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## **Abstract:**

The traditional ageing of wine spirits is done in wooden barrels, however, high costs have led to the search for alternative technologies, such as the use of stainless steel tanks with wooden staves and the application of micro-oxygenation. This work evaluates the changes in the major volatile compounds of wine spirits aged for 6, 12 and 18 months in wooden barrels and stainless steel tanks with micro-oxygenation. For both ageing technologies, two types of wood (Limousin oak and Portuguese chestnut wood) were used. The samples were analysed concerning their alcohol strength (electronic densimetry) and volatile composition, namely of methanol, acetaldehyde, ethyl acetate and other major volatile compounds ((GC-FID) and near-infrared spectroscopy (NIR)). The results show that the ageing technology was more influential than the wood species for the volatile composition of wine spirits, namely acetaldehyde, methanol, 2-methylpropan-1-ol and 2+3-methylbutan-1-ol. However, the opposite behaviour was found for the spectral data. The ageing process was accelerated by using the alternative ageing technology, especially with chestnut wood staves. The most informative spectral regions to discriminate samples were around 6859  $\text{cm}^{-1}$  and from 5200  $\text{cm}^{-1}$  to 4200  $\text{cm}^{-1}$ . NIR is a promising technique to identify different technologies and different wood species used in the ageing process of wine spirits.

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Article

# Screening of Different Ageing Technologies of Wine Spirit by Application of Near-Infrared (NIR) Spectroscopy and Volatile Quantification

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**Abstract:** The traditional ageing of wine spirits is done in wooden barrels, however, high costs have led to the search for alternative technologies, such as the use of stainless steel tanks with wooden staves and the application of micro-oxygenation. This work evaluates the changes in the major volatile compounds of wine spirits aged for 6, 12 and 18 months in wooden barrels and stainless steel tanks with micro-oxygenation. For both ageing technologies, two types of wood (Limousin oak and Portuguese chestnut wood) were used. The samples were analysed concerning their alcohol strength (electronic densimetry) and volatile composition, namely of methanol, acetaldehyde, ethyl acetate and other major volatile compounds ((GC-FID) and near-infrared spectroscopy (NIR)). The results show that the ageing technology was more influential than the wood species for the volatile composition of wine spirits, namely acetaldehyde, methanol, 2-methylpropan-1-ol and 2+3-methylbutan-1-ol. However, the opposite behaviour was found for the spectral data. The ageing process was accelerated by using the alternative ageing technology, especially with chestnut wood staves. The most informative spectral regions to discriminate samples were around  $6859\text{ cm}^{-1}$  and from  $5200\text{ cm}^{-1}$  to  $4200\text{ cm}^{-1}$ . NIR is a promising technique to identify different technologies and different wood species used in the ageing process of wine spirits.

**Keywords:** wine spirit; NIR; major volatile compounds; ageing technology; micro-oxygenation

## 1. Introduction

The traditional ageing of wine spirits consists of placing the drink, after the distillation, in wooden barrels for a more or less prolonged period of time. During this stage, and as a result of physical, chemical and sensory changes, the quality of the drink greatly increases. The beverage is usually sold after this process. According to an EU regulation [1], the minimum time required for the ageing of wine spirits is six months.

After the distillation, the wine spirit is mainly composed of ethanol and water, and also of several volatile compounds, which mainly result from the grapes and from the fermentation process [2]. Quantitatively, the main volatile compounds, usually called major volatiles, are acetaldehyde, ethyl acetate, methanol and fusel alcohols. The methanol results from pectin dimethyl esterification

catalysed by pectin methylesterases in the grapes, while the other compounds are metabolites of yeast fermentation [3]. Their contents are also influenced by the distillation [4]. Some of these compounds have a remarkable impact on the aroma of the beverage before and after the ageing process [5,6].

During the ageing process, the distillate's composition changes due to several reactions that take place inside the wooden barrel resulting from the contact between the distillate and the wood [7]. Oxygen, which enters through the barrels or can be applied and controlled through micro-oxygenation, plays a crucial role in such reactions [8]. Therefore, the volatile profile of spirits changes due to the extraction of various compounds from the wood [9,10], and the contents of major volatiles also undergo modifications over the ageing period [11,12].

The aforementioned changes are influenced by several factors, such as the kind of wood, the heat treatment of the barrels and the ageing time [13,14].

Near-infrared spectroscopy (NIR) has been used in several studies as a method to predict the quality of different foods and beverages due to the minimum sample preparation, low cost and speed of analysis [15–17]. In addition, the use of this analytical technique gives rise to a characteristic spectrum for each sample according to the molecular bonds of its chemical constituents [18]. Vibrational techniques have, in general, been used to assess different characteristics of different spirits. Nordon et al. [19] compared NIR and Raman spectrometry to evaluate the alcohol strength of whiskies, vodkas and other alcoholic drinks. NIR has also been used to determine the alcohol and methanol contents or other constituents of whiskies [19,20], gin, vodka [21], rum, brandies [22] and other distilled beverages [14,22,23]. Research on aged wine spirits and brandies using NIR is scarce; as far as we know, there was only one study on wine spirit. Hanousek-Cica et al. [24] used partial least squares regression to calibrate and predict the contents of major volatile compounds and phenols in the wine spirits.

The traditional ageing technology, using wooden barrels, is costly and time consuming. For these reasons, in recent years, some research has been done about alternative technologies for the ageing of alcoholic beverages, namely the addition of wood fragments to the beverages stored in stainless steel tanks. In this context, several works have been carried out, particularly on wine spirits [9,10]. The association of wood fragments with micro-oxygenation, which consists of adding small amounts of oxygen over time, have been also studied, namely in red wines [25,26]. The first study about this subject on the ageing of wine spirits showed that the use of micro-oxygenation and staves promotes greater extraction of several phenolic compounds than the wooden barrels [8].

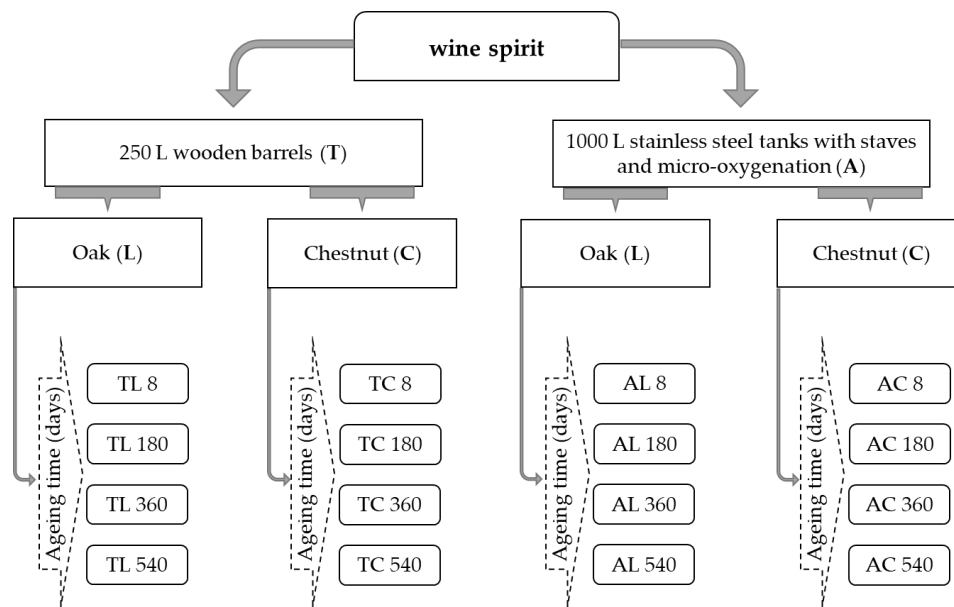
The aim of this study was to investigate the potential of near-infrared spectroscopy (NIR) as a rapid technique to differentiate aged wine spirits according to the two different ageing technologies—wooden barrels and an alternative using micro-oxygenation and staves—and two different wood species—chestnut and Limousin oak. For this approach, the spectral properties of wine spirits and their relationship with the main volatile compounds' contents were examined.

