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Study of a laboratory-scaled new method for the accelerated continuous ageing of wine spirits by applying ultrasound energy

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ABSTRACT

During the ageing of brandies, many physicochemical processes take place involving the distilled spirit and the wood of the casks. Because of these reactions, the polyphenolic content of brandies and their content of organic acids increase with the ageing. These reactions are slow, and the ageing of high-quality brandies takes several years. In this paper, the development of a system that uses the circulation of the wine distillate through encapsulated American oak chips and the application of ultrasound energy with the aim of producing aged wine spirits has been carried out, and the influences of the operation variables over the characteristics of the produced drink have been measured. With that proposal, the influence of different powers of ultrasound, and also the influence of the movement of the liquor through oak chips, was determined first. This way, the results show that higher powers of ultrasound, of nearly 40 W/L, in addition with the movement of the spirit, improve the extraction of phenolic compounds in a 33.94%, after seven days of ageing. Then, applying Youden and Steiner's experimental design, eight experiments of ageing were performed, and the samples obtained by this new method were analysed to obtain information related to their physicochemical and oenological characterisation in order to determine the experimental conditions that produce the best ageing results. This way, the best spirit produced by this new method of ageing is obtained with a high alcoholic strength of the distilled wine and a high quantity of oak chips, and with room temperature and high flow rate. In addition, the presence of oxygen in the sample and the absence of light increase the quality of the produced spirit. Finally, the application of ultrasound energy in large pulses is related with the improvement of two important ageing markers: the intensity of the colour and the TPI. As a last experiment, we applied this ageing method to five varietal spirits. The sensorial analysis of aged samples showed the aged spirits had better ratings than the initial distilled wine.

1. Introduction

Sherry brandy is matured through the traditional criaderas and soleras system [1], during which the spirit extracts its principal components from the interior surface of the oak casks. In result, the polyphenolic content of brandies, as well as their organic acids content, increase with the age [2,3].

The ageing of high-quality brandies can take several years. In Cadiz province, the Specific Designation "Brandy de Jerez" takes a very important place in the economy. Those are the reasons why the producers are looking for other processes that allows them to obtain a similar beverage but in a faster way, in order to develop new products or improve the characteristics of the existing ones. Several authors have published about accelerated methods of ageing that involve the using of ultrasound energy to improve the extraction of the cask compounds with the aim of producing wines [4–7] and brandies [8–10], with positive results.

Ultrasounds (US) are pressure waves with frequencies between 20 kHz and 10 MHz that have been highly used to accelerate extraction processes [4,11–13]. US cause tissue rupture and improving the extraction of intracellular substances into the solvent by cavitation forces. Cavitation is a phenomenon that occurs when we apply high energy ultrasound in a liquid possessing

Abbreviations: TPI, total polyphenol index; USEA, ultrasound energy application; GAE, gallic acid equivalent; ABV, alcohol by volume.

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elastic properties. The expansion of the liquid molecules, by the force of ultrasound, creates bubbles or cavities and can explosively collapse, generating localized pressures to alter the plant tissue, favouring extraction processes of bioactive compounds from these tissues.

Ultrasounds can also produce free radicals during sonolysis solvent: sonication of pure water produces hydroxyl and hydrogen peroxide [14]. This may induce other oxidizing species, participating in some extraction processes based on oxidation reactions, such as ageing of wine and brandy in wood casks [15].

We have found in the bibliography methods of wine and brandy ageing by US which take place in a continuous way [4,5,10]. They have been developed in a stationary way: the initial beverages and the oak chips were introduced in a tank where the ultrasound energy was applied. This system is simple and effective when used on a laboratory scale, but it is difficult to scale if we ageing large quantities of wine or brandy.

In processes of ageing, some factors like the presence of light, the temperature or the presence of oxygen may affect the characteristics of the final product. For that reason, in order to get to know the influence of the experimental conditions over the products of this new method, it was necessary to perform an experimental design.

In 1975, Youden and Steiner proposed a fractional factorial experimental design [16], which allows estimating the influence of seven chosen parameters on the results of analysis by performing eight experiments. This procedure has been applied, e.g. by Fretz et al. to determine the impact of different parameters on the development of flavour compounds in wine [17].

In the present work a new laboratory-scale accelerated method of ageing based in the application of ultrasound energy has been developed. In this process, the extraction of the components that are present in the oak wood is carried out in a dynamic way by making the wine distillate flow through the chips. Then, by using the Youden and Steiner's experimental design, the influences of seven experimental variables over the characteristics of the produced spirit were quantified.

2. Materials and methods

2.1. Reagents

The solvent used in all analysis was distilled water of Milli-Q quality (Millipore, Bedford, USA).

For the Folin-Ciocalteu TPI analysis, the Folin-Ciocalteu reagent and sodium carbonate (Merck, Darmstadt, Germany) were employed. The calibration curve was constructed with gallic acid (Sigma-Aldrich, Madrid, Spain).

For the HPLC analysis, the solvents employed were prepared with trifluoroacetic acid and bis-tris buffer (Sigma-Aldrich, Madrid, Spain) and EDTA disodium dehydrate (Panreac, Barcelona, Spain). The solvents were filtered through membranes of 0.45 μm pore size (Micron Separation, Westborough, USA).

The calibration curves for HPLC were constructed for citric acid monohydrated and acetic acid (Panreac, Barcelona, Spain), tartaric acid, succinic acid and lactic acid (Fluka, Buchs, Switzerland), malic acid (Sigma-Aldrich, Madrid, Spain) and formic acid (Scharlau, Barcelona, Spain).

For the UHPLC analysis, the solvents employed were prepared with acetonitrile (Fisher chem, Loughborough, United Kingdom) and acetic acid (Panreac, Barcelona, Spain). The solvents were filtered through Micron Separation membranes of 0.22 μm pore size (Micron Separation, Westborough, USA).

