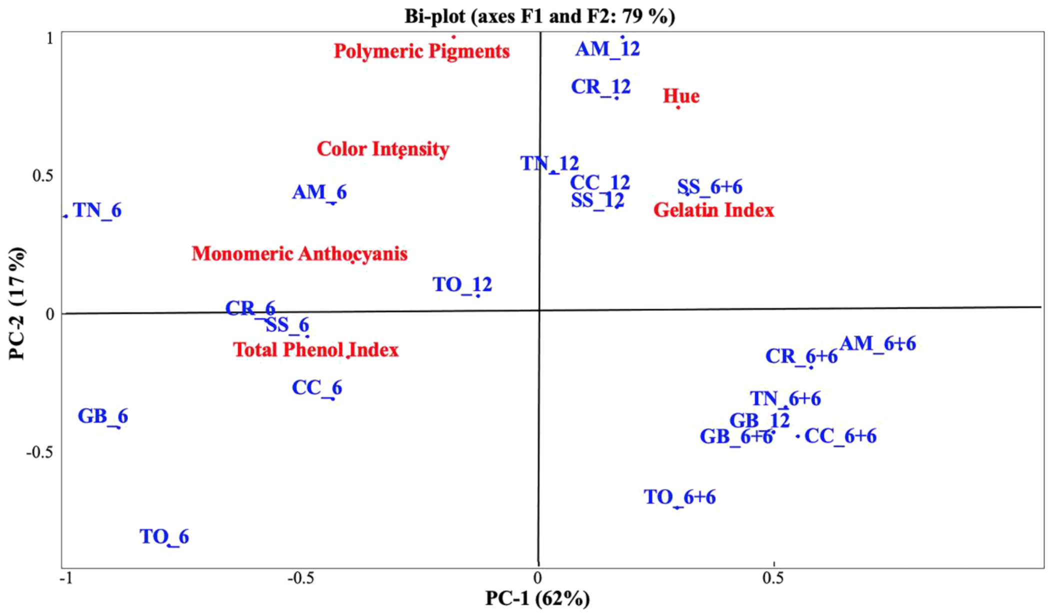

Figure 1. Principal component analysis (PCA): scores and loadings plot of the polyphenol compounds, color indices, and gelatin index measured in the Sangiovese red wine during aging (_6: 6 months aging in tank; _12: 12 months aging in tank; _6 + 6: 6 months aging in tank plus 6 months of bottle aging; TO: used oak barrel; TN: new oak barrel; CR: uncoated concrete; CC: epoxy coated concrete; SS: stainless steel; AM: raw earthenware amphorae; GB: glass bottle with wine bottled at the beginning of the experiment and used as a reference).

new barrel, suggesting that, to reach a similar level of wine color stability, it could need a longer time of contact between wine and tank. The TN wine maintained a high level of polymeric pigments also after 12 months, both in TN_12 and TN_6 + 6 wines. It could be assumed that during the first 6 months of aging, this wine reached the maximum content of stable polymers, with no further evolution in the subsequent period, whether it was in wood and in bottle.

While 6 months aging seemed to be sufficient to reach the highest level of polymeric pigments formation in the wine aged in the new oak barrel, more time seemed to be necessary to reach the same results in the wine aged for 12 months in amphorae (AM_12). In fact, while this last one showed an high formation of polymeric pigments, the 6 months in glass bottle after 6 months in amphorae (AM_6 + 6) did not show any increase of this kind of compounds.

The CR wine showed a different color evolution compared to all the other samples. In fact, both the CR_12 and CR_6 + 6 wines had a high formation of polymeric pigments compared to the CR_6 wine and similar to the same wine aged in the oak barrel. This might be due to the contact of wine with the raw concrete for 6 months, allowing the release of elemental and permeation of oxygen that could be responsible of the polymerization reactions both in bottle and tank aging. The CC wine (CC_12 and CC_6 + 6), similarly to the GB wine reference, probably due to the presence of coating that prevents the release of elementals and the contact with oxygen, appeared to be less reactive toward polymerization reactions.

With regards to the wine aged in the stainless steel tank (SS_12), the high level of polymerization of tannins detected after 12 months cannot fail to be related to the exposure to air carried out after 6 months by the racking. In fact, the same wine bottled after 6 months before racking and without exposure had a low content of polymeric pigments. Concerning the perceivable color of wines, the CIELab coordinates and the ΔE in Table 2 showed that after 12 months aging, the TO_12 wine was still different from all the others and that the TN_12 wine was different from CR_12. The AM wine showed, as previously seen, the lowest a^* and the highest b^* coordinates after 12 months (AM_12) and after 6 months in bottles (AM_6 + 6) and was the only one that maintained its difference from all the other wines, all along the observation period. With regard to the other kinds of wines, the ΔE of the _6 + 6 wines evidenced that there were not any more perceivable differences between them.

Figure 1 reports the bi-plot relative to all the samples and chemical parameters related to the wine color. The total explained variance was 75.03% (PC1 60.81%, PC2 14.22%), and the wines were separated in three groups, according to the time and modality of aging (tanks and bottles), along the first dimension (PC1). In fact, all the _6 months aging wines were on the left side of the plot and characterized by monomeric anthocyanins, TPI and CI, while all _6 + 6 wines were grouped on the right side and related to the polymeric pigments, hue, and gelatin index. The _12 wines were positioned between the two aforementioned groups indicating an intermediate color composition and level of evolution.

The distribution of the wines in the bi-plot showed that the _6 samples were more spread compared to the _12 and _6 + 6, meaning that the detected differences within each group, decreased during aging both in tanks and bottles. Anyway, the TO and AM wines maintained always an opposite position according to the color composition given that the AM showed the highest hue value and the TO showed the lowest value for the entire period of the study. Lastly, the _12 wines were the most correlated to the polymeric pigments evidencing that a longer tank aging enhanced the reactions related to the color stabilization.[4]

3.1.2. Elemental Content and Tartaric Stability of Wines. All wines analyzed were below the maximum acceptable limits for the elements for which the OIV has been set to this limit (B, 80 mg/L; Cu, 1 mg/L; Zn, 5 mg/L; As, 0.2 mg/L; Cd, 0.01 mg/L; and Pb, 0.15 mg/L).

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Table 3. Elemental Content Measured in Sangiovese Red Wine during Aging (_6 and _12 Months) in Different Tanks (LSD, Least Significant Difference Test; 95% Significance Level; Different Letters in the Same Column Indicate Statistical Significances; ND, Not Detected)