## 2. Materials and Methods

### 2.1. Samples

The aged wine spirits were produced on an industrial scale according to the scheme shown in Figure 1. The same wine spirit was used to fill Limousin oak (*Quercus robur* L.) 250 L new barrels, Portuguese chestnut (*Castanea sativa* Mill.) 250 L new barrels, 1000 L stainless steel tanks with Limousin oak staves and 1000 L stainless steel tanks with chestnut staves, both combined with micro-oxygenation. The barrels and the wood pieces were made by J. M. Gonçalves cooperage (Palaçoulo, Portugal) with medium plus toasting level (90 min at an average temperature of 240 °C). The barrels were heated over a fire of wood offcuts, and the staves were heated in an industrial oven, both strictly controlling the wood's temperature to assure the same toasting level. The quantity of staves (91 cm length × 5 cm width × 1.8 cm thickness) used in the stainless steel tanks was calculated based on the surface area to volume ratio of a 250 L barrel (85 cm<sup>2</sup>/L). Micro-oxygenation was applied, as described by Canas et al. [8], using pure oxygen (X50S Food, Gasin, Portugal), which was supplied at a flow rate of

2 mL/L/month through a multiple diffuser micro-oxygenator (VISIO 6, Vivelys, France) with ceramic diffusers. Sampling was made at 8, 180, 365 and 540 days of ageing. Forty samples were analysed: 24 from barrels (two wood species  $\times$  four ageing times  $\times$  three replicates); 16 from stainless steel tanks (two wood species  $\times$  four ageing times  $\times$  two replicates).



**Figure 1.** Scheme of the assay representing the different experimental units according to the ageing technology, the wood used and the ageing time; three replicates were used for each barrel modality and two replicates were used for each stainless steel tank with micro-oxygenation modality.

The wine spirit samples were coded as follows (Figure 1): TC—aged in 250 L chestnut new barrels; TL—aged in 250 L oak new barrels; AC—aged in 1000 L stainless steel tanks with chestnut wood staves and micro-oxygenation; AL—aged in 1000 L stainless steel tanks with oak wood staves and micro-oxygenation.

The wooden barrels and the stainless steel tanks were placed in the cellar of Adegas Cooperativa da Lourinhã in similar environmental conditions.

## 2.2. Analytical Procedures

Alcohol strength was determined by distillation and electronic densimetry [27], using an electronic densimeter Model 5000 DMA brand Anton Paar (Graz, Austria). The results are presented as the volumetric percentage of ethanol in the beverage.

The volatile compounds (methanol, acetaldehyde, ethyl acetate and major volatile compounds) were analysed by gas chromatography–flame ionisation detection (GC-FID) according to a validated method [28]. Chromatographic analysis was provided by the direct injection of the distillate, obtained in the distillation performed for alcohol strength determination. Prior to injection, 1 mL of internal standard solution (4-methylpentan-2-ol) was added to 10 mL of each sample. The GC-FID analysis was carried out using a Focus GC gas chromatograph (Thermo Finnigan, Milan, Italy), equipped with a flame ionisation detector (FID) (250 °C) and a fused silica capillary column of polyethylene glycol (DB-WAX, JW Scientific, Folsom, CA, USA), 60 m length, 0.32 mm i.d., 0.25  $\mu$ m film thickness. The carrier gas was hydrogen (3.40 cm<sup>3</sup>/min). The samples were loaded (~1  $\mu$ L) on the injector (200 °C) in split mode (split ratio 1:6). The oven temperature program was 35 °C (for 8 min), then increased by 10 °C/min to 200 °C, and held at this temperature for 1 min. The quantification was done by analysing the hydroalcoholic solutions of standards with known concentrations of different volatile compounds, under the same conditions. The results were expressed as mg/L.

### 2.3. Spectroscopic Measurements

The near infrared spectra of the samples were obtained according the methodology proposed by Yang et al. [23], in a NIR spectrometer (MPA Bruker) using transmitted light, collected in 1 mm quartz cells at 25 °C for 2 min in the instrument before scanning and using air as a background. The samples were measured with a spectral resolution of 8 cm<sup>-1</sup> and 32 scans in the wavenumber from 12,500 to 4000 cm<sup>-1</sup>.

### 2.4. Data Analysis

A two-way analysis of variance (ANOVA) was applied to the chemical results, which were assessed with two factors (wood: chestnut and oak; technology: traditional and alternative), and the differences between the experimental modalities (TC, TL, AC, AL) were evaluated with the Fisher's least significant difference (LSD) test with a *p*-value of 0.05. Differences between sampling time (8, 180, 360 and 540 days) were also examined with the LSD test.

Principal component analysis (PCA) was performed using the NIR spectra of wine spirits in order to distinguish the different samples analysed. Six replicated spectra for each wine spirit samples were collected, and the analysis was performed with the average spectra of these measurements. For NIR data analysis, only the region between 9000 and 4000 cm<sup>-1</sup> was used and the first derivative of Savitzky–Golay was applied as a pre-process.

The data analysis was carried out using UnscramblerX 10.5 (CAMO, Oslo, Norway) software and Statistica from StatSoft.

## 3. Results and Discussion

### 3.1. Spirits' Volatile Composition

In general, the ageing technology was more influential than the wood botanical species, which is in accordance with Caldeira et al. [13]. The results of the ANOVA (Tables 1 and 2) show that, for almost all of the volatile compounds, the technology had a higher significant effect, which explains the total variation of between 35% and 97%. However, the wood species significantly influenced the concentration of some volatile compounds in the wine spirits, such as acetaldehyde, considering the ageing time up to 360 days; this factor affected almost all of the analysed compounds for the period up to 540 days of ageing (Tables 1 and 2). Nevertheless, for 540 days of ageing, the percentage of variance given by the ANOVA is higher for the factor of wood. Indeed, some research pointed out the influence of the wood botanical species on the volatile composition of aged wine spirits [10,13,29].

**Table 1.** Differences in alcohol strength, methanol, acetaldehyde and ethyl acetate of the wine spirits aged with Limousin oak and chestnut wood in two different technologies.