The calibration curves for UHPLC were constructed for 5-hydroxymethylfurfuraldehyde and furfuraldehyde (Sigma-Aldrich, Madrid, Spain), 4-hydroxybenzoic acid (Chem Fabric, Wolfen, Germany), vanillic acid, 4-hydroxybenzaldehyde, 5-methylfurfuraldehyde, vanillin, *p*-coumaric acid and syringaldehyde (Fluka, Buchs, Switzerland) and syringic acid (Kodak, New York, USA).

2.2. Samples and chips used

The sample employed in the different studies was a wine distillate (usually named as *holanda* in Jerez area) with an alcoholic strength of 65% ABV, obtained from a winery associated to the *Protected Designation of Origin of Jerez-Xérèz-Sherry y Manzanilla de Sanlucar de Barrameda*. This spirit was diluted in order to obtain another sample with the same characteristics but with an alcoholic strength of 40**%**.

The chips used came from the variety *Quercus Alba*, they were medium-sized (64 cm^2/L) and they were pre-treated by applying a medium toast (Nutritec, Barcelona, Spain). Before the experiments, the chips were introduced in Sherry wine as it was described by Schwartz Rodríguez et al. [18], so that the wood could absorb some of the wine's compounds.

2.3. Statistical analysis

All statistical procedures were carried out by using Microsoft Excel 2010 (Redmond, USA).

2.4. Reactor of ageing based in ultrasound energy's application

As it was not possible to find and acquire a commercial system that allows carrying out the proposed experiments, it was necessary to develop it.

Fig. 1 shows a diagram of the used system with its principal parts. The spirit was introduced in a 5 L glass tank that was connected to a glass tube, in which the oak chips were introduced. The glass tube was submerged in a P20 ultrasound bath (J.P. Selecta, Barcelona, Spain) that applied power of 40W/L with a frequency of 40 KHz. In addition, it was connected to an Aquarius Universal 2000 pump (Oase, Hörstel, Germany) that made the spirit return into the tank, with two possible flow rates: 40 L/h or 50 L/h. All the connections were established with silicon tubes.

The temperature of the system was controlled using a recirculating cooler F12 (Julabo, Seelbach, Germany). The ultrasound energy was applied in time intervals that were controlled by a programmed computer system.

2.5. Experimental design

2.5.1. Preliminary studies

Previously to experimental design, three preliminary studies were performed: first, determining the influence of different powers of ultrasound; second, determining the influence of ultrasound pulses and continuous flow, and third, establishing the optimal duration of the ageing process.

In these studies, the conditions used were: 25 °C of temperature and 5 g/L of oak chips. Ultrasound pulses, if applied, were programmed in cycles of time intervals of 6 min and then 24 min of rest, during seven days. For experiments with movement of the spirit, the flow rate was 50 L/h. In addition, the ageing experiments were carried out in presence of light. A sampling procedure was made every day, and their TPI was measured in triplicate.

In the first study, in order to clarify the effect of different powers of ultrasound, two ageing processes have been carried out over 5 L of a 65% ABV *holanda* during seven days, without movement of the spirit: (1) with a power of ultrasound of 40 W/L and (2) with a power of ultrasound of 26.7 W/L. In addition, a reference

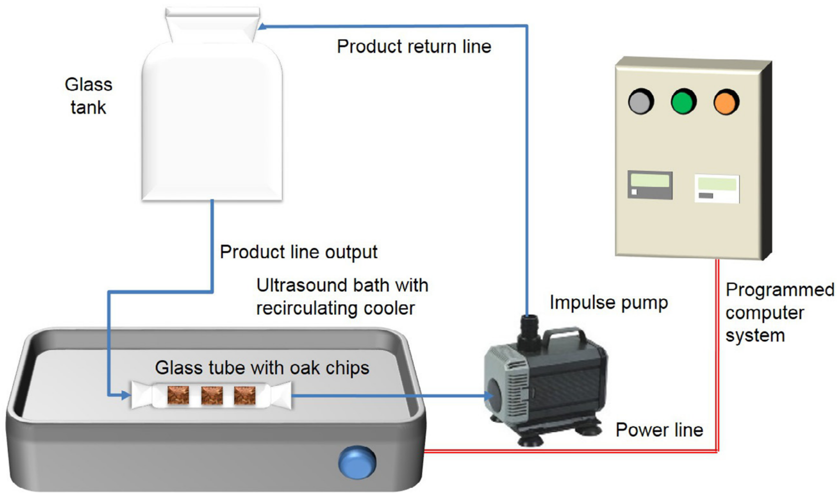

Fig. 1. Accelerated ageing system.

experiment was carried out without ultrasounds application. We tried to carry out an accelerated ageing with higher powers of ultrasound, (60 W/L and 100 W/L), but the refrigerated circulator was not able to keep the temperature of the *holanda* stable and the temperature rapidly increase during the ultrasound energy applications, which may cause an alteration of the results. For this reason these powers of ultrasound were not added to our paper.

In the second study, in order to determine the influence of the application of ultrasound pulses and the continuous flow over the sample, three ageing processes have been carried out over 5 L of a 65% ABV *holanda* during seven days: (1) with continuous flow and with ultrasound pulses at 40 W/L; (2) without flow and with ultrasound pulses at 40 W/L; (3) with continuous flow and without ultrasound pulses. In addition, a reference experiment was carried out without flow and without ultrasounds application.

Finally, in the third study, in order to determine the optimal duration for experimentation, we have accelerated aged during seven days two *holandas*: one of them had an alcoholic strength of 40% ABV, and the other one had 65% ABV.

2.5.2. Studied parameters

All parameters were chosen because their importance in extraction processes (temperature, flow rate, mass of chips per litre of *holanda*, USEA's application) and in oxidation processes (alcoholic strength of *holanda*, light and aeration) that may affect the properties of brandies and spirits.