code[a,b]	^{11}B	^{23}Na	^{24}Mg	^{27}Al	^{39}K	^{40}Ca	^{52}Cr	^{55}Mn	^{56}Fe	^{59}Co	^{60}Ni	^{63}Cu	^{66}Zn	^{75}As	^{112}Cd	^{207}Pb
TO_6	5.000 e	7.485 c	86.374 b	0.707 d	831.756 b	65.793 b	nd	1.257 c	3.276 ab	nd	0.028 b	0.052 b	1.006 ab	nd	nd	0.009 a
TN_6	4.764 b	6.942 a	88.762 d	0.581 a	845.181 c	76.402 e	nd	1.322 d	2.738 a	nd	0.031 e	0.083 b	0.882 a	nd	nd	0.018 a
CR_6	4.883 d	18.01 f	83.496 a	0.613 ab	899.698 e	50.541a	nd	1.223 b	3.397 b	nd	0.030 de	0.062 ab	0.997 ab	nd	nd	0.025 a
CC_6	4.520 a	7.214 b	87.862 c	0.663 cd	844.467 c	72.625 d	nd	1.251 c	3.000 a	nd	0.028 bc	0.022 a	1.039 ab	nd	nd	0.001 a
SS_6	5.000 e	6.953 a	87.254 c	0.476 a	833.257 b	72.010 d	nd	1.238 bc	3.156 a	nd	0.029 cd	0.023 a	1.023 ab	nd	nd	0.004 a
AM_6	5.000 e	8.993 e	89.716 e	3.021 e	890.775 d	89.100 f	nd	1.562 e	4.704 c	nd	0.032 e	0.021 a	1.123 b	nd	nd	0.001 a
GB_6	4.827 c	8.356 d	85.388 b	0.652 abc	801.562 a	69.293 c	nd	1.148 a	3.074 ab	nd	0.022 a	0.019 a	0.095 ab	nd	nd	0.001 a
p value	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05		<0.05	<0.05		<0.05	<0.05	0.5673 ns			ns
TO_12	4.790 d	7.697 b	100.901 e	0.458 ab	825.129 c	56.594 d	0.048 a	1.125 a	2.652 a	0.004 b	0.015 a	0.049 d	0.849 a	0.042 ab	0.004 a	0.012 a
TN_12	4.263 b	7.159 ab	100.008 c	0.467 ab	807.458 a	58.142 e	0.019 a	1.198 b	2.527 a	0.004 ab	0.022 bcd	0.034 c	0.859 a	0.040 a	0.002 a	0.011 a
CR_12	4.012 a	19.824 d	99.205 a	3.921 c	898.408 f	43.169 a	0.039 a	1.130 a	5.817 b	0.004 b	0.023 cd	0.049 d	1.0037 c	0.046 ab	0.007 a	0.007 a
CC_12	4.010 a	7.365 ab	99.987 c	0.912 ab	816.447 b	51.621 b	0.056 a	1.133 a	2.468 a	0.003 a	0.018 ab	0.027 b	1.022 bc	0.044 ab	0.003 a	0.005 a
SS_12	4.010 a	6.706 a	99.359 b	0.322 a	846.752 d	54.811 c	0.024 a	1.09 a	2.487 a	0.003 a	0.025 d	0.034 c	0.871 a	0.066 cd	0.005 a	0.005 a
AM_12	4.303 b	9.271 c	103.679 f	1.871 b	849.572 e	61.657 f	0.019 a	1.487 c	2.980 a	0.004 b	0.015 a	0.021 a	0.977 b	0.057 bc	0.003 a	0.004 a
GB_12	4.459 c	9.153 c	100.640 e	0.580 ab	816.143 b	52.009 b	0.013 a	1.115 a	2.297 a	0.004 ab	0.017 abc	0.021 ab	0.861 a	0.083 d	0.007 a	0.008 a
p value	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.54 ns	<0.05	<0.05	ns	<0.05	<0.05	<0.05	<0.05	0.68 ns	0.39 ns

[a]TO: used oak barrel; TN: new oak barrel; CR: uncoated concrete; CC: epoxy coated concrete; SS: stainless steel; AM: raw earthenware amphorae; GB: glass bottle with wine bottled at the beginning of the experiment and used as a reference. [b]_6: 6 months aging in tank; _12: 12 months aging in tank.

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Table 3 reports the detected elemental content of the wines after 6 and 12 months aging; Cr, Co, As, Cd, and Pb appeared under the detection limit and were not reported.

3.1.3. The Amphorae (AM) and Uncoated Concrete (CR) Tanks Affect the Wines the Most in Terms of Elemental Release. The wine aged in the uncoated concrete tank presented significant differences for the concentration of Na, Al, Ca, Fe, and K in comparison to all the other wines. In fact, CR wine had the highest content of Na and K and the lowest content of Ca both after 6 and 12 months, differently for Al and Fe contents that were the highest only at 12 months. The AM wine appeared to be the highest for Al and Ca content at 6 months, while at 12 months, they were still high even if there was a decrease. Concerning the K, both at 6 and 12 months, the AM wines had the highest content together with the CR wines. According to other authors,[3] the larger amounts of elementals could be due to the release phenomena from the raw material, while the salification with tartaric acid and the consequent precipitation could affect the their decrease. This was confirmed by the pH values (Table 4) that resulted higher for the wines aged in CR and AM tanks, and that could be considered a direct consequence of the salification reactions that involved the high content of Ca and K. Moreover, even if the wine used for the experiment was stable to the mini-contact test performed both at the beginning of the experiment and at 6 months aging (delta μS <5%, data not shown), in _12 and _6 + 6 wines, it was registered to be a significant variation in conductivity drop, in particular for wine aged in amphorae, which showed the highest tartaric stability in both _12 and _6 + 6 wines. For these kinds of tanks, it could be assumed that already during the first 6 months of aging, it released an important amount of elementals compared to the other tanks (Table 3). Between 6 and 12 months, on the other hand, there was a decrease that could be attributed to the salification with tartaric acid, confirmed by higher levels of tartaric stability of the wines (Table 4). Moreover, as noted by other authors,[3] wines bottled after 6 months in amphorae had a similar behavior to the 12 months, demonstrating that the release of metals was already important at the moment of the first survey, at 6 months.

Table 4. Values of pH and Drop in Electric Conductivity ($\Delta\sigma$, Expressed as μS/cm) Measured in Sangiovese Red Wine during Aging (_12 and _6 + 6 Months) in Different Tanks (LSD, Least Significant Difference Test; 95% Significance Levell Different Letters in the Same Column Indicate Statistical Significances) ($\Delta\sigma$ < 30 Was Considered Very Stable; 30 to 50 Was Stable; 50 to 70 Was Warning Level; and > 70 Was Not Stable)

code[a,b]	pH	$\Delta\sigma$ %	$\Delta\sigma$
TO_12	3.41a	5.3%	79.9 b
TN_12	3.45c	6.9%	105.7 e
CR_12	3.54f	5.7%	89.3 bc
CC_12	3.46e	7.3%	108.2 e
SS_12	3.46d	6.8%	100.3 de
AM_12	3.55 g	3.7%	56.4 a
GB_12	3.42b	6.1%	91.1 cd
p value	0.0000		0.0002
TO_6 + 6	3.47c	5.4%	83.2b
TN_6 + 6	3.43b	6.0%	92.2d
CR_6 + 6	3.57e	6.4%	100.8e
CC_6 + 6	3.44b	6.9%	104.4f
SS_6 + 6	3.40a	6.0%	88.4c
AM_6 + 6	3.51d	4.0%	62.0a
GB_6 + 6	3.44b	6.1%	91.1d
p value	0.0000		0.0000

[a]TO: used oak barrel; TN: new oak barrel; CR: uncoated concrete; CC: epoxy coated concrete; SS: stainless steel; AM: raw earthenware amphorae; GB: glass bottle with wine bottled at the beginning of the experiment and used as a reference. [b]_6: 6 months aging in tank; _12: 12 months aging in tank; _6 + 6: 6 months aging in tank plus 6 months of bottle aging.

The Fe content was the highest for the AM wine at 6 months but the lowest at 12 months followed by the CR wine at 6 months that appeared instead the highest at 12 months. The detected Fe concentration did not necessarily imply a metal instability risk, but the function of iron as a catalyst for oxidative reactions that involve polyphenols could be evidenced. In fact, this could explain the high amount of polymeric pigments in the AM and the CR wines, similar to that of the wood barrels, as discussed in the Phenolic Profile and Color Indices section. In fact, while the tannin polymerization reactions are enhanced by ellagitannins and oxygen in wooden barrel,[30] it is well known that elements such as Fe and Cu can participate, in the presence of oxygen, to the catalytic conversion of wine's hydrogen peroxide into hydroxyl radical. This reaction could produce many electrophilic oxidation products, such as ethanal, that could further react with polyphenols creating bonds between tannins or anthocyanins which can in turn be incorporated into larger phenolic structures, resulting in color stabilization.[8] As evidenced by Gil i Cortiella *et al.*,[3] there is a great diversity of mineralogical compositions for concrete and clay, and if a release of inorganic compounds from tanks to wine could take place, the specific chemical composition of the concrete or clay of which the tanks are made could impact the extent of the extraction phenomenon.

3.1.4. Volatile Profile of Wines. This analysis was performed to evaluate the relation between the kind of tank material and the volatile profiles of the wines. Thirty-five free volatile compounds were identified and quantitated, including six acetates, five esters, four terpenes, eight alcohols, three fatty acids, four ketones, and one aldehyde. Results relative to wine volatiles composition at _6, _12, and _6 + 6 months aging are reported in Tables 5, 6, and 7 respectively.