Samples		Alcohol Strength (%)	Methanol (mg/mL)	Acetaldehyde (mg/mL)	Ethyl Acetate (mg/mL)
8 Days	TC	77.2 ± 0.0	405.1 ± 7.0	27.4 ± 1.5	458.5 ± 5.3
	TL	77.3 ± 0.2	406.2 ± 7.8	28.4 ± 0.2	446.2 ± 2.8
	AC	77.0 ± 0.0	397.7 ± 0.9	28.5 ± 0.8	455.1 ± 10.3
	AL	77.1 ± 0.1	397.0 ± 11.1	27.4 ± 0.4	460.1 ± 9.1
Technology (Ty)		n.s.	n.s.	n.s.	n.s.
Wood (W)		n.s.	n.s.	n.s.	n.s.
Ty x W		n.s.	n.s.	n.s.	n.s.
residual		–	–	–	–
180 Days	TC	76.4 ± 0.1 a	373.3 ± 6.1 a	34.6 ± 0.3 b	433.2 ± 2.3
	TL	76.6 ± 0.1 a	380.0 ± 5.6 a	31.0 ± 1.9 a	434.5 ± 10.3
	AC	77.0 ± 0.3 b	390.9 ± 5.7 b	35.8 ± 0.5 b	447.0 ± 14.7
	AL	77.0 ± 0.1 b	394.8 ± 0.1 b	35.6 ± 0.8 b	444.0 ± 18.8
Technology (Ty)		69.4 *	81.1 **	56.8 **	n.s.
Wood (W)		n.s.	n.s.	21.7 *	n.s.
Ty x W		n.s.	n.s.	n.s.	n.s.
residual		30.6	18.9	21.5	–

Table 1. Cont.

360 Days	TC	76.5 ± 0.3	344.4 ± 4.1 a	51.4 ± 0.9 b	499.8 ± 30.4
	TL	76.8 ± 0.1	351.3 ± 7.2 a	38.4 ± 4.1 a	485.1 ± 17.4
	AC	77.0 ± 0.0	390.1 ± 1.1 b	68.5 ± 0.2 c	478.7 ± 4.2
	AL	76.9 ± 0.0	393.5 ± 7.3 b	55.5 ± 0.9 b	452.6 ± 7.0
Technology (Ty)		n.s.	96.6 ***	60.0 ***	n.s.
Wood (W)		n.s.	0.0	34.4 **	n.s.
Ty x W		n.s.	0.0	0.0	n.s.
residual		–	3.4	5.6	–
540 Days	TC	76.2 ± 0.3 a	343.5 ± 4.1 a	79.8 ± 0.3 b	503.4 ± 34.3 a
	TL	76.8 ± 0.0 b	355.7 ± 4.5 b	71.2 ± 0.5 a	532.7 ± 1.7 b
	AC	76.8 ± 0.2 b	370.1 ± 4.1 c	89.3 ± 2.3 c	488.3 ± 1.1 ab
	AL	77.2 ± 0.0 b	353.0 ± 6.3 ab	81.1 ± 1.8 b	441.1 ± 7.2 a
Technology (Ty)		42.4 **	34.8 **	56.4 ***	55.5 **
Wood (W)		45.0 **	3.0 *	41.6 ***	0.9 *
Ty x W		0.0	51.3 **	0.0	26.4 *
residual		12.6	10.9	2.0	17.2

TC—aged in 250 L chestnut new barrels; TL—aged in 250 L oak new barrels; AC—aged in 1000 L stainless steel tanks with chestnut wood staves and micro-oxygenation; AL—aged in 1000 L stainless steel tanks with oak wood staves and micro-oxygenation. Mean values with the same letter in a column, for each ageing time, did not statistically differ. n.s.,  $p > 0.05$ ; \*  $0.01 < p < 0.05$ ; \*\*  $0.001 < p < 0.01$ ; \*\*\*  $p < 0.001$ .

**Table 2.** Differences in major volatile compounds of the wine spirits aged with oak and chestnut wood in two different technologies for 540 days.

Samples		propan-1-ol (mg/mL)	2-methylpropan-1-ol (mg/mL)	butan-1-ol (mg/mL)	2+3-methylbutan-1-ol (mg/mL)
8 Days	TC	175.2 ± 2.7 b	864.7 ± 8.6 b	6.4 ± 0.3	2063.7 ± 24.8 b
	TL	175.9 ± 2.9 b	865.6 ± 8.5 b	6.4 ± 0.3	2063.7 ± 34.0 b
	AC	169.7 ± 1.6 a	850.7 ± 4.6 a	6.3 ± 0.6	2017.0 ± 15.1 a
	AL	170.3 ± 0.9 a	852.0 ± 1.4 a	5.9 ± 0.1	2016.2 ± 7.6 a
Tec		69.6 *	60.4 *	n.s.	59.5 *
W		n.s.	n.s.	n.s.	n.s.
Tec x W		n.s.	n.s.	n.s.	n.s.
residual		30.4	39.4	–	40.5
180 Days	TC	159.2 ± 1.2 a	793.7 ± 7.3 a	5.9 ± 0.4	1853.9 ± 19.9 a
	TL	161.6 ± 2.2 a	806.7 ± 15.6 ab	6.3 ± 0.3	1904.3 ± 29.2 ab
	AC	165.8 ± 1.6 b	817.2 ± 5.1 b	6.3 ± 0.6	1953.0 ± 12.4 b
	AL	166.7 ± 0.3 b	819.8 ± 1.5 b	5.8 ± 0.1	1954.9 ± 9.6 b
Tec		86.2 **	57.3 *	n.s.	71.8 **
W		n.s.	n.s.	n.s.	n.s.
Tec x W		n.s.	n.s.	n.s.	n.s.
residual		13.8	42.7	–	28.2
360 Days	TC	155.0 ± 2.5 a	777.6 ± 14.1 a	5.5 ± 0.6	1871.7 ± 13.7 a
	TL	156.7 ± 0.8 a	778.7 ± 8.8 a	5.6 ± 0.3	1881.0 ± 25.4 a
	AC	165.5 ± 3.7 b	797.8 ± 3.2 b	6.2 ± 0.3	1926.2 ± 24.8 b
	AL	165.9 ± 3.3 b	802.2 ± 8.6 b	5.9 ± 0.2	1930.3 ± 23.0 b
Tec		87.6 ***	66.2 *	n.s.	71.9 **
W		n.s.	n.s.	n.s.	n.s.
Tec x W		n.s.	n.s.	n.s.	n.s.
residual		12.4	33.8	–	28.1
540 Days	TC	157.0 ± 2.0	798.8 ± 5.0 b	5.0 ± 0.0	1927.4 ± 17.0 b
	TL	159.9 ± 3.0	801.7 ± 5.6 b	5.0 ± 0.3	1931.9 ± 17.6 b
	AC	158.6 ± 1.3	795.2 ± 1.4 b	5.4 ± 0.6	1917.0 ± 0.4 b
	AL	152.9 ± 1.2	772.2 ± 3.6 a	5.3 ± 0.1	1861.7 ± 3.9 a
Tec		n.s.	47.1 **	n.s.	46.2 **
W		n.s.	16.5 *	n.s.	16.9 *
Tec x W		n.s.	28.5 **	n.s.	24.3 *
residual		–	7.9	–	12.6

TC—aged in 250 L chestnut new barrels; TL—aged in 250 L oak new barrels; AC—aged in 1000 L stainless steel tanks with chestnut wood staves and micro-oxygenation; AL—aged in 1000 L stainless steel tanks with oak wood staves and micro-oxygenation. Mean values followed by the same letter in a column, for each ageing time, are not statistically different. n.s.,  $p > 0.05$ ; \*  $0.01 < p < 0.05$ ; \*\*  $0.001 < p < 0.01$ ; \*\*\*  $p < 0.001$ .