The ultrasound pulses were applied in cycles in a relation of 1 min of ultrasound pulses every 5 min. This relation was chosen because ultrasound energy could have raise the temperature of the system if there were not time of rest between ultrasound pulses, making the temperature a parameter that would be difficult to control. In order to maintain the relation and to know the effect of ultrasound pulses in the accelerated aging process, this variable was defined as (a) 1 min of ultrasound pulses and then 4 min of rest, and (b) 6 min of ultrasound pulses and then 24 min of rest. These cycles were maintained for 3 day, that is, for 4320 min.

In order to control the seven variables of interest, the accelerated process of ageing was modified in each experiment as follows: For the variable named "alcoholic strength of the *holanda*", the glass tank was filled up with five litres of two different spirits: one of them was at 40% ABV and the other one was at 65% ABV. The variable named as "mass of chips per litre" was controlled by adding two different amounts of chips to the system: 20 g for the low parameter, and 25 g for the high parameter. The temperature was controlled by programming the recirculating cooler. The flow rate was controlled by changing the nominal flow rate of the pump. For the variable named as "USEA's time intervals", the ultrasound bath was programmed in order to apply ultrasound energy in A: 1 min, then 4 min of rest; B: 6 min, then 24 min of rest. The experiments without exposure to light were carried out in darkness by introducing the system in an opaque plastic container specially prepared for the investigation. The variable named as "aeration" was controlled by changing the position of the end of the tube that makes the spirit return into the glass tank: for experiments with aeration, the end of the tube was left over the spirit's surface, so the falling of the liquid would produce air bubbles. For experiments without aeration, the end of the tube was submerged into the spirit's bosom.

2.5.3. Youden and Steiner study

In order to determine the influence of many experimental conditions over the characteristics of the aged spirit produced by this new method a Youden-Steiner experimental design was applied using seven variables of interest with two values: a high value and a low value. Table 1 shows the variables controlled, and their values used, in this study. Eight experiments of ageing were performed in the same order as it is shown in Table 2. The conditions used in these experiments are given by the factorial design of parameters according to the Youden and Steiner's method (Table 2).

Then, the obtained products were analysed with the objective of quantify different oenological parameters of interest, and in order to calculate the differences associated with every variable in each analysis, as it is described in the Youden's procedure [13,14].

To determine the influence of each chosen variable in the final result, the mean of the four values that corresponding to the capital letters (high value) was compared to the mean of the four values that corresponding to the lowercase letters (low value) for each oenological parameter analysed.

The following equation was employed, for example, to evaluate the effect of the aeration in the TPI:

$$Effect\ Aeration_{PTI} = \frac{PTI_{Y1} + PTI_{Y4} + PTI_{Y7} + PTI_{Y8}}{4} - \frac{PTI_{Y2} + PTI_{Y3} + PTI_{Y5} + PTI_{Y6}}{4} \quad (1)$$

where PTI_{Y1} is the result of PTI in sample Y1. Sample Y1 is the sample obtained to apply the experiment factorial combination number

Table 1
Controlled variables, and their values used, for the evaluation of accelerated continuous ageing method of wine spirits.

Controlled variables		High value		Low value	
A/a	Aeration	With aeration	A	Without aeration	a
B/b	Exposure of light	With light	B	Without light	b
C/c	USEA's time intervals	6 min US, 24 min rest	C	1 min US, 4 min rest	c
D/d	Flow rate	50 L/h	D	40 L/h	d
E/e	Temperature	25 °C	E	13 °C	e
F/f	Mass of chips per litre	5 g/l	F	4 g/l	f
G/g	Alcoholic strength	65°	G	40°	g

Table 2
Factorial combination of controlled variables for evaluation by Youden and Steiner's method.

	Factorial combination							
	1	2	3	4	5	6	7	8
Aeration	A	a	a	A	a	a	A	A
Exposure of light	B	B	B	B	b	b	b	b
USEA's time intervals	c	C	c	C	c	C	C	c
Flow rate	d	D	d	D	D	d	d	D
Temperature	e	e	E	E	e	E	e	E
Mass of chips per litre	f	f	F	F	F	f	F	f
Alcoholic strength	G	g	g	G	G	G	g	g
Sample name	Y1	Y2	Y3	Y4	Y5	Y6	Y7	Y8

1. The minimal difference, in absolute value, that must be obtained in each analysis to consider critical a variable was the 10% of the mean calculated in that analysis for all the experiments of ageing.

According to Youden's procedure, obtaining a positive difference for a variable in an analysis means that a high value of that variable is related with a high result measured in that analysis. On the other hand, a negative difference means that a high value of the variable is related with a low result measured in the analysis.

2.6. Total Polyphenols Index determination

TPI was determined using Folin-Ciocalteu method modified by Alonso Borbarán et al. [19], using a Helios Gamma UV–Vis spectrophotometer (UNICAM, Cambridge, United Kingdom). The calibration curve was performed with gallic acid, and the results are expressed in mg GAE per litre of sample. All measurements were performed in triplicate.

2.7. Colour parameters determination

The determination of the colour parameters was performed by visible spectrometry. The sample was introduced directly in a cuvette of 1 mm weigh, and the visible spectrum was measured using a Helios Gamma UV–Vis spectrophotometer, (UNICAM, Cambridge, United Kingdom), in triplicate.

Then, by applying the method proposed by the International Organization of Vine and Wine (OIV) [20], the CIE L*a*b* parameters were obtained using an angle of observer of 10° and the illumination standard D65.

2.8. Organic acids analysis

The quantitative analysis of the organic acids content were carried out using a Millipore HPLC system (Waters, Milford, USA) with a LDC conductimetric detector (Milton Roy, Florida, USA). The separation was conducted in a Rezex ROA-Organic ion-exclusion column (Phenomenex, Torrance, USA).