At 6 months, wines showed significant differences according to the different tanks. In particular, the TN_6 wine had the highest value of ketones (whiskey lactone and cis-oak lactone) and terpenes like 4-terpineol and to a lesser extent of norisoprenoids (vitispirane II and riesling acetal). The AM wine was characterized by high values of esters (ethyl butanoate, ethyl hexanoate, and ethyl lactate) and norisoprenoids (TDN). Moreover, the AM wine resulted very rich in phenylmethanol (floral-rose, phenolic, balsamic, almond note) for which it was possible to detect values 5 to 10 times higher than all the other wines. There are evidences that phenylmethanol can be produced as an intermediate of the reaction between acetaldehyde and flavanols.[8] In fact, the AM, together with the TN wine, showed also the lowest values of ethanal that was probably due to the consumption of this molecule in favor of polymeric pigments synthesis (Table 1). These results are in agreement with the findings of Saucier *et al.*[41] who found that ethanal-mediated condensation reactions are the main contributor to polymeric pigment formation in oxidative

Table 5. List of Volatile Compounds Measured in the HS-SPME-GC–MS of Sangiovese Red Wine at 6 Months Aging in Different Tanks and Olfactive Detection Threshold (LSD, Least Significant Difference Test; 95% Significance Level; Different Letters in the Same Column Indicate Statistical Significances); All Data Are Expressed in μg/L[a]

compound no.	volatile compounds	ODT[c]	TO_6		TN_6		CR_6		CC_6		SS_6		AM_6		GB_6		p value
1	ethyl acetate[2]	12270[31]	63.219	bc	77.915	e	60.572	ab	71.941	d	59.031	a	64.433	c	73.108	de	<0.05
2	hexyl acetate	670[33]	0.573	ab	0.517	ab	0.735	d	0.881	e	0.618	bc	0.697	cd	0.411	a	<0.05
3	ethyl 3-methylbutanoate	3[31]	12.306	bc	11.474	b	11.040	b	14.137	d	13.048	cd	11.599	b	2.797	a	<0.05
4	3-methylbutyl acetate	30[31]	365.243	c	292.169	b	339.003	c	345.076	c	354.507	c	368.236	c	134.102	a	<0.05
5	diethyl butanedioate (diethyl succinate)[b]	200000[31]	4.574	e	3.715	abc	3.580	ab	3.856	bcd	4.075	d	3.409	a	4.153	cde	<0.05
6	2-phenylethyl acetate (β-phenethyl acetate)	250[31]	33.272	abc	30.174	a	36.471	cd	34.213	bcd	37.338	d	35.410	bcd	30.376	a	<0.05
	total acetates[b]		68.204	c	81.965	g	64.539	b	76.190	e	63.511	a	68.258	d	77.429	f	<0.05
7	ethyl butanoate	20[31]	58.978	b	59.335	bc	57.365	bc	81.827	c	47.813	a	61.365	c	39.370	a	<0.05
8	ethyl hexanoate	14[31]	818.788	ab	748.122	a	915.525	c	895.247	c	889.825	bc	925.224	c	730.550	a	<0.05
9	ethyl octanoate	580[31]	27.831	b	25.456	ab	46.686	c	28.455	b	21.651	a	24.222	ab	47.848	c	<0.05
10	ethyl nonanoate	850[38]	0.312	ab	0.239	a	0.378	ab	0.436	ab	0.461	b	0.389	ab	0.577	ab	ns
11	ethyl 2-hydroxypropanoate (ethyl lactate)[b]	154000[31]	62.146	c	55.093	a	56.663	b	78.083	f	68.078	d	102.088	g	76.857	e	<0.05
	total esters[b]		63.052	c	55.926	a	57.683	b	79.089	f	69.038	d	103.099	g	77.675	e	<0.05
12	3.7-dimethylocta-1.6-dien-3-ol (β-linalol)	25[31]	3.261	a	4.150	b	4.399	b	4.064	b	4.037	b	4.105	b	3.968	ab	<0.05
13	3.7-dimethyloct-6-en-1-ol (β-citronellol)	100[31]	1.893	a	2.173	ab	2.370	bc	2.501	c	2.567	cd	2.326	bc	2.443	bc	<0.05
14	4-allyl-2-methoxyphenol (eugenol)	6[32]	0.081	bc	0.065	ab	0.063	ab	0.089	c	0.084	c	0.065	ab	0.047	a	<0.05
15	2-(4-methylcyclohex-3-en-1-yl)propan-2-ol p-menth-1-en-8-ol (4-terpineol)	250[35]	1.085	a	1.681	d	1.162	ab	1.435	c	1.289	bc	1.285	b	0.937	a	<0.05
	total terpens		6.320	a	8.069	f	7.994	e	8.089	g	7.977	d	7.781	c	7.395	b	<0.05
16	2.2.6.8-tetramethyl-7.11-dioxatricyclo (6.2.1.0)-1.6-undec-4-ene (Riesling acetal)	n.f.	0.126	c	0.129	c	0.100	a	0.130	c	0.133	cd	0.109	ab	0.128	bc	<0.05
17	1.1.6-trimethyl-1.2-dihydronaphthalene (TDN)	20[37]	0.001	ab	0.001	abc	0.001	bc	0.0004	a	0.001	a	0.002	c	0.0003	ab	<0.05
18	(2*R*,5*R*)-2.6.6-trimethyl-10-methylidene-1-oxaspiro[4.5]dec-8-ene (vitispirane I)	800[36]	0.054	a	0.091	b	0.065	ab	0.081	ab	0.064	ab	0.071	ab	0.037	a	ns
19	(2*S*,5*R*)-2.6.6-trimethyl-10-methylidene-1-oxaspiro[4.5]dec-8-ene (vitispirane II)	800[36]	0.012	a	0.022	cd	0.015	abc	0.021	bcd	0.015	ab	0.025	e	0.007	a	<0.05
	total norisoprenoids		0.192	c	0.244	g	0.181	b	0.232	f	0.213	e	0.207	d	0.172	a	<0.05
20	hexan-1-ol	8000[33]	442.877	ab	426.493	a	446.442	ab	435.506	a	465.459	ab	428.320	a	455.935	ab	ns
21	eptan-1-ol	3[34]	548.180	b	699.223	d	586.163	bc	595.520	bc	472.155	a	572.170	bc	658.343	cd	<0.05
22	2-phenylethanol (β-phenylethanol)[b]	14000[32]	56.124	b	47.731	ab	53.404	b	53.124	b	56.766	b	41.921	a	53.481	ab	ns
23	phenylmethanol	200000[31]	27.670	ab	24.641	a	43.009	bc	48.359	c	31.050	ab	207.386	d	29.016	abc	<0.05
24	propan-1-ol[b]	306000[35]	18.115	d	16.787	a	17.086	b	18.625	f	16.791	ab	17.625	c	18.247	de	<0.05
25	2-methylpropan-1-ol[b]	40000[33]	59.068	d	57.274	c	56.263	bc	59.467	d	55.559	b	53.883	a	56.772	bc	<0.05
26	2-methylbutan-1-ol[b]	65000[33]	72.511	d	67.005	a	68.537	b	70.101	c	68.000	ab	70.287	c	73.988	d	<0.05
27	3-methylbutan-1-ol[b]	30000[33]	315.842	c	293.749	a	313.408	c	312.819	c	299.793	b	313.406	c	315.240	c	<0.05
	total alcohols[b]		522.680	g	483.697	a	509.773	d	515.217	e	497.879	b	498.330	c	518.871	f	<0.05
28	*n*-pentadecanoic acid	500[39]	5.645	b	2.825	a	5.902	b	6.424	b	6.274	b	7.137	b	4.944	b	<0.05
29	octanoic acid	500[31]	152.536	bc	138.884	b	66.898	a	153.450	bc	173.719	c	142.511	b	129.948	ab	<0.05
30	nonanoic acid	1100[40]	53.495	d	40.829	b	55.960	d	43.358	bc	56.593	d	51.618	cd	18.640	a	<0.05
	total fatty acids		211.676	f	182.539	c	128.760	a	203.232	e	236.587	g	201.267	d	153.533	b	<0.05
31	octan-2-one	500[41]	9.711	ab	9.658	a	9.570	a	9.710	a	9.370	a	9.663	a	9.234	a	ns