Some major volatile compounds are very important because they contribute to the flavour and aroma of the wine spirits. Actually, odour notes like sweetish, sliced apple or nut are assigned to acetaldehyde, a glue-like aroma to ethyl acetate, a herbaceous aroma to 2-methyl-1-propan-1-ol, and solvent to 2+3-methylbutan-1-ol [6,30,31]. Therefore, the amounts of these volatile compounds have a significant influence on the final product's quality [31,32]. These compounds depend on the raw material, fermentation or distillation conditions, but they can also be influenced by the different conditions of the ageing process [32,33]. In the present study, the raw material, the fermentation and the distillation conditions were fixed, while the ageing process varied according to the technology and the kind of wood used.

The results reported in Table 2 indicate that the technology had a significant effect only for propan-1-ol, 2-methylpropan-1-ol and 2+3-methylbutan-1-ol contents in the wine spirits after 8 days of ageing. Canas et al. [8] found some statistical differences in the non-volatile phenolic compounds in the early period of ageing (six months).

Table 3 exhibits the results of LSD tests on the ageing time for each sample group (TC, TL, AC, AL).

**Table 3.** Differences observed for each sample group (technology vs. wood) during the ageing time.

Days	Aged in 250 L New Barrels								Aged in 1000 L Stainless Steel Tanks with Staves and Micro-Oxygenation							
	with Chestnut				with Oak				with Chestnut				with Oak			
	8	180	360	540	8	180	360	540	8	180	360	540	8	180	360	540
Alcohol strength (%)	B	A	A	A	B	A	A	A	A	A	A	A	AB	AB	A	B
Methanol (g/mL)	C	B	A	A	C	B	A	A	B	B	B	A	B	B	B	A
Acetaldehyde (mg/mL)	A	B	C	D	A	AB	B	C	A	B	C	D	A	B	C	D
Ethyl acetate (mg/mL)	A	A	B	B	A	A	B	C	A	A	B	B	A	A	A	A
Propan-1-ol (mg/mL)	B	A	A	A	B	A	A	A	B	B	B	A	B	B	B	A
2-methylpropan-1-ol (mg/mL)	B	A	A	A	B	A	A	A	B	A	A	A	C	B	B	A
butan-1-ol (mg/mL)	B	AB	AB	A	A	A	B	B	B	B	B	A	B	B	B	A
2+3-methylbutan-1-ol (mg/mL)	C	B	A	A	B	A	A	A	B	AB	A	A	C	B	B	A

Mean values with the same letter in a row, for each sample group (TC, TL, AC and AL), did not statistically differ.



Methanol is naturally present in alcoholic beverages; its amount mainly depends on the raw material [3,34]. This constituent is a hazardous compound to health [35]. However, its content in wine spirits is much lower than those observed in other spirits, namely fruit spirits or grape marc spirits [36]. According to EU regulation [1], the maximum methanol concentration in wine spirits or brandy is 200 g per hectolitre of 100% alcohol volume.

The ethyl acetate concentration was similar for both technologies and wood species used up to six months of ageing (Tables 1 and 3). Thereafter, a significant increase was observed, except for the wine spirits aged by the alternative technology with Limousin oak (Table 3).

The amount of acetaldehyde increased over time, resulting from the oxidation reactions [34]; higher amounts of this compound were observed for the alternative technology, especially with chestnut wood staves. Similar results were also reported by other authors [9,11]. The measurement and control of acetaldehyde in wine spirits must be tightly monitored because high amounts of this compound may have a negative influence on the quality of the wine spirits [31]. In addition, the acetaldehyde content in wine spirits is usually acceptable during the ageing process if it is performed adequately.

For 1-butanol, no significant differences between ageing technology or wood species were identified when the ageing period was analysed separately (Table 2). However, comparing each group of samples (TC, TL, AC and AL), a statistical decrease in the concentration of 1-butanol was found. This decrease was more pronounced, with statistical differences, when the alternative technology was used in the ageing process (Table 3). For this reason, this parameter was included in the PCA performed with analytical results in Section 3.3.

Significant differences related to the ageing technologies were observed between 2-methyl-1-propanol, 2+3-methyl-1-butanol and 1-propanol (Table 2). Such differences were also significantly affected by the ageing time after 8 days of ageing (Table 3). Similar results were reported by Caldeira et al. [9,13].

It is well known that the release of wood compounds is more pronounced in the first months of ageing due to the higher concentration gradient between the wood and the distillate [35], which explains the differences observed over time.

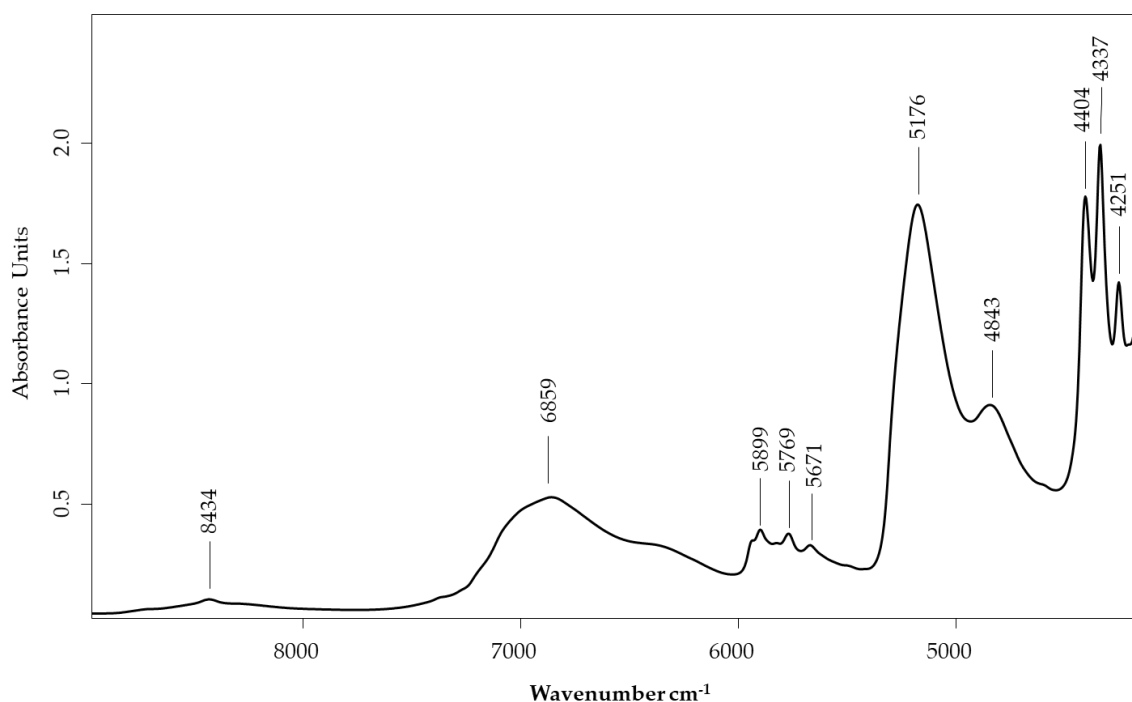
Regarding the analytical data, some changes also occur over time. The contents of major volatiles in wine spirits become more discriminative, as observed previously with the LSD test. At the end of the ageing time, the alternative technology promoted higher amounts of acetaldehyde, 1-butanol, alcohol strength and methanol (Tables 1 and 2). One hypothesis for some of these results is a lower evaporation in the alternative technology, since the evaporation that takes place in the traditional technology promotes losses of ethanol but also of other volatile compounds [36].