The chromatographic conditions were: 0.5 mL/min of flow-rate, 40 μL of injection volume, 60 °C of temperature. The mobile phase used was a 2.5 mM solution of trifluoroacetic acid, and a solution consisting of 2.5 mM of trifluoroacetic acid, 20 mM of bis-tris buffer and 100 mM of EDTA was added at the outlet of the column, in order to increase the detection sensibility. These conditions were applied previously by our group with the proposal of determine the concentration of organic acids in brandies [21]. The results were expressed in mg of organic acid per litre of sprit. All measurements were carried out in triplicates.

2.9. Phenolic and furanoid compounds analysis

The quantitative analysis of the phenolic and furanoid content was carried out using an Acquity Waters UHPLC system (Millipore, Milford, USA) with a photodiode array UV-Vis detector. The column used was an Acquity Waters UPLC (BEH C18, 100 × 2.1 mm).

The chromatographic conditions were 0.7 mL/min of flow-rate, 2.5 μL of injection volume, and 47 °C of temperature. The eluents used were A: a solution consisting of 3% acetonitrile, 2% acetic acid, 95% distilled water, and B: a solution consisting of 85% acetonitrile, 2% acetic acid, 13% distilled water. These conditions were applied previously by our group with the proposal of determine the concentration of phenolic and furanoid compounds in brandies [2] and wines [22].

The detection by UV absorption was conducting by scanning between 250 and 400 nm, with a resolution of 1.2 nm, and the quantification was conducted at 255 nm for the derivatives of p-hydroxybenzoic acid and vanillic acid, 320 nm for the derivatives of vanillin, p-coumaric acid and syringaldehyde, and 280 nm for the rest of the phenols and furanoids. The results were expressed in mg of compound per litre of spirit. All measurements were carried out in triplicates.

2.10. Sensory analysis

In order to evaluate the produced spirits, a quantitative descriptive analysis was carried out by applying the methods established by ISO 4121 [23]. Eight trained judges, five men and three women, whose ages ranged between 20 and 55 years, evaluated the samples. Assessment took place in a normalized room at 22 °C [24], using official cups [25] with 15 mL of sample into each one.

The evaluation of every analytical descriptor and visual, gustatory and olfactory impressions were noted down on a normalized tasting sheet, by using a nine-pointed scale (0: absent; 2: light;

4: medium; 6: intense; 8: very intense) for analytical descriptors, and another nine-pointed scale (0: bad; 2: mediocre; 4: acceptable; 6: good; 8: very good) for sensory impressions. Then, by using a two factor ANOVA (judges × samples), the homogeneity of the panel was studied with the proposal of obtaining the maximum information of the sensory analysis. This sensory method had been applied e. g. by Cejudo Bastante [26] over vinegar samples in order to quantify their analytical descriptors.

3. Results and discussion

3.1. Preliminary results

3.1.1. Influence of power of ultrasound

In order to determine the influence of different powers of ultrasound in the extraction process, we have plotted the total polyphenol index versus time (expressed in days of experiments) in the three processes of aging we have done as a first preliminary study.

As it can be observed in Fig. 2a, higher powers of ultrasound are related with higher polyphenol contents, as the TPI obtained after seven days was mildly higher in experiment with 40 W/L of power. These results are consistent with the results obtained by Y. Tao et. al. on their study over the extraction, assisted by ultrasounds, of phenolics from wine lees [6].

As the best results were obtained with a power of ultrasound of 40 W/L, the next experiments were carried out with that power.

3.1.2. Influence of ultrasound pulse and continuous flow

In oder to determine the influence of ultrasonic pulses and the flow of the *holanda* in the extraction process, we have plotted the total polyphenol index versus time (expressed in days of experiments) in the four processes of aging we have done as a second preliminary study.

As it can be observed in Fig. 2b, in seven days the best extraction was obtained in experiment (1), with continuous flow and with ultrasound pulses, followed by experiment (2), without flow and with ultrasound pulses at 40 W/L and experiment (3), with continuous flow and without ultrasound pulses. Finally, the worst extraction was obtained in experiment (3), without flow and without ultrasound pulses. In this way, we can conclude that the movement of the *holanda* and the application of ultrasound pulses have a synergic effect that increases the extraction of the wood's compounds in a 33.94%, as it was expected. On the other hand, the movement of the spirit and the application of ultrasound energy have similar effects separately.

These results are comparable to those obtained by Meullemiestre et al. [27] in their study of the use of ultrasound on solid-liquid extraction of phenolic compounds from maritime pine sawdust waste. They found higher values of total phenolic compounds in the extracts obtained by ultrasound-assisted maceration than those obtained by conventional maceration. Other authors [4,11,12] attribute this fact to the ultrasonic cavitation phenomenon, which is responsible to accelerate extraction processes.

3.1.3. Optimization of the optimal duration for experimentation

When the optimal duration for experimentation was studied, as it is shown in Fig. 2c, the 80% of the TPI measured after seven days was obtained in the first three days, irrespective of the alcoholic strength of the *holanda*. This is the reason why, in the present study, we consider that three days is enough to obtain a reasonably aged product for both *holandas*.