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Table 5. continued

compound no.	volatile compounds	ODT[c]	TO_6		TN_6		CR_6		CC_6		SS_6		AM_6		GB_6		p value
32	ethanal[b]	500[37]	5.192	e	0.988	ab	2.443	c	3.127	d	1.281	ab	0.905	a	1.927	bc	<0.05
33	3-hydroxy-2-butanone (acetoin)[b]	150000[31]	22.584	d	2.005	ab	2.790	b	3.386	b	10.659	c	0.654	a	4.551	b	<0.05
34	5-butyl-4-methyloxolan-2-one (whiskey lactone)	67[31]	1.615	b	14.795	c	nd	a	nd	a	nd	a	nd	a	nd	a	<0.05
35	5-butyl-4-methyloxolan-2-one (*cis*-oak lactone)	790[31]	8.524	b	26.101	c	nd	a	nd	a	nd	a	nd	a	nd	a	<0.05
	total ketones and aldehydes[b]		27.795	g	3.043	b	5.242	c	6.523	e	11.950	f	1.568	a	6.488	d	<0.05

[a]TO: used oak barrel; TN: new oak barrel; CR: uncoated concrete; CC: epoxy coated concrete; SS: stainless steel; AM: raw earthenware amphorae; GB: glass bottle with wine bottled at the beginning of the experiment and used as a reference; n.f., not found. [b]Expressed as mg/L. [c]ODT: olfactive detection threshold (μg/L) according to different authors.[31−40]

conditions. Instead, the TO wine showed the highest value in ethanal and 3-hydroxy-2-butanone (acetoin) and to a lesser extent, of fatty acids (nonanoic acid) and alcohols (propan-1-ol, 2-methylpropan-1-ol, and 2-methylbutan-1-ol). The CC wine resulted rich in acetates (ethyl acetate and ethyl 3-methylbutanoate), esters (ethyl lactate), terpenes (eugenol), and alcohols (propan-1-ol). Regarding the CR wine, the only relevant note was relative to the high content of terpenes (β-citronellol). The SS wine appeared to be the lowest for acetates (ethyl acetate) and the highest for fatty acids (octanoic and nonanoic acids).

The analysis of volatiles after 12 months aging in the different tanks highlighted that the wines were more characterized according to the tank materials, even if the trend was similar to the one observed at 6 months aging. In particular, the TN wine was rich in compounds derived by oak (whiskey lactone and *cis*-oak lactone), esters (ethyl octanoate, ethyl nonanoate, ethyl lactate), and alcohols (propan-1-ol). The wine in amphorae (AM) appeared to be the richest in ethanal and very rich in norisoprenoids (riesling acetal), while it showed a very low amounts of esters (ethyl lactate) and acetates (diethyl succinate, ethyl acetate, ethyl 3-methylbutanoate). The TO wine was still the richest in 3-hydroxy-2-butanone (acetoin), rich in alcohols (3-methylbutan-1-ol), ethanal, and esters (ethyl octanoate, ethyl lactate), but it resulted also the poorest in terpenes (β-linalool, β-citronellol, 4-allyl-2-methoxyphenol). After 12 months, CR and CC wines had similar composition since they were the richest in terpenes (4-terpineol), acetates (3-methylbutylacetate for CR and diethyl succinate for CC), and fatty acids content (nonanoic acid for CR and *n*-pentadecanoic acid for CC). The CC wine was also one of the richest in esters (ethyl lactate) and norisoprenoids (vitispirane I and II). Given its reductive status, the SS wine was subjected to a pumping over with air exposure at 6 months of aging, so the composition of volatiles at 12 months was probably affected by this practice and it was not considered for comments.

After 6 months of aging in tanks and 6 months in glass bottle, the TN wine showed the highest level of acetates (ethyl acetate), esters (ethyl lactate), and to a lesser extent of terpenes (4-terpineol, β-linalol, and eugenol). On the contrary, it had the lowest amount of total alcohols (3-methylbutan-1-ol, 2-methylbutan-1-ol, 2-methylpropan-1-ol), ketones (acetoin), and aldehydes (ethanal). The TO wines had a high value of acetates (ethyl 3-methylbutanoate, diethyl succinate), while it appeared to be the poorest in terpenes (β-linalol and β-citronellol). The CR and AM wines had a similar volatile profile, showing low amounts of esters and norisoprenoids and a high level of alcohols. In particular, the AM wine showed the highest level of phenylmethanol, as already observed for the 6 and 12 month wines, and the highest value of ethanal. The CC wine showed intermediate values for all the detected compounds. The SS wine showed high values of acetates (ethyl acetate, β-phenyl acetate), terpenes (all the detected compounds), norisoprenoids (all the detected compounds), alcohols (hexan-1-ol, eptan-1-ol), fatty acids (octanoic acid), and aldehydes (ethanal). The GB wine had a similar composition of the SS wine, except for the acetates content showing the lowest value.

In order to highlight a hidden but existing trend, a PCA was carried out using the data corresponding to the three detection sampling (_6, _12, and _6 + 6). Figure 2 shows the bi-plot

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Table 6. List of Volatile Compounds Measured in the HS-SPME-GC−MS of Sangiovese Red Wine at 12 Months Aging in Different Tanks (LSD, Least Significant Difference Test; 95% Significance Level; Different Letters in the Same Column Indicate Statistical Significances) (All Data Are Expressed in μg/L)[a]