Some research reported a significant effect on the volatile compounds of the wine spirits aged with oak wood when compared to the wine spirits aged with chestnut wood [6,9]. The results suggest that the latter presents greater differences from the wine spirits aged with oak, and the evolution of the ageing process of chestnut is higher and the stabilisation occurs earlier than for oak. These different behaviours could be explained by the higher porosity observed in chestnut wood compared to oak wood, which increase the extraction process of the different compounds from wood to beverage [37].

It is well known that the wine spirit has a high concentration of ethanol, a richness of minor volatile compounds and phenolic compounds other than volatile phenols [9], which lead to a differentiation in the ageing technologies and wood species used in the ageing process. Besides, the wood contact during the ageing process leads to wood phenolic compound enrichment in wine spirits, namely of those of low molecular weight.

### 3.2. Characterisation of Wine Spirit Spectra

Figure 2 exhibits a representative spectrum of the wine spirits acquired by NIR. The NIR absorption spectra of wine spirits (Figure 2) were similar to those obtained for other alcohol beverages, such as whisky [19,20], beer [38] and vodka [21].



**Figure 2.** Absorption spectra of a representative wine spirit sample in near infrared region measured against a background of air.

The NIR spectrum is complex since it shows several overlapping bands that are difficult to assign to a specific chemical group. It comprises the first and second overtones, and the combination of two or more fundamental vibration regions. Furthermore, the NIR spectrum has a strong absorbance in the region of  $4000\text{--}4300\text{ cm}^{-1}$  and  $4450\text{--}10,000\text{ cm}^{-1}$ , resulting from the water present in the samples.

The peaks near  $8400\text{ cm}^{-1}$  were ascribed to the 2nd overtone C-H stretch of ethanol, one of the main compounds in wine spirits and a combination of the O-H bend, and the 1st overtone of the O-H stretch given by the influence of the water [38]. Carbohydrates also contribute to this spectral region, in which the 2nd overtone of C-H stretch region is observed [39]. In this region, the carbonilic and aromatic compounds usually contribute to its second overtone absorption [40]. The abovementioned groups of compounds are also present in this kind of beverage but at low concentration.

The strong band characteristic of wine spirits occurs at  $5176\text{ cm}^{-1}$ . This band is assigned to the O-H combinations and O-H first overtones of water and ethanol and C-H stretch first overtones. The 2nd overtone O-H stretch of water and ethanol occurs at  $6859\text{ cm}^{-1}$ .

The bands at  $4404\text{ cm}^{-1}$  and  $4337\text{ cm}^{-1}$  are attributed to the absorbance of methanol [23]. The ethanol, sugars and phenolic compounds also have an absorption band at  $4404\text{ cm}^{-1}$  related to C-H combinations and O-H stretch overtones at  $4338\text{ cm}^{-1}$  to C-H overtones [41]. The band at  $4251\text{ cm}^{-1}$  is related to the combination of stretch and deformation of C-H groups [42].

The spectral range between  $6000\text{--}5600\text{ cm}^{-1}$  corresponds to the first overtone of the C-H stretching vibrations in  $-\text{CH}_3$  and  $-\text{CH}_2$  groups; this region is usually associated with sugars and aromatic groups [43,44].

### 3.3. Analysis of Spectral Information vs. Analytical Data

It is well known that significant differences in the volatile composition of wine spirits with different ageing times exist. Nevertheless, it is important to know whether it is possible to distinguish wine spirits with the same ageing time, according to the ageing technology and the wood species used. A PCA with all chemical parameters for all ageing times has been performed (data not shown); however, the result became very confusing and difficult to draw conclusions from, given the great influence of ageing time, which overlapped with the differences promoted by the wood species and

the ageing technologies. For this reason, the analysis was performed individually for 8, 120, 360 and 540 days of ageing.

The PCA was done with an average of 10 spectra for each sample of wine spirits measured in each ageing period, applying baseline correction and first derivative as pre-processes with 17 smoothing points, to examine qualitative differences between the samples group (TC, TL, AC, AL). After performing PCA, the data were plotted in a graph of first principal component (PC1) vs. second principal component (PC2), as shown in Figures 3a, 4a, 5a and 6a. Concerning these PCAs performed with NIR spectral information, a stronger influence by the kind of wood was observed. For these PCAs, the first two components accounted for 98%, 97%, 98% and 99% of the total variation for 8, 180, 360 and 540 days of ageing, respectively. The results obtained for the analytical data represent, for the first two PCs, 65.5%, 72.2%, 70.2% and 69.1% of the variation in the spectra for the previous ageing periods, respectively.

The PCA eigenvectors were analysed to investigate the source of the observed spectral differentiation between the four groups of wine spirits analysed (Figures 3b, 4b, 5b and 6b). For spectral analysis, and considering the wine spirit composition, is important to take into account all of the aforementioned absorption bands. For this reason, we decided to use all of the spectral regions from  $9000\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  in the further analysis. Moreover, Figures 3b, 4b, 5b and 6b reveal that the wavelengths from  $5500$  to  $4500\text{ cm}^{-1}$  are the most representative in discriminating the samples, for all ageing periods.

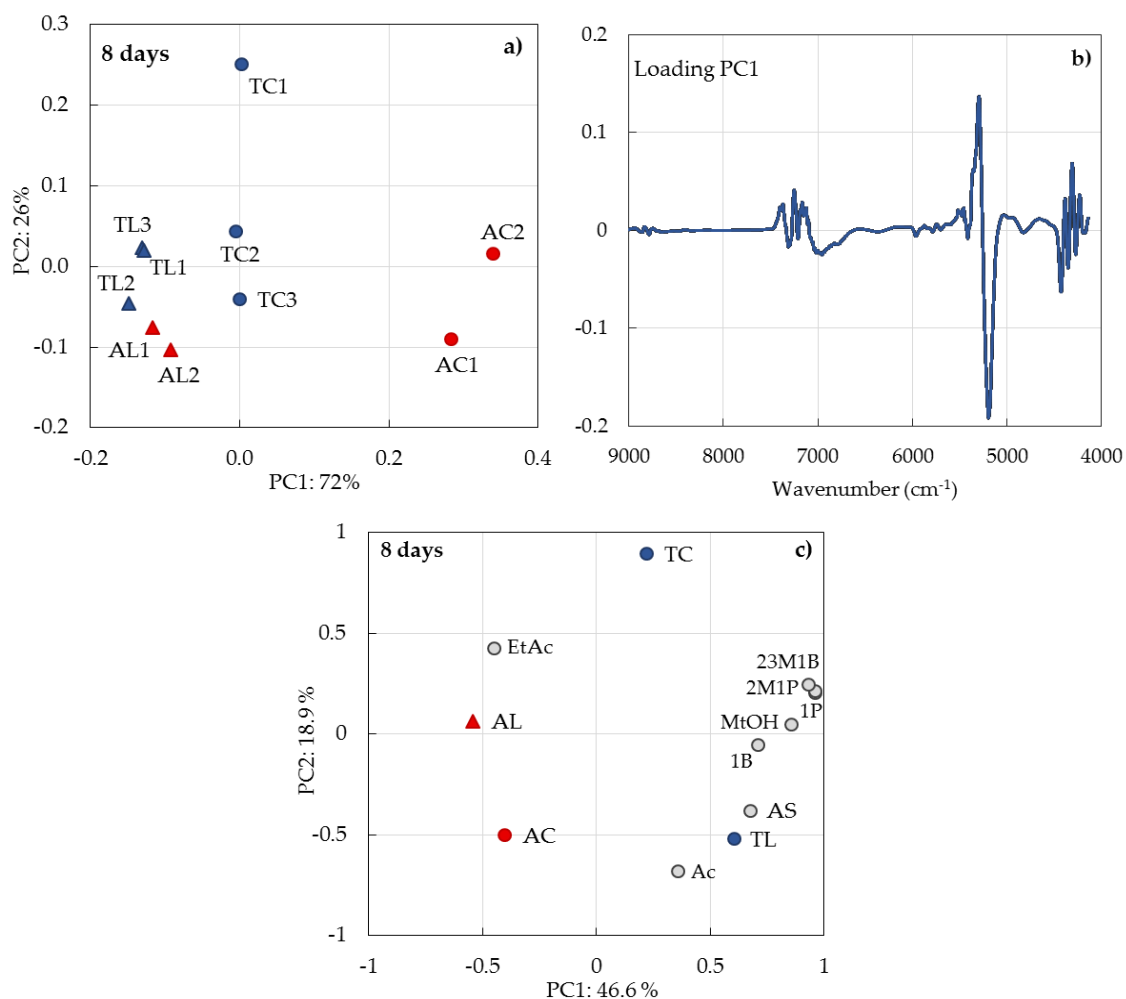
A PCA with the chemical results was also performed (Figures 3c, 4c, 5c and 6c). Generally, there was a separation of the samples according to the wood species and especially the ageing period.