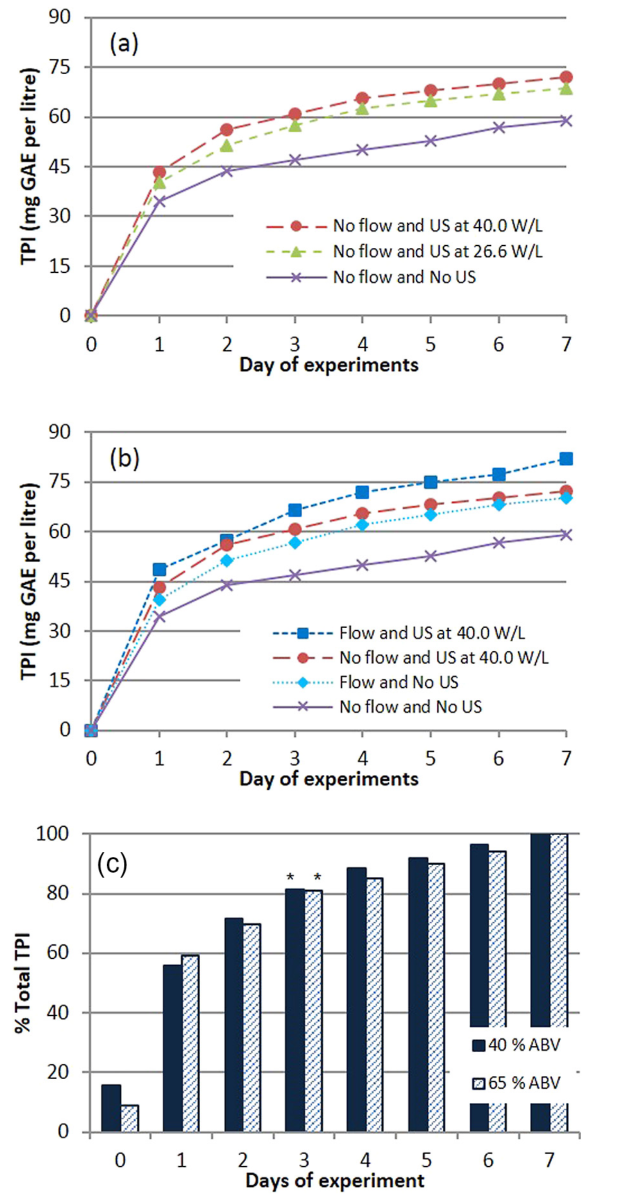

Fig. 2. Preliminary studies of the accelerated method of ageing. (a) Comparison of two extraction studies based on the power of ultrasounds: 40 W/L and 26.7 W/L. A reference experiment without ultrasound pulses application have been added. (b) Comparison of four extraction studies: with continuous flow and with ultrasound pulses (Flow and US), without flow and with ultrasound pulses (No flow and US), with continuous flow and without ultrasound pulses (Flow and No US), and without flow and without ultrasound pulses (No flow and No US). (c) Determination the optimal duration for experimentation: with *holanda* at 40% ABV and with *holanda* at 65% ABV. Note: *First day at which the TPI is the 80% of the total TPI obtained after seven days of ageing.

3.2. Total polyphenol index

Fig. 3 shows Folin-Ciocalteu Index results. The sample Y4 is the one that presents the maximum quantity of polyphenols. The samples Y7 and Y8 present a high TPI value too. These three samples correspond with experiments that were carried out with aeration of the spirit. In these cases, the results are consistent with that indicated by Pueg et al. [15], some polyphenols, like vanilline and syringaldehyde, are obtained from oxidative processes that involve the lignine of the wood and the dissolved oxygen that is present in the liquor.

As we can observe in Fig. 4, all the variables except the alcoholic strength of the *holanda* critically affect the final product. In

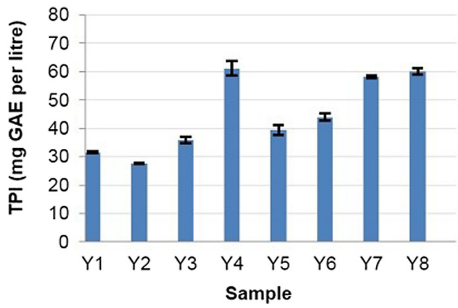

Fig. 3. TPI results obtained for each aged sample in the Youden's procedure.

addition, all the variables, except the exposure of light, affect positively to the presence of polyphenols in the product. These results are consistent with the idea that all critical variables improve the extraction of the wood's compounds. As it is well defined that moderate temperatures, high flow rates, and higher masses of wood per litre of liquor make the extraction process to be carried out faster, provided that there is a minimum of free liquid, as in our case [27]. Increased temperature favours the release of phenolic compounds to increase the diffusivity and solubility of these compounds in the brandy [28]. As it was predicted, higher times of ultrasound pulses also improve the extraction of phenolic compounds.

Finally, as it can be observed, the exposure of light affects negatively to total polyphenol index. This effect is clearly related to the catalytic effect that presents light in the oxidation and polymerization process of certain polyphenolic compounds [29,30].

3.3. Colour parameters

The samples, which were obtained by the eight accelerated processes of ageing, present yellow and green colours, and they drift