compound no.	volatile compounds	ODT[c]	TO_12		TN_12		CR_12		CC_12		SS_12		AM_12		GB_12		p value
1	ethyl acetate[b]	12270[31]	43.294	b	47.703	b	48.599	b	46.813	b	43.974	b	31.786	a	68.057	c	<0.05
2	hexyl acetate	670[33]	4.117	bc	0.313	a	0.494	c	0.999	d	0.379	ab	2.185	e	0.310	ab	<0.05
3	ethyl 3-methylbutanoate	3[31]	6.686	d	4.580	bc	3.104	ab	3.419	ab	5.457	cd	2.312	a	1.491	a	<0.05
4	3-methylbutyl acetate	30[31]	96.583	bc	91.107	bc	121.047	c	80.513	ab	120.771	c	109.398	bc	26.886	a	<0.05
5	diethyl butanedioate (diethyl succinate)[b]	200000[31]	5.250	d	4.135	ab	3.936	a	4.557	c	4.336	bc	3.951	a	8.069	e	<0.05
6	2-phenylethyl acetate (β-phenethyl acetate)	250[31]	25.685	bc	22.354	a	27.598	c	24.876	b	25.936	bc	27.022	bc	36.238	d	<0.05
	total acetates[b]		48.678	c	51.956	d	52.688	e	51.479	d	48.463	b	35.878	a	76.191	f	<0.05
7	ethyl butanoate	20[31]	12.347	ab	11.909	ab	16.176	b	16.632	b	18.121	b	16.476	b	1.535	a	ns
8	ethyl hexanoate	14[31]	711.529	a	675.731	a	740.390	a	690.738	a	704.686	a	689.503	a	609.135	a	ns
9	ethyl octanoate	580[31]	33.318	d	30.055	bcd	31.658	cd	31.450	cd	28.842	abc	26.795	ab	22.302	a	<0.05
10	ethyl nonanoate	850[38]	0.262	c	0.296	d	0.270	c	0.268	c	0.204	a	0.237	b	1.049	e	<0.05
11	ethyl 2-hydroxypropanoate (ethyl lactate)[b]	154000[31]	77.464	d	81.304	e	73.384	c	77.384	d	76.372	d	42.227	a	68.228	b	<0.05
	total esters[b]		78.222	g	82.022	f	74.173	c	78.123	e	77.124	d	42.960	a	68.862	b	<0.05
12	3.7-dimethylocta-1.6-dien-3-ol (β-linalol)	25[31]	2.691	a	3.039	b	3.354	cd	3.241	bc	3.045	b	3.521	d	3.312	bcd	<0.05
13	3.7-dimethyloct-6-en-1-ol (β-citronellol)	100[31]	2.096	a	2.147	a	2.799	b	2.571	b	2.315	bc	2.574	bc	3.757	d	<0.05
14	4-allyl-2-methoxyphenol (eugenol)	6[32]	0.143	a	0.172	a	0.173	a	0.181	a	0.214	a	0.136	a	0.293	a	ns
15	2-(4-methylcyclohex-3-en-1-yl)propan-2-ol p-menth-1-en-8-ol (4-terpineol)	250[35]	1.291	ab	1.599	cd	1.556	cd	1.717	d	1.253	a	1.470	abc	1.700	bcd	<0.05
	total terpens		6.221	a	6.956	c	7.882	f	7.710	e	6.828	b	7.700	d	9.062	g	<0.05
16	2.2.6.8-tetramethyl-7.11-dioxatricyclo (6.2.1.0)-1.6-undec-4-ene (Riesling acetal)	n.f.	0.136	a	0.132	a	0.129	a	0.144	a	0.129	a	0.269	b	0.192	a	<0.05
17	1.1.6-trimethyl-1.2-dihydronaphthalene (TDN)	20[37]	0.018	ab	0.040	bc	0.015	ab	0.020	abc	0.011	a	0.008	a	0.061	c	ns
18	(2*R*,5*R*)-2.6.6-trimethyl-10-methylidene-1-oxaspiro[4.5]dec-8-ene (vitispirane I)	800[36]	0.165	b	0.190	cd	0.168	bc	0.197	d	0.129	a	0.128	a	0.337	e	<0.05
19	(2*S*,5*R*)-2.6.6-trimethyl-10-methylidene-1-oxaspiro[4.5]dec-8-ene (vitispirane II)	800[36]	0.060	**b**	0.075	c	0.063	b	0.074	c	0.045	a	0.044	a	0.138	d	<0.05
	total norisoprenoids		0.378	c	0.436	d	0.375	b	0.435	e	0.313	a	0.448	f	0.728	g	<0.05
20	hexan-1-ol	8000[33]	375.366	a	371.377	a	379.888	a	376.105	a	375.531	a	353.300	a	233.277	a	ns
21	eptan-1-ol	3[34]	319.727	c	267.759	ab	279.788	ab	277.239	ab	296.420	bc	258.171	a	407.038	d	<0.05
22	2-phenylethanol (β-phenylethanol)[b]	14000[32]	53.043	b	44.851	a	50.461	b	52.020	b	49.767	b	49.743	b	74.932	c	<0.05
23	phenylmethanol	200000[31]	32.946	a	45.051	b	51.806	c	52.968	c	41.638	b	184.471	e	62.069	d	<0.05
24	propan-1-ol[b]	306000[35]	18.105	bc	19.992	cd	20.971	d	18.207	bc	19.374	cd	13.779	a	15.864	ab	<0.05
25	2-methylpropan-1-ol[b]	40000[33]	60.739	cd	51.379	b	63.337	d	54.840	bc	57.521	bcd	42.483	a	54.590	bcd	<0.05
26	2-methylbutan-1-ol[b]	65000[33]	72.760	cd	61.797	b	75.565	d	66.350	bc	67.143	bc	50.745	a	61.823	abc	<0.05
27	3-methylbutan-1-ol[b]	30000[33]	317.683	f	267.907	a	318.218	g	285.936	c	301.920	e	286.445	d	273.174	b	<0.05
	Total alcohols[b]		523.059	e	496.386	d	529.264	f	478.059	b	496.439	d	443.990	a	481.085	c	<0.05
28	*n*-pentadecanoic acid	500[39]	5.282	ab	4.279	a	6.728	c	6.831	cd	6.280	bc	7.935	d	10.789	e	<0.05
29	octanoic acid	500[31]	150.879	ab	139.508	a	172.180	c	159.156	ab	155.925	ab	153.832	ab	186.500	c	ns
30	nonanoic acid	1100[40]	81.881	c	65.746	a	91.509	d	74.583	bc	74.313	bc	67.584	ab	64.044	ab	<0.05
	total fatty acids		238.043	d	209.534	a	270.418	g	240.569	e	236.518	c	229.350	b	261.333	f	<0.05
31	octan-2-one	500[40]	7.918	b	6.683	ab	7.175	b	7.145	b	7.286	b	7.360	b	4.600	a	ns

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Table 6. continued

compound no.	volatile compounds	ODT[c]	TO_12		TN_12		CR_12		CC_12		SS_12		AM_12		GB_12		p value
32	ethanal[b]	500[37]	3.849	bc	2.489	ab	4.330	c	3.592	bc	3.733	bc	4.153	c	0.943	a	<0.05
33	3-hydroxy-2-butanone (acetoin)[b]	150000[31]	20.856	c	3.205	a	3.284	a	4.633	a	8.168	b	5.269	a	2.774	a	<0.05
34	5-butyl-4-methyloxolan-2-one (whiskey lactone)	67[31]	1.864	b	12.667	c	nd	a	nd	a	nd	a	nd	a	nd	a	<0.05
35	5-butyl-4-methyloxolan-2-one (*cis*-oak lactone)	790[31]	6.651	b	31.008	c	nd	a	nd	a	nd	a	nd	a	nd	a	<0.05
	total ketones and aldehydes[b]		24.722	g	5.744	b	7.622	c	8.232	d	11.910	f	9.430	e	3.722	a	<0.05

[a]TO: used oak barrel; TN: new oak barrel; CR: uncoated concrete; CC: epoxy coated concrete; SS: stainless steel; AM: raw earthenware amphorae; GB: glass bottle with wine bottled at the beginning of the experiment and used as a reference; n.f., not found. [b]Expressed as mg/L. [c]ODT: olfactive detection threshold (μg/L) according to different authors.[31−40]

(total explained variance of PC1 and PC2 50.63%), with the distribution of wines and the relative volatile compounds.

As already observed for the phenolic compounds, the wines appeared to be separated in three distinctive groups according to the different times and modality of aging (tanks and bottles). In particular, on the left of the graph, there were the _6 wines; in the middle, the _12 wines; and on the right, the _6 + 6 wines. This last group resulted the most different from the _6 wines and characterized by the higher content of norisoprenoids (#16, #17, #18, #19) and terpenes (#14, #15), and to a lesser extent of acetates (#5) and esters (#30). On the other hand, _6 wines were richer in esters and acetates (#4, #6, #7, #8) and less in alcohols (#20, #21) and terpenes (#12). According to other authors,[42] it was evidenced an increase in eugenol (#14) in all wines both in tanks and in the bottle after 12 months aging.

It could be observed that during wine aging, both in the tank and bottle, there was a decrease in esters, mainly acetates, except for the ethyl esters of diprotic acids such as ethyl lactate (#11) and diethyl succinate (#5).[43] In particular, it was possible to observe an increase of diethyl succinate (#5) in the _6 + 6 wines in comparison with the same wines aged for 12 months in tanks.

Higher alcohols maintained the same concentration in all wines (_6, _12 and _6 + 6) confirming that as reported in the literature,[43] their concentration usually do not change very much with aging.

3-Methylbuthyl acetate, which has been described as one of the most important compounds for wine aroma,[43] showed a substantial decrease during aging both in tank and in bottle, and _6 wines resulted the richest. Ethanal, the main aldehyde formed as a direct result of the oxidative chain reactions, is also the major aldehyde present and in higher concentration in _12 and _6 + 6 wines, in comparison to the _6 wines. Its contribution to the wine sensory profile is to provide a fruity flavor at low concentrations (~30 mg/L) and rotten-like flavor at higher levels (~100 mg/L).[44]

All these findings allowed presuming that reductive condition of the 6 months bottle aging induced reactions that enabled the synthesis of varietal volatiles, in particular, norisoprenoids by acidic hydrolysis of the precursors. These findings were in accordance with other authors.[15] On the contrary, the more oxidative conditions of the tanks seemed to have reduced the speed of these kinds of reaction and, consequently, the 12 month wines resulted more similar to the 6 month wines.

3.2. Sensory Characterization and Differentiation of Sangiovese Wines Aged in Different Tank Materials.

Figure 3 shows the results of the descriptive analysis of the wines aged in the different tanks after 6 months. The PCA explained the 71.97% of the total variance (PC1 54.33%; PC2 17.65%), with the significative attributes (berry jam, cherry, reductive, vanilla, wood, and spicy odor; vegetal, spicy, wood, vanilla, and butter in-mouth flavor) as loadings.