Score and loading plot for the two significant principal components (Figure 3a) of NIR spectra of wine spirits aged for 8 days describes 98% of the total variation (72% for PC1 (8-NIR) and 26% for PC2 (8-NIR)). Figure 3a shows a tendency of separation by the kind of wood. Considering the alternative vs. traditional technology, the difference is more evident for the beverages aged with chestnut wood.

Regarding the loading plot for PC1 (8-NIR), the more representative component, which had higher influence in this separation, was the region around  $6859\text{ cm}^{-1}$  and from  $5200\text{ cm}^{-1}$  to  $4200\text{ cm}^{-1}$ .

Figure 3c represents the PCA performed with analytical parameters (AP) (scores and loadings) that explain 67% of the total variation. Examining PC1 (8-AP), it was possible to observe a trend to discriminate samples according to the technology.

Eight days is a very short period of ageing, but even so, NIR found some differences, especially related to the wood species used in the ageing process. Some slight differences also begin to be detected between the technologies used. It is well reported in previous works of our research team that ageing with chestnut is faster than with Limousin oak [8,45]. Canas et al. [29] reported significant differences between the phenolic compounds, except for vanillic acid, even in this early stage of ageing.

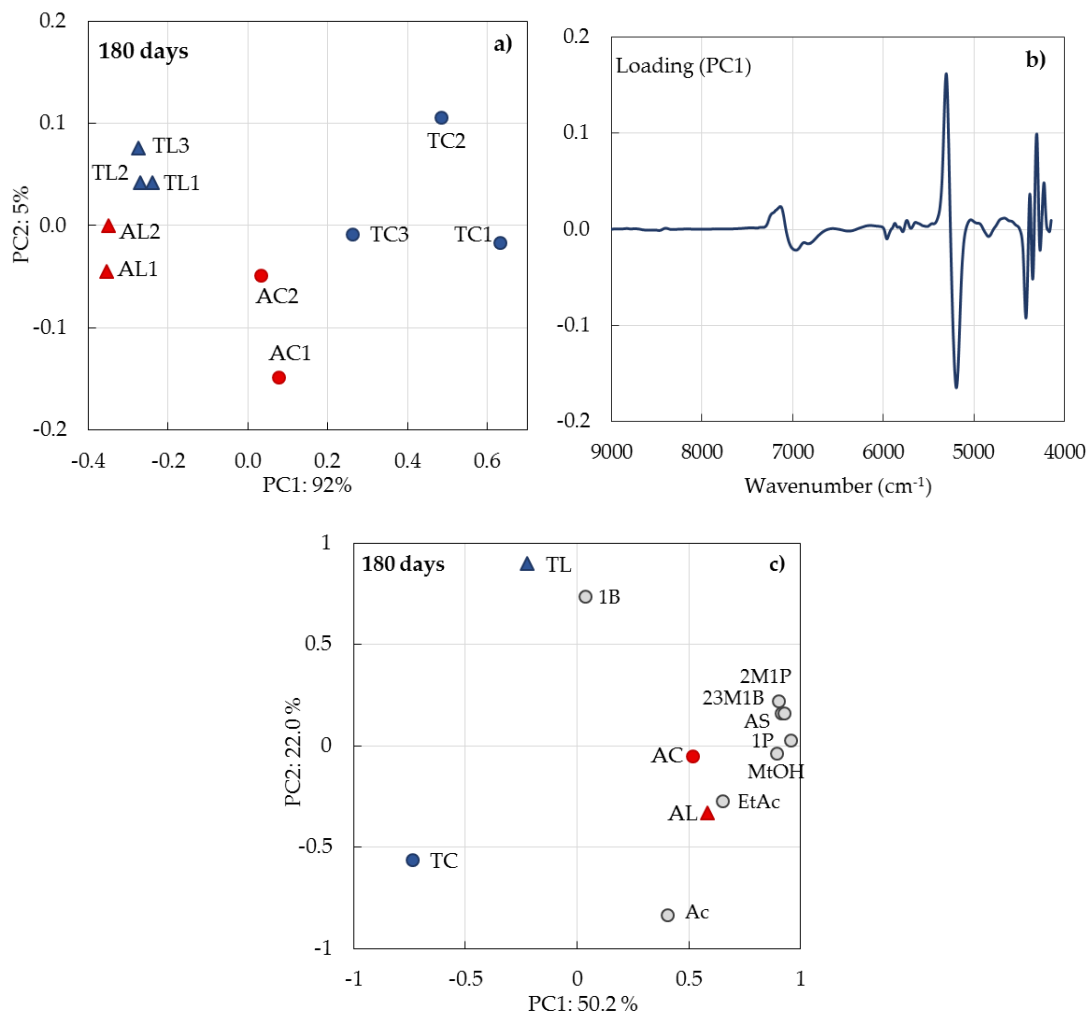


**Figure 3.** Principal component analysis of wine spirit aged by the traditional and alternative technologies with chestnut and oak wood for 8 days for: (a) scores of near-infrared spectroscopy (NIR) spectral information; (b) loadings of NIR spectral information; (c) standardised scores and loadings of analytical parameters measured. TC—aged in 250 L chestnut new barrels; TL—aged in 250 L oak new barrels; AC—aged in 1000 L stainless steel tanks with chestnut wood staves and micro-oxygenation; AL—aged in 1000 L stainless steel tanks with oak wood staves and micro-oxygenation. AS—alcohol strength (%); MtOH—methanol (g/mL); Ac—acetaldehyde (mg/mL); EtAc—ethyl acetate (mg/mL); 1P—propan-1-ol (mg/mL); 2M1P—2-methylpropan-1-ol (mg/mL); 23M1B—2+3-methylbutan-1-ol (mg/mL); 1B—butan-1-ol (mg/mL).