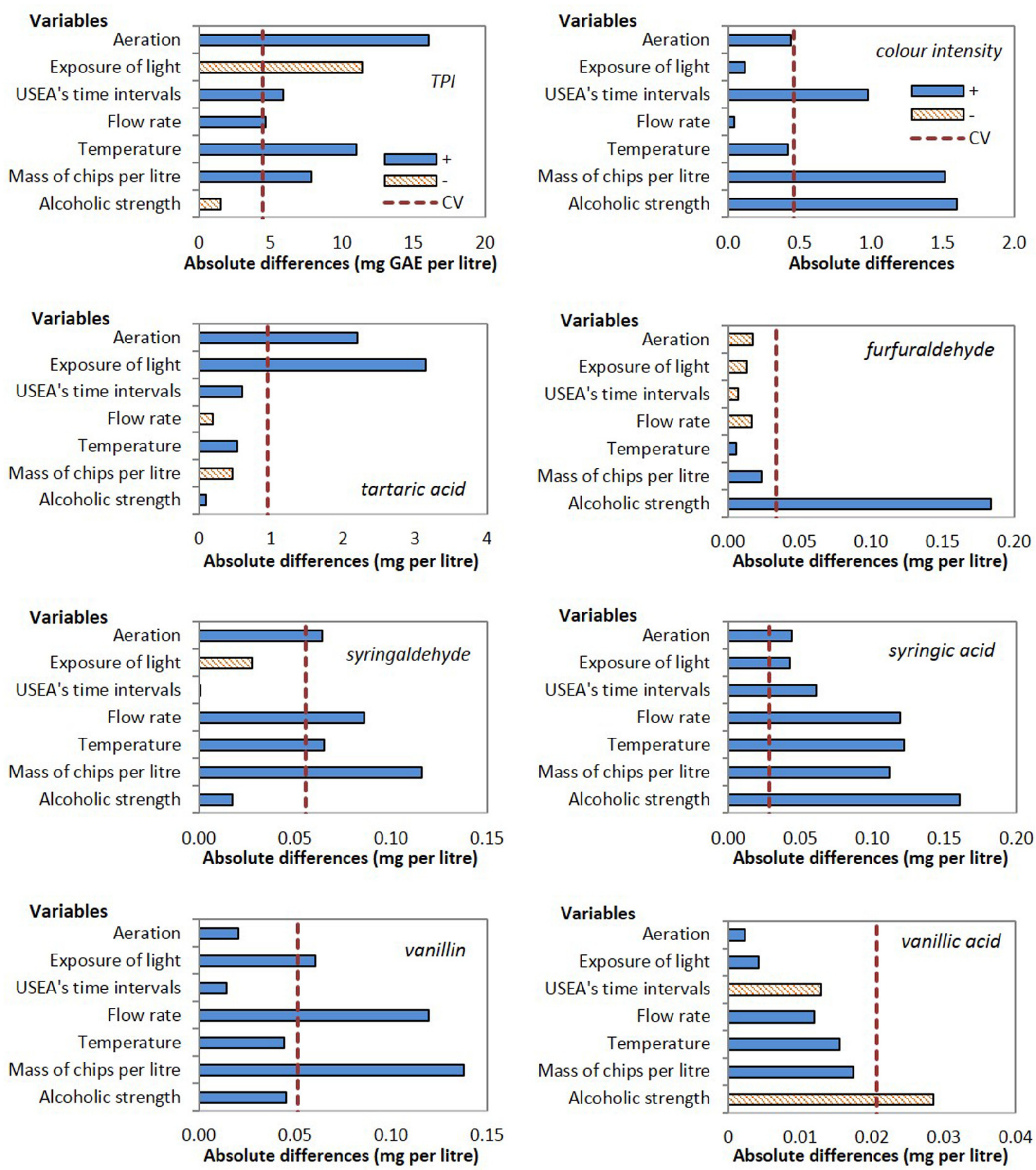

Fig. 4. Youden and Steiner's method applied over TPI results, colour intensity results, tartaric acid's concentration results, and phenols and furanoids compounds' concentration results: furfuraldehyde, syringic acid, syringaldehyde, vanillin, and vanillic acid. (+): The variable affects positively to that parameter; (−): the variable affects negatively to that parameter; CV: value from which it is considered that the studied variable is critical (10% of the mean calculated using the eight experiments of Youden and Steiner's method)

apart of the red and violet tones, they present negative a* parameters (between −1.0 and −0.4), and positive b* values (between 2.5 and 7.0). In addition, they present light colours; the luminosity is almost 100, the maximum value, in every case.

The C* and the H* parameters confirm that the samples tend to a greenish yellow colour. The hue is about 100°, and the chroma is between 2.5 and 7.5. They present few intense colours, almost transparent ones. The sample Y2 presents a different tendency, and it drifts apart the yellow tones, approaching the greenish ones. The samples Y5, Y6 and Y7 group together, reaching a C* parameter of about 5.0. These samples correspond with the experiments that were carried out in darkness.

The variables that critically affect to the chroma of the samples are, in order, the alcoholic strength of the *holanda*, the mass of chips, and the USEA's time intervals, as it is shown in Fig. 4. Although the exposure of light was obtained as not-critical variable, in this case we expected that the exposure of light would decrease the intensity of the colour, as it was described by Espejo et al. [31]. The absolute difference for aeration is at the limit of value that could be considered critical. The presence of small amounts of oxygen enable polymerisation processes that increase the colour of wine aged in wooden barrels [32].

Finally, the hue is not critically affected by any of the studied variables. The hue is a colour parameter that it is affected only on the absorbance of the compounds, and it is not affected by their concentration.

3.4. Organic acids

The organic acids in brandies are mainly obtained by the ageing process because most of them, like the tartaric acid and the malic acid, are present in the wine that is previously used for impregnate the wood of the casks. In addition, some organic acids, like the lactic acid and the acetic acid, are obtained from the distillation process, and they are present in the *holanda* [33].

Only three of the studied compounds were determined in the samples: the lactic acid, the acetic acid and the tartaric acid.

In this case, no variable is critical to the extraction of the acetic acid and the lactic acid, although the exposure of light and the aeration of the *holanda* affect the most to the extraction capacity of the tartaric acid, as it is shown in Fig. 4. This last result is interesting because, although we could not find related information in other papers, we could relate the extraction of tartaric acid with oxidative mediums.

3.5. Phenolic and furanoid compounds

Only five phenolic and furanoid compounds were detected and identified in the samples: furfuraldehyde, vanillic acid, syringic acid, vanillin and syringaldehyde.

The phenolic compounds are mainly obtained in the ageing process, being extracted from the wood. Vanillin and syringaldehyde are produced by oxidation of the lignin that is present in the wood, and the subsequent oxidation produces their carboxylic acids, like the vanillic acid and the syringic acid [15]. On the other hand, furanoid compounds, like furfuraldehyde, are mainly present in the wood because its toast pre-treatment [34].

As it can be observed in Fig. 4, the variable that critically affects to the results, in relation to the concentration of furfuraldehyde, is the alcoholic strength of the *holanda*. Its content ranged from 0.406 mg/l to 0.447 mg/l in the samples obtained from *holandas* at 65% ABV, and in the samples obtained from *holandas* at 40% ABV the concentration vary between 0.219 mg/l and 0.272 mg/l. Samples obtained from *holandas* at 65% ABV exhibit almost double that samples obtained from *holandas* at 40% ABV. When we calculated the furfuraldehyde concentration by absolute ethanol in the samples, this difference is practically nil for all controlled variables.

The critical variables for vanillic acid is also the alcoholic strength, but in this case the variable affects negatively to that parameter.