Wines were clearly separated along the first dimension in three main groups: the TN_6 wine on the left of the graph, the AM_6, SS_6, CC_6, and CR_6 in the middle, and the GB_6 on the right. As expected, the TN_6 wine was related to all the woody attributes (spicy, wood, vanilla, and butter). The TO_6 wine was positioned between the TN_6 and the central group because of its intermediate characteristics. In fact, it was related to a lesser extent to the woody attributes and also to berry jam and cherry odor that were in turn also related to the AM_6

Table 7. List of Volatile Compounds Measured in the HS-SPME-GC-MS of Sangiovese Red Wine at _6 + 6 Months Aging in Different Tanks (LSD, Least Significant Difference Test; 95% Significance Level; Different Letters in the Same Column Indicate Statistical Significances) (All Data Are Expressed in μg/L)[a]

compound no.	volatile compounds	ODT[c]	TO_6 + 6		TN_6 + 6		CR_6 + 6		CC_6 + 6		SS_6 + 6		AM_6 + 6		GB_6 + 6		p value
1	ethyl acetate[b]	12270[31]	67.220	a	96.125	d	70.922	ab	71.176	b	76.996	c	70.400	ab	67.141	ab	<0.05
2	hexyl acetate	670[33]	0.286	a	0.242	a	0.242	a	1.093	b	0.403	a	1.306	b	0.195	a	<0.05
3	ethyl 3-methylbutanoate	3[31]	13.221	c	10.783	abc	9.306	bc	9.777	bc	3.737	bc	6.168	ab	3.330	a	<0.05
4	3-methylbutyl acetate	30[31]	93.156	d	56.569	c	66.733	c	66.882	c	67.317	a	38.254	b	10.593	a	<0.05
5	diethyl butanedioate (diethyl succinate)[b]	200000[31]	9.070	b	4.790	ab	4.127	a	4.668	a	4.980	ab	4.295	a	6.658	ab	<0.05
6	2-phenylethyl acetate (β-phenethyl acetate)	250[31]	20.174	a	23.395	ab	25.343	bc	23.832	ab	28.904	c	26.922	bc	36.170	d	<0.05
	total acetates[b]		76.417	e	101.006	g	75.151	c	75.945	d	82.076	f	74.768	b	73.814	a	<0.05
7	ethyl butanoate	20[31]	6.702	b	6.578	b	6.015	b	12.793	c	6.483	b	3.063	a	0.857	a	<0.05
8	ethyl hexanoate	14[31]	751.397	c	666.598	b	659.436	b	760.923	c	840.028	d	590.100	a	591.323	a	<0.05
9	ethyl octanoate	580[31]	57.735	b	39.439	a	36.113	a	40.634	a	71.983	c	38.760	a	48.151	ab	<0.05
10	ethyl nonanoate	850[38]	0.203	ab	0.151	a	0.155	a	0.194	b	0.663	b	0.143	a	0.961	c	<0.05
11	ethyl 2-hydroxypropanoate (ethyl lactate)[b]	154000[31]	60.055	a	80.310	c	56.964	a	59.752	a	59.128	a	58.139	a	66.041	b	<0.05
	total esters[b]		60.871	e	81.022	g	57.666	a	60.566	d	60.047	c	58.771	b	66.683	f	<0.05
12	3.7-dimethylocta-1.6-dien-3-ol (β-linalol)	25[31]	1.954	a	3.121	d	2.949	c	2.656	b	2.844	c	3.168	d	3.260	d	<0.05
13	3.7-dimethyloct-6-en-1-ol (β-citronellol)	100[31]	1.499	a	2.067	b	2.274	b	2.077	b	2.783	c	2.391	bc	3.856	d	<0.05
14	4-allyl-2-methoxyphenol (eugenol)	6[32]	0.150	ab	0.213	d	0.134	a	0.148	ab	0.205	cd	0.176	bc	0.276	e	<0.05
15	2-(4-methylcyclohex-3-en-1-yl)propan-2-ol p-menth-1-en-8-ol (4-terpineol)	250[35]	1.347	b	1.770	d	1.209	a	1.364	b	1.661	c	1.305	b	1.703	cd	<0.05
	total terpens		4.950	a	7.171	e	6.567	c	6.246	b	7.493	f	7.041	d	9.095	g	<0.05
16	2.2.6.8-tetramethyl-7.11-dioxatricyclo (6.2.1.0)-1.6-undec-4-ene (Riesling acetal)	n.f.	0.152	c	0.155	c	0.120	a	0.136	ab	0.171	d	0.130	ab	0.179	d	<0.05
17	1.1.6-trimethyl-1.2-dihydronaphthalene (TDN)	20[37]	0.038	c	0.022	b	0.013	a	0.022	b	0.049	d	0.022	b	0.061	d	<0.05
18	(2*R*,5*R*)-2.6.6-trimethyl-10-methylidene-1-oxaspiro[4.5]dec-8-ene (vitispirane I)	800[36]	0.282	d	0.215	bc	0.165	a	0.229	c	0.335	e	0.198	b	0.342	e	<0.05
19	(2*S*,5*R*)-2.6.6-trimethyl-10-methylidene-1-oxaspiro[4.5]dec-8-ene (vitispirane II)	800[36]	0.127	c	0.101	b	0.068	a	0.134	c	0.151	d	0.093	b	0.137	cd	<0.05
	total norisoprenoids		0.600	e	0.493	c	0.366	a	0.521	d	0.705	f	0.442	b	0.719	g	<0.05
20	hexan-1-ol	8000[33]	310.329	ab	340.272	d	327.431	bcd	335.572	cd	345.030	d	306.061	a	312.290	abc	<0.05
21	eptan-1-ol	3[34]	337.255	bc	315.120	b	351.983	cd	288.380	a	364.926	d	278.585	a	385.014	d	<0.05
22	2-phenylethanol (β-phenylethanol)[b]	14000[32]	48.511	a	55.198	b	50.613	a	55.063	b	55.160	b	54.575	b	69.158	c	<0.05
23	phenylmethanol	200000[31]	35.613	a	62.773	a	46.765	a	46.979	a	45.405	a	156.517	b	54.983	a	<0.05
24	propan-1-ol[b]	306000[35]	16.482	b	16.749	bc	15.232	a	16.724	bc	16.805	bc	17.204	c	15.544	a	<0.05
25	2-methylpropan-1-ol[b]	40000[33]	52.405	a	51.838	a	55.833	a	51.772	a	53.807	a	53.662	a	51.770	a	ns
26	2-methylbutan-1-ol[b]	65000[33]	64.683	c	60.981	a	67.334	d	62.548	b	61.966	ab	65.190	c	60.587	a	<0.05
27	3-methylbutan-1-ol[b]	30000[33]	279.227	ab	269.143	a	289.925	b	269.243	a	280.025	ab	272.789	a	265.497	a	ns
	total alcohols[b]		461.993	c	454.627	a	479.664	g	456.021	b	468.518	f	464.162	e	463.308	d	<0.05
28	*n*-pentadecanoic acid	500[39]	5.661	b	5.121	ab	3.682	a	3.127	ab	5.239	b	3.882	ab	11.012	c	<0.05
29	octanoic acid	500[31]	125.388	a	138.619	ab	141.256	ab	147.517	abc	161.706	bc	158.636	bc	189.384	c	ns
30	nonanoic acid	1100[40]	71.295	ab	57.676	a	59.926	a	63.980	a	92.053	b	59.604	a	62.979	ab	<0.05

Table 7. continued

compound no.	volatile compounds	ODT[c]	TO_6 + 6		TN_6 + 6		CR_6 + 6		CC_6 + 6		SS_6 + 6		AM_6 + 6		GB_6 + 6		p value
	total fatty acids		202.344	b	201.416	a	204.864	c	214.625	d	258.998	f	222.123	e	263.375	g	<0.05
31	octan-2-one	500[40]	5.730	b	5.788	b	5.608	b	5.880	b	5.984	b	4.975	a	4.196	a	<0.05
32	ethanal[b]	500[37]	3.465	d	0.987	a	2.822	c	1.992	b	3.757	d	4.181	e	1.330	a	<0.05
33	3-hydroxy-2-butanone[b]	150000[31]	15.274	b	1.814	a	2.319	a	1.001	a	4.507	a	3.012	a	2.435	a	<0.05
34	5-butyl-4-methyloxolan-2-one (whiskey lactone)	67[31]	1.371	b	10.969	c	nd	a	nd	a	nd	a	nd	a	nd	a	<0.05
35	5-butyl-4-methyloxolan-2-one (*cis*-oak lactone)	790[31]	9.041	b	28.761	c	nd	a	nd	a	nd	a	nd	a	nd	a	<0.05
	total ketones and aldehydes[b]		18.755	g	2.847	a	5.147	d	2.999	b	8.270	f	7.198	e	3.770	c	<0.05

[a]TO: used oak barrel; TN: new oak barrel; CR: uncoated concrete; CC: epoxy coated concrete; SS: stainless steel; AM: raw earthenware amphorae; GB: glass bottle with wine bottled at the beginning of the experiment and used as a reference; n.f., not found. [b]Expressed as mg/L. [c]ODT: olfactive detection threshold (μg/L) according to different authors.[31−40]

wine. The SS_6, CC_6 and CR_6 could not be directly related to any of these attributes. On the right of the graph, the GB_6 wine was related to reductive odor and vegetal flavor attributes.