The PCA eigenvectors were also analysed to understand the source of the observed spectral discrimination. The most representative region for the variation observed between samples was from  $5500\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  (Figure 3b), in which the influence of the higher number of compounds present in the beverages was noticed. Concerning the analytical data (Figure 3c), the results show a higher influence of the wood used in the ageing process than that observed with the PCA performed with spectral data: separation by the wood explains 19% of the total variation and the separation by technology explains 47%. In this case, the more variable compounds in this early stage were acetaldehyde and ethyl acetate.

Regarding the data collected for 180 days of ageing, the first component splits the wine spirits according to the wood species, explaining 92% of the total variation (Figure 4a). It seems that a slightly separation of the samples based on the ageing technologies across PC2 (180-NIR) exists, but this component only explains 5% of the total variation.

The most representative NIR spectral regions for the differentiation of the samples aged for 180 days was similar to those observed for 8 days of ageing time (Figure 4b). Concerning the results of the analytical data, the PCA (180-AP) explains 72.2% of the total variation and split the data in PC1 (180-AP) (50%) according the ageing technology (Figure 4c).



**Figure 4.** Principal component analysis of wine spirit aged by the traditional and alternative technologies with chestnut and oak wood during 180 days for: (a) scores of NIR spectral information; (b) loadings of NIR spectral information; (c) standardised scores and loadings of analytical parameters measured. TC—aged in 250 L chestnut new barrels; TL—aged in 250 L oak new barrels; AC—aged in 1000 L stainless steel tanks with chestnut wood staves and micro-oxygenation; AL—aged in 1000 L stainless steel tanks with oak wood staves and micro-oxygenation. AS—alcohol strength (%); MtOH—methanol (g/mL); Ac—acetaldehyde (mg/mL); EtAc—ethyl acetate (mg/mL); 1P—propan-1-ol (mg/mL); 2M1P—2-methylpropan-1-ol (mg/mL); 23M1B—2+3-methylbutan-1-ol (mg/mL); 1B—butan-1-ol (mg/mL).

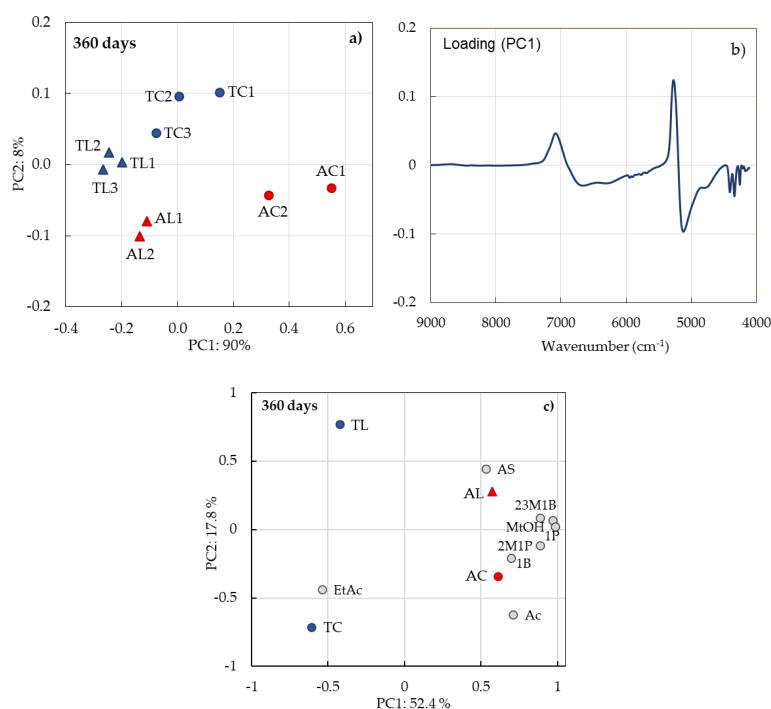
The wine spirit samples after 360 days of ageing and produced with different wood species and ageing technologies were separated across PC1 (360-NIR), which explained 90% of the total variation (Figure 5a). The ageing technology seems to separate the samples across PC2 (360-NIR); however, it only explains 8% of the total variance. The NIR loading plot for PC1 (360-NIR) reveals those previously reported for the other ageing times.

The PCA (360-AP) made with the analytical parameters (Figure 5c) exhibited a clear separation between the ageing technologies across PC1 (360-AP), which explains 52% of the total variation, as observed for 8 and 180 days of ageing.

For 180 days of ageing, it was evident that PC1 (92% of the total variation) allowed the wine spirits to be separated by the wood species used in the ageing process, but more markedly than that observed for 8 days of ageing time, as expected (Figure 4a). In addition, PC2, which explains 5% of the variation, indicates a trend in the sample separation by the ageing technology.

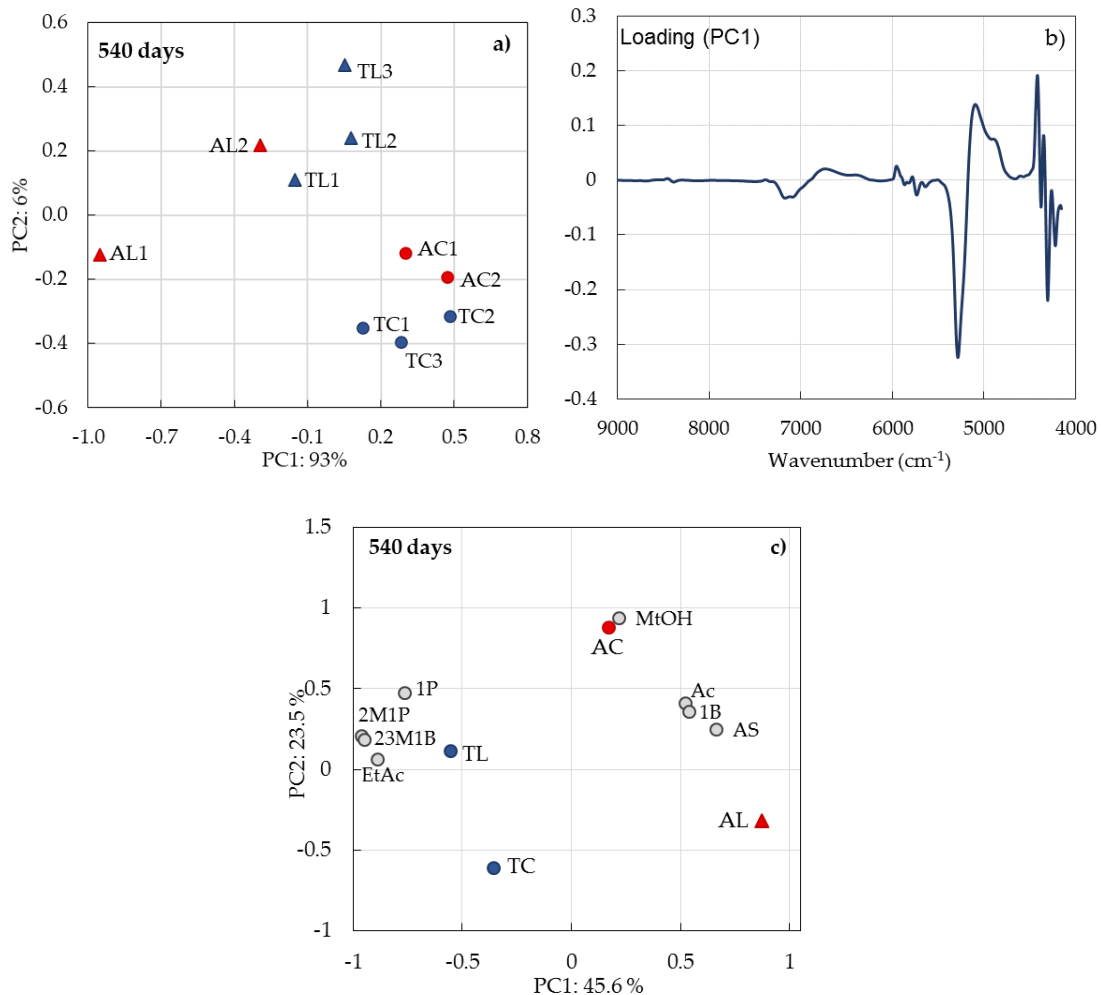
As previously observed, the peak at  $5176\text{ cm}^{-1}$  is the eigenvector influenced by  $-\text{OH}$ , that is, it was affected by the water content of the sample and also by the ethanol (the main component of the wine spirits) and other alcohols. The peaks between  $4300\text{ cm}^{-1}$  and around  $4100\text{ cm}^{-1}$  also had an important contribution (Figures 4b and 5b). This spectral region, as mentioned, is due to the absorbance of methanol and ethanol in higher concentrations, and also sugars and phenolic compounds present in the beverages in lower concentrations, but it was decisive to identify some differences between the samples. Velvarská et al. [46] used the spectral region  $5424\text{--}4000\text{ cm}^{-1}$  for the NIR determination of acetaldehyde. The studies on major volatile compounds and NIR are scarce, however, using Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR), accurate calibration models for these compounds, in similar regions to the calibration models for ethanol and methanol, were performed [47]. Moreover, another study used the same region of ethanol absorption to find a good discrimination between honey spirit samples, using Raman methodology [48].