The mass of chips, the exposure of light and the flow rate are critical variables for the concentration of vanillin. The mass of chips, the flow rate, the temperature and the aeration are the critical variables for the concentration of syringaldehyde. These two cases make sense because the vanillin and the syringaldehyde are compounds that are obtained in the deterioration, produced by oxygen, of the lignin presented in the wood chips, and the critical variables are related to the oxygenation and the turbulent flow of the spirit [15]. A similar behaviour for vanillin, and syringialdehide was observed by Pizarro et al. [35], the level of these compound increased with increasing the chip dose.

Finally, all variables are critical in the presence of syringic acid in the samples. This behaviour may be because this acid is involved in many oxidation and polymerization reactions (Nishimura et al., 1983) and its content may be greatly affected by the conditions of extraction. In Youden samples, the content ranged from 0.448 to 0.716 mg/l, these values are consistent with those obtained by Canas et al. [36] to brandy subject to traditional ageing and the brandy aged with staves.

3.6. Sensory analysis

The results of the sensory analysis can be divided in two ways: on one hand, obtained values associated with visual and olfactory impressions and olfactory analytical descriptors, and on the other hand, the results of gustatory impressions and analytical descriptors.

As we can observe in Fig. 5, the olfactory impression tends to be between the values 4 and 6 ("acceptable" and "good", respectively). The only sample that has a high value of an olfactory defect is the sample Y3. The defect was recognized as "green wood". This smell may be produced by the absence of oxygen in the system, because Y3 is the sample produced with less movement and turbidity of the proposed ones: the experiment was carried out with low flow rate, low USEA's time intervals, and without aeration. In addition, the sample was produced with presence of light. Visual impression was positive in all the cases, and the same colour hues were written down: greenish yellow, almost transparent, with green highlights. Gustatory impression was positive in samples that correspond to experiments that were carried out without light presence. On the other hand, the samples Y1, Y3 and Y4 had worse gustatory impression that the initial *holanda* (samples that were obtained in experiments with presence of light).

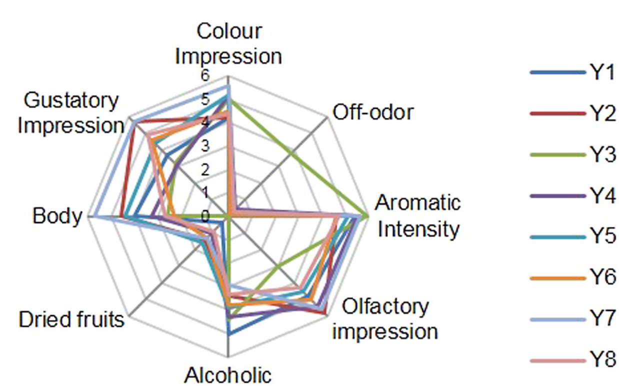

Fig. 5. Visual, olfactory, and gustatory impressions obtained for each aged sample in the Youden's procedure.

Table 3
Variables that critically affects to oenological parameters of interest in Youden and Steiner's study.

Parameters studied	Controlled variables						
	Alcoholic strength	Mass of chips per litre	Temperature	Flow rate	USEA's time intervals	Exposure of light	Aeration
TPI		(+)	(+)	(+)	(+)	(−)	(+)
Colour intensity	(+)	(+)		(+)			
Tartaric acid						(+)	(+)
Furfuraldehyde	(+)						
Syringaldehyde		(+)	(+)	(+)			(+)
Syringic acid	(+)	(+)	(+)	(+)	(+)	(−)	(+)
Vanillin		(+)		(+)		(+)	
Vanillic acid	(−)						

(+): The variable affects positively to that parameter. (−): the variable affects negatively to that parameter.

In general, the aged samples obtained better results than the initial *holandas* by sensory analysis, although the exposure to light seems to be an experimental condition that produces bad taste. In addition, samples that were aged with high quantity of chips present higher aromatic intensities and better visual impressions, as well as greater values of body's descriptor. Finally, samples obtained with high USEA's time intervals present higher notes of dried fruits and lower alcohol flavour.

3.7. Summary of accelerated ageing experiments

According to the results of the Youden's experiments, that are summarized in Table 3, the influences of the experimental conditions, as well as their preferable values, are listed below.

For the alcoholic strength of the *holanda*, the best results are obtained with *holandas* at 65% ABV, as the colour intensity and the extraction of furfuraldehyde and syringic acid are increased with that alcoholic strength.

Regarding to the mass of chips per litre of *holanda*, with 5 g/L of chips the best results are obtained, because the colour intensity, the TPI and the extraction of vanillin, syringaldehyde and syringic acid are increased. In addition, the samples obtained with a high value of this variable present better aromatic intensities and visual impressions.

The best characteristics are obtained with room temperature (at 25 °C), the high studied value, as the TPI, the extraction of syringaldehyde and syringic acid are increased. These results are similar with the obtained with a high flow rate.

For the USEA's time intervals, the application of ultrasound energy in longer pulses is preferable than the most-fragmented application. This conclusion is obtained because the colour intensity, the TPI and the extraction of syringic acid are increased with a time interval of 6 min of ultrasound waves and then 24 min of rest. In addition, high values of this variable produce spirits with higher notes of dried fruits and lower alcohol flavour.

The exposure of light does not present good results, as the TPI and the extraction of tartaric acid and syringic acid are decreased in experiments that were carried out in presence of light, although the extraction of vanillin is increased with the same condition. On the other hand, the aeration of the sample is preferable, as the TPI and the extraction of tartaric acid, syringaldehyde and syringic acid are increased with presence of oxygen.

3.8. Applying the process of ageing over five varietal holandas

In order to verify and to validate the process of ageing, five varietal *holandas*, obtained by the distillation method of spinning cone column, were aged and analysed. The variety of the *holanda* is related with the variety of the grape that was used for the production of the wine that was lately distilled. The five varieties were: Zalema, Palomino fino, Muscat, Colombard, and Pedro Ximénez.