Because of the important impact of wood barrel on wine sensory characteristics, different PCA elaborations have been carried out on the Sangiovese red wine during 12 months aging in tank and 6 months aging in tank plus 6 months of bottle aging. In particular, two different PCAs were performed: the first for the CC, CR, AM, and SS wines (_12 and _6 + 6) and the second for the TO and TN wines (_12 and _6 + 6). In both the PCAs, the wines were compared with the GB wine.

Figure 4 shows the PCA bi-plot of the descriptive analysis data of SS, CC, CR, AM, and GB wines at _12 and _6 + 6. The total explained variance was of 88.98% (PC1 69.40% and PC2 19.58%).

Twelve months aging (_12) were more similar between them with respect to the 6 months aging (_6 + 6) wines. In fact, all the _6 + 6 wines were positioned near the limit of the graph, far from each other, while the _12 wines were, on the contrary, near the center and close to each other. Regarding the relation between the wines and the attributes, the graph showed that the AM and SS wines were similar in both the aging time modality (_6 + 6 and _12), while the CR wines showed the highest differences between the two kinds of aging. The CC_6 + 6 and CR_6 + 6 appeared to be similar and associated to the floral flavor, floral odor, sweetness attributes, and to a lesser extent to acidity, while the SS_6 + 6 and the AM_6 + 6 to the berry jam odor.

Interestingly, the results of the sensory evaluation were similar to the distribution of wines according to the aforementioned chemical composition. In fact, the distribution of these wines underlined that the bottle aging affected the perceived quality of wines and showed that the _6 + 6 wines were perceived significantly more different as compared to the _12 months wines.

The results of the descriptive analysis of the TO and TN wines are reported in Figure 5. The PCA explained the 88.36% of the total variance (PC1 71.04%; PC2 17.32%).

In this case, the evolution of the wines seemed more influenced by the kind of the tank in the case of the TN and, even if to a lesser extent, for the TO wine. In fact, the TN_ 6 + 6 and TN_12 wines appeared to be similar and directly related to all the woody attributes (wood and vanilla flavor and odor, spicy odor, and butter flavor) and also to floral and cherry odor attributes. The TO wine appeared to be more influenced by the kind of aging, given that the difference between the TO_6 + 6 wine and TO_12 and their less relation (overall for TO_6 + 6) with the woody attributes. The TO_12 wine at last was also related to the cherry odor.

So far, the impact on the chemical and sensory characteristics of wine determined by the use of different aging tank materials has been the subject of numerous scientific works. However, most of them have been limited to the contextual comparison of two or at most three types of containers and considering white wines.[3,5,10−13] Based on this, with the present work, a simultaneous comparison of most of the types of containers currently used in the cellars was carried out. Therefore, new-alternative and traditional tank materials have been compared during the aging at the industrial scale of a single variety red wine and the impact on the chemical and sensory characteristics of the wine has been evaluated.

The present study allowed to highlight that earthenware raw amphorae and uncoated concrete promoted the wine color

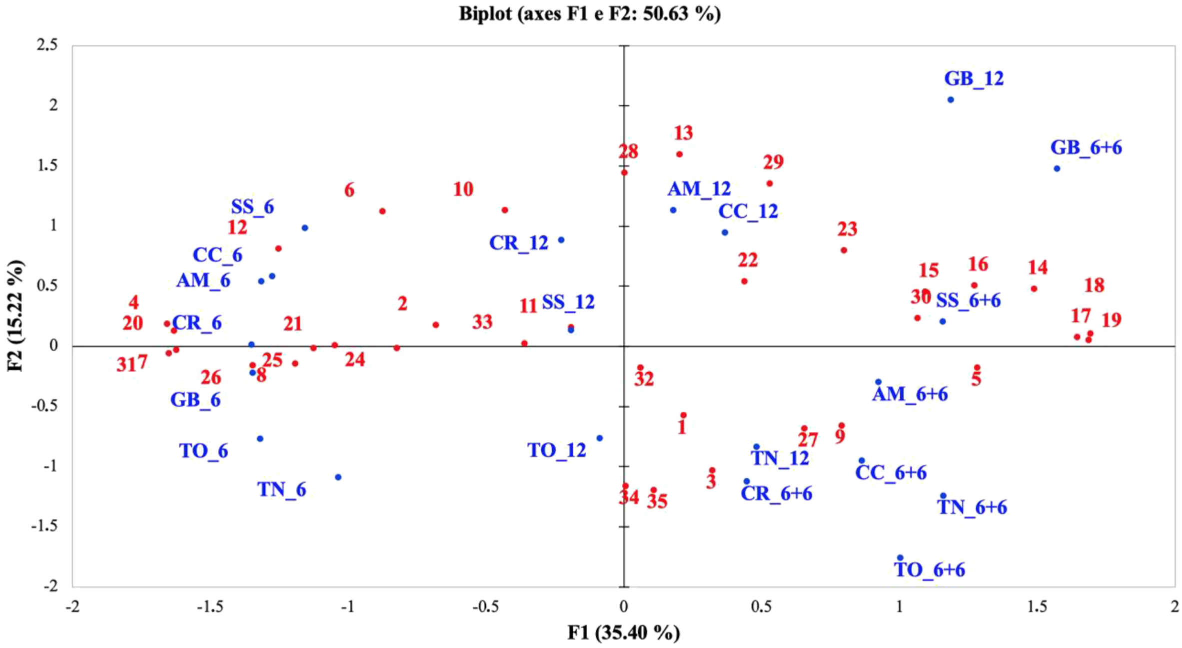

Figure 2. Principal component analysis (PCA): scores and loadings plot of the volatile compounds, measured in Sangiovese red wine during aging (_6: 6 months aging in tank; _12: 12 months aging in tank; _6 + 6: 6 months aging in tank plus 6 months of bottle aging; TO: used oak barrel; TN: new oak barrel; CR: uncoated concrete; CC: epoxy coated concrete; SS: stainless steel; AM: raw earthenware amphorae; GB: glass bottle with wine bottled at the beginning of the experiment and used as a reference). See Table 5 for the volatile compounds code.