Concerning the analytical data, a good separation between the samples from different ageing technologies was found after 360 days of ageing (PC1 = 52% of the total variation); high values of major volatile compounds in the wine spirits aged with an alternative technology were found, which are located on the same side of this component (Figure 5c).



**Figure 5.** Principal component analysis of wine spirits aged by the traditional and alternative technologies with chestnut and oak wood for 360 days for: (a) scores of NIR spectral information; (b) loadings of NIR spectral information; (c) standardised scores and loadings of analytical parameters measured. TC—aged in 250 L chestnut new barrels; TL—aged in 250 L oak new barrels; AC—aged in 1000 L stainless steel tanks with chestnut wood staves and micro-oxygenation; AL—aged in 1000 L stainless steel tanks with oak wood staves and micro-oxygenation. AS—alcohol strength (%); MtOH—methanol (g/mL); Ac—acetaldehyde (mg/mL); EtAc—ethyl acetate (mg/mL); 1P—propan-1-ol (mg/mL); 2M1P—2-methylpropan-1-ol (mg/mL); 23M1B—2+3-methylbutan-1-ol (mg/mL); 1B—butan-1-ol (mg/mL).

Figure 6a,b shows the PCA (540-NIR) scores that explain 99% of the total variation (93% for PC1 (540-NIR) vs. 6% for PC2 (540-NIR)). There was a clear separation of the samples according to the wood species used, but at the end of the ageing period, the samples were still separated according to the technology used in ageing.



**Figure 6.** Principal component analysis of wine spirits aged in traditional and alternative technologies in chestnut and oak wood aged for 540 days for: (a) scores of NIR spectral information; (b) loadings of NIR spectral information; (c) standardised scores and loadings of analytical parameters measured. TC—aged in 250 L chestnut new barrels; TL—aged in 250 L oak new barrels; AC—aged in 1000 L stainless steel tanks with chestnut wood staves and micro-oxygenation; AL—aged in 1000 L stainless steel tanks with oak wood staves and micro-oxygenation. AS—alcohol strength (%); MtOH—methanol (g/mL); Ac—acetaldehyde (mg/mL); EtAc—ethyl acetate (mg/mL); 1P—propan-1-ol (mg/mL); 2M1P—2-methylpropan-1-ol (mg/mL); 23M1B—2+3-methylbutan-1-ol (mg/mL); 1B—butan-1-ol (mg/mL).

For 360 and 540 days of ageing, the PCAs explain 98% and 99% (Figures 5a and 6a) of the total variation in both cases and the conclusion is similar to that reported for 6 months. The highest differences were closely related to the wood used in the ageing process. In the initial period of ageing, the effect of the wood was more significant, then the effect of technology, which became more significant. In addition, for the 540 days of ageing, the wine spirits became more complex [9,10] and the eigenvector revealed a higher influence in the region mentioned as important for the PCA (Figures 3b, 4b, 5b and 6b).

The samples from the traditional ageing technology were placed in the opposite part of the PCA, corresponding to higher concentrations of propan-1-ol, 2-methylpropan-1-ol, 2+3-methylbutan-1-ol and ethyl acetate.

As mentioned in Section 3.1, the wood contact during the ageing process leads to wood phenolic compound enrichment in wine spirits, namely those of low molecular weight (Figure 6c). These compounds also influence the NIR spectra and give richer information than the major volatiles when isolated.

Therefore, the results suggested that specific chemical constituents, such as ethanol, water, sugars and phenolic compounds, do not contribute individually to the wine spirit differentiation between the ageing technologies and wood species used.

In the final period of the ageing time, the first two PCs account for 99% of the variation in the spectra (Figure 6a). PC1 (540-NIR) explains 93% of the total variance in the wine spirit samples, and the source of the observed spectral discrimination was found around  $5176\text{ cm}^{-1}$  (Figure 6b). This region was associated with the O–H combinations and O–H first overtones of water and ethanol and C–H stretch first overtones [41,42]. Moreover, at  $4404$  and  $4337\text{ cm}^{-1}$ , two important eigenvectors were observed, which were related to C–H combinations and O–H stretch overtones ascribed to the absorbance of methanol, ethanol, sugars and phenolic compounds present in the wine spirits [8].

#### 4. Conclusions

This study has shown that near-infrared spectroscopy has the potential to discriminate between wine spirits according to the wood species used, as well as the ageing technologies, for a specific ageing time with an accuracy up to 90%.

The ageing technology was more influential than the wood botanical species for the wine spirit volatile composition. At the end of the ageing time (540 days), the alternative technology produced wine spirits with higher levels of alcohol strength, acetaldehyde, 1-butanol and methanol. However, concerning the spectral data, the wood botanical species was more influential than the ageing technology. The spectral regions around  $6859\text{ cm}^{-1}$  and from  $5200\text{ cm}^{-1}$  to  $4200\text{ cm}^{-1}$  were the most representative of the sample differentiation.

Regarding the spectral information, it is possible to conclude that the concentration of volatile compounds plays a crucial role in the wine spirit discrimination according to the ageing technology, the kind of wood and ageing time. Nevertheless, other compounds, such as sugars and phenolics existing at low concentrations in this kind of spirit beverage, are also important discriminators. Further research is needed on this topic.

The identification of the more relevant NIR spectral region, which gave discriminative information, is very important to future studies that will focus on calibration models.

This research is an exploratory study and requires, in the future, more samples of other spirits obtained at industrial scales to validate the results.

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