The accelerated conditions of ageing used were 55° of alcoholic strength of the *holanda*, 5 g/L of oak chips, 25 °C of temperature and 50 L/h of flow rate. The ultrasound energy was applied in time intervals of 6 min and then 24 min of rest. The processes were carried out with aeration and in darkness.

The results of the analysis are shown in Table 4 for the determinations of TPI, colour parameters, organic acids content and phenolic and furanoid content, in Fig. 6a for the tasting evaluation, and in Fig. 6b for the gustatory impressions.

Table 4
Oenological parameters obtained for each single-varietal spirit sample.

	Single-varietal spirits				
	Zalema	Palomino	Muscat	Colombard	Pedro Ximénez
	Holanda				
TPI (mg GAE/L)	12.83 ± 2.90	10.15 ± 3.53	9.04 ± 2.29	9.15 ± 2.60	13.50 ± 4.77
Hue	NQ	NQ	NQ	NQ	NQ
Colour intensity	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Acetic acid (mg/L)	138.54 ± 49.49	138.48 ± 22.76	578.32 ± 23.08	232.43 ± 1.17	133.35 ± 15.63
Furfuraldehyde (mg/L)	NQ	0.38 ± 0.01	0.22 ± 0.01	NQ	0.22 ± 0.02
Syringaldehyde (mg/L)	NQ	NQ	NQ	NQ	NQ
Vanillin (mg/L)	NQ	NQ	NQ	NQ	NQ
	Aged Spirit				
TPI (mg GAE/L)	30.80 ± 3.84	31.14 ± 5.38	21.31 ± 2.91	27.12 ± 3.85	29.80 ± 2.91
Hue	96.52 ± 1.22	94.06 ± 0.28	95.72 ± 0.10	96.79 ± 1.45	96.21 ± 1.18
Colour intensity	5.76 ± 0.26	7.44 ± 0.19	5.09 ± 0.07	5.68 ± 0.16	5.59 ± 0.05
Acetic acid (mg/L)	107.23 ± 6.16	345.42 ± 65.07	121.18 ± 4.87	214.57 ± 33.22	143.58 ± 17.08
Furfuraldehyde (mg/L)	0.22 ± 0.01	0.31 ± 0.01	0.24 ± 0.01	NQ	0.43 ± 0.01
Syringaldehyde (mg/L)	0.85 ± 0.04	0.92 ± 0.03	0.93 ± 0.01	0.90 ± 0.02	0.91 ± 0.01
Vanillin (mg/L)	0.37 ± 0.03	0.34 ± 0.00	0.28 ± 0.01	0.32 ± 0.00	0.28 ± 0.00

NQ: Non-Quantifiable.

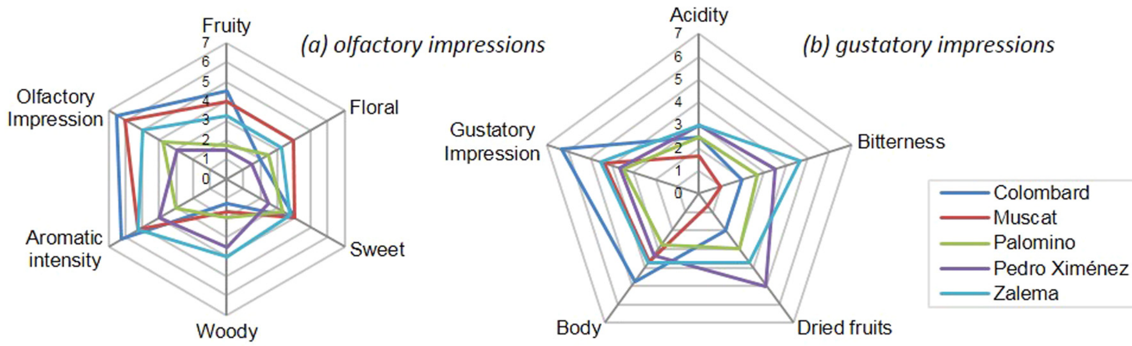

Fig. 6. The most significant notes of (a) olfactory impressions, and (b) gustatory impressions in sensorial analysis of aged varietal *holandas*.

As it can be observed, TPI results, colour intensity results, and concentrations of acetic acid, vanillin, syringaldehyde and furfuraldehyde increased in average with the process of ageing, as it was expected. This is a positive result because wineries look for the rising of these oenological parameters with the ageing.

Tasting evaluation of varietal *holandas* and their aged spirits were made too. Using ranking test [37] no-aged samples and aged samples, have been compared. The aims of this study have been, first, know the assessor's preferences and, then, identify the more significant descriptors of samples.

Organoleptic analyses showed that all varietal *holandas* were very aromatic, particularly *holandas* from Zalema, Colombard and Muscat varieties. We assume that is due to the distillation process used to obtain them. Fig. 6a shows data of *holanda* descriptors with more discriminative capacity.

Aged spirit of variety Colombard presents medium insensitive values of fruity and sweet flavour, mild intensities to floral, oak and bitter, and a pronounced aromatic intensity. Aged spirit of Zalema and Muscat present high values of aromatic intensity, too. These aged spirits also present a differenced floral note, medium fruity, and mild sweet.

In relation to the wood note, Muscat presents a faint taste, and Zalema reaches average values. The bitter taste is perceived intense in Zalema and weak in Muscat. Palomino and Pedro Ximénez brandy are having a worse rating of all evaluated.

Regarding the gustatory impression, these samples were better valued than starting spirits: they have clear notes of ageing in wood, such as wood notes, lower acidity, or a minor sensation alcoholic strength. In this case, Pedro Ximénez brandy is the one with a better value in dried fruit note.

In conclusion, we can say that the use of this new method for the accelerated continuous ageing of wine spirits by applying ultrasound energy allows us to get spirits with characteristics of aged spirits by traditional methods in only three days.

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