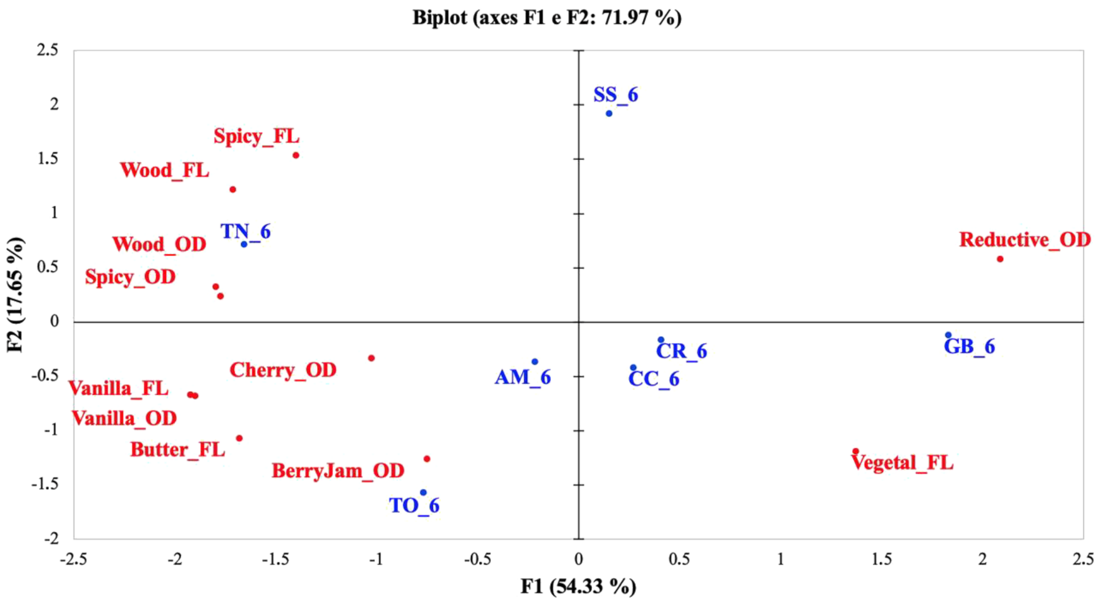

Figure 3. Principal component analysis (PCA): scores and loadings plot of the significative sensory attributes evaluated in Sangiovese red wine at 6 months of tank aging (TO: used oak barrel; TN: new oak barrel; CR: uncoated concrete; CC: epoxy coated concrete; SS: stainless steel; AM: raw earthenware amphorae; GB: glass bottle with wine bottled at the beginning of the experiment and used as a reference).

stabilization similarly to the new oak barrel already after 6 months aging. This aspect was confirmed by the wine composition after 6 months of bottle aging as they showed the highest content in polymeric pigments, even when compared to the same wines aged for 12 months in the same tanks. Moreover, earthenware raw amphorae and uncoated concrete released in wines a relevant amount of elementals causing an acidity decrease, affecting also the sensory profile. The bottle aging, combined with different tank materials, enhanced the complexity of the wine volatile profile thanks to the reductive status inside the bottle that seemed to promote the varietal precursors hydrolysis. These findings could be useful for winemakers since the tank material represents an important choice in the wine production process as a function of the oenological aim and definition of the wine style. In fact, in order to obtain a color stability of the red wine, materials such uncoated concrete or earthenware raw amphorae could be a good alternative to wood when peculiarity of the varietal character needs to be preserved without conferring to the wine the volatile compounds that are typical of the toasted oak. Further research will be necessary in order to highlight the elementals release trend and the oxygen

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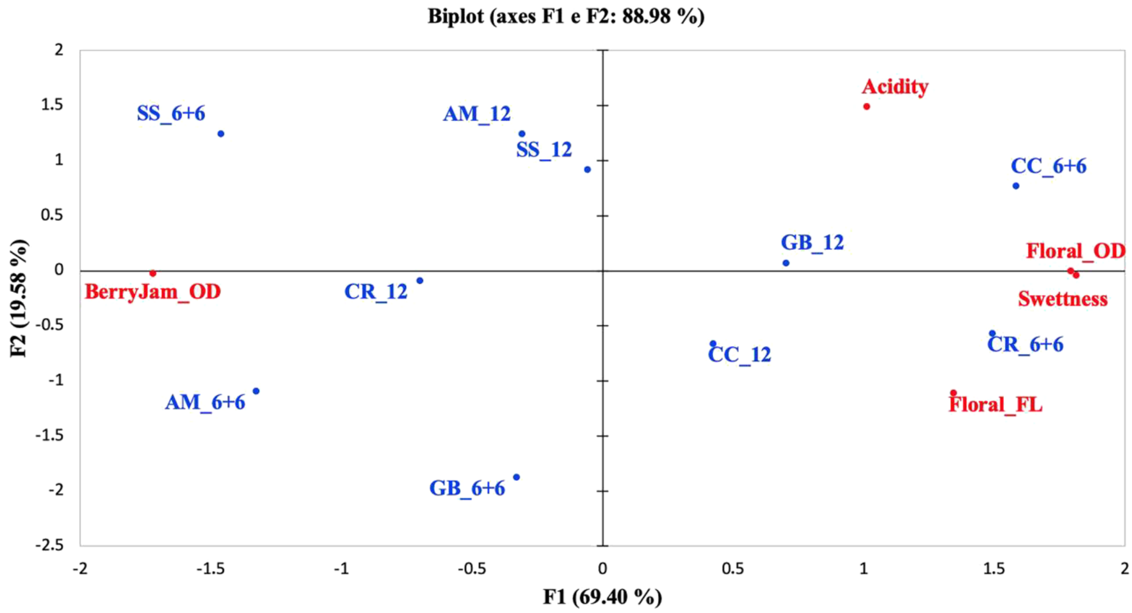

Figure 4. Principal component analysis (PCA): scores and loadings plot of the significative sensory attributes evaluated in the Sangiovese red wine at 12 months aging (_12: 12 months aging in tank; _6 + 6: 6 months aging in tank plus 6 months of bottle aging; CR: uncoated concrete; CC: epoxy coated concrete; SS: stainless steel; AM: raw earthenware amphorae; GB: glass bottle with wine bottled at the beginning of the experiment and used as a reference).

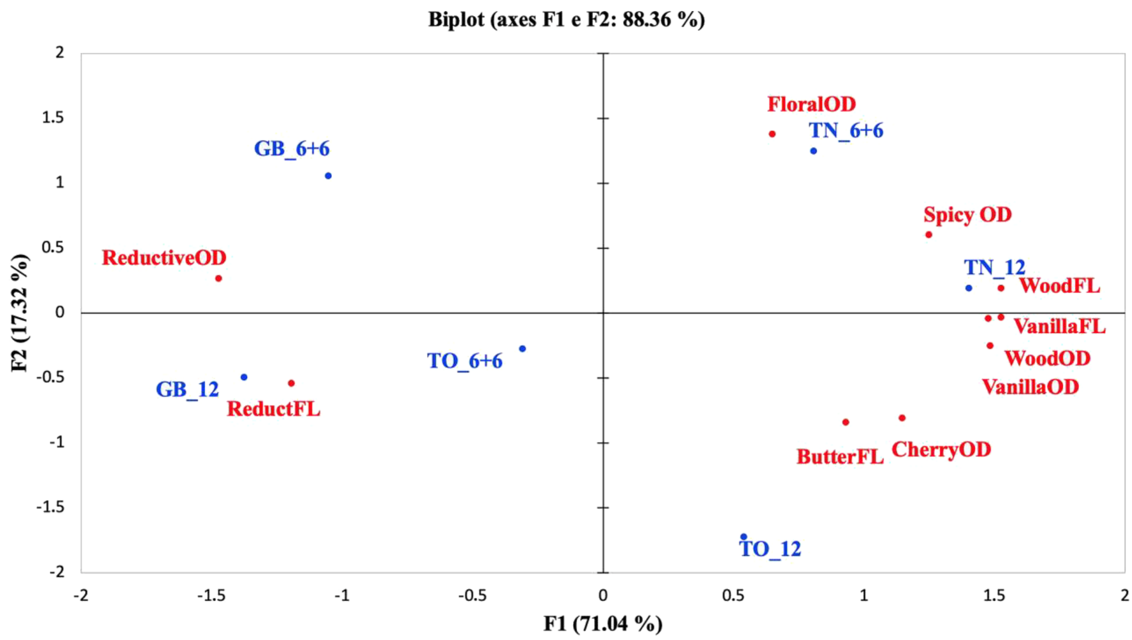

Figure 5. Principal component analysis (PCA): scores and loadings plot of the significative sensory attributes evaluated in Sangiovese red wine at 12 months aging (_12: 12 months aging in tank; _6 + 6: 6 months aging in tank plus 6 months of bottle aging; TO: used oak barrel; TN: new oak barrel; GB: glass bottle with wine bottled at the beginning of the experiment and used as a reference).

permeation dynamic during time and, similarly to the study available in the literature for oak barrel, according to the subsequent re-fill of the tank.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsfoodscitech.1c00329.

Chemical characteristics of the 2018 Sangiovese wine used for the study; list of compounds measured in the HS-SPME-GC-MS and GC-FID, retention time, and linear retention index for the HP-Innowax column; and attributes and reference standards for the panel training (PDF)

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Notes

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