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Authentication and Discrimination of Whiskies of High Commercial Value by Pattern Recognition

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Authentication and Discrimination of Whiskies of High Commercial Value by Pattern Recognition

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ABSTRACT

A analytical method for a rapid and non-destructive classification and authentication of whiskies of high commercial value based on trademark and years of aging is presented. Molecular absorption spectroscopy was performed with a minimum manipulation of the sample. Different conditions previous to the chemometric analysis, such as dilution and pH effect were studied. Fifteen commercial trademarks of whiskies with different years of aging were acquired from the local market. The pattern recognition was performed using principal component analysis (PCA), linear discriminant analysis (LDA) and partial least squares discriminant analysis (PLS-DA) to obtain models that allowed the classification and discrimination of whiskies based in trademarks and years of aging respectively. Results show that by LDA, a mean of 99.15% of samples were correctly classified according to trademark. On the other hand, by PLS-DA a 100% of correct classification and discrimination was achieved with several aging labels (6, 8, 12 and 15 years of aging).

KEYWORDS: Whiskies; Trademark; Years of aging; Classification; Discrimination; Pattern recognition.

INTRODUCTION

The authenticity of food and food ingredients is a major issue at present (Arvanitoyannis and Tzouros 2005; Lachenmeier 2007), they are of vital consideration, as there are often news related to food fraud. An authentic product is those that agree exactly with the description provided by the manufacturer. The adulterations of beverage occur not only in the factories, but also in establishments such as bars and restaurants, it affects the credibility of the producers, customer satisfaction and sometimes even health thereof.

The authenticity of the food and drink is an issue of vital consideration today, as they often are disclosed news related to food fraud. Falsifications occur mostly in illegal factories and retail establishments such as bars and restaurants, and affect not only the credibility of the producers, but also the satisfaction of customers and sometimes even health (Nagato et al. 2001). Counterfeiting occurs mostly in beverages of high commercial value, such as imported whiskies. Conversely, other types of drinks are also susceptible, because despite having lower value, because its consumption is high. Traditional strategies are generally based on the chemical analysis which identifies one or more parameters, such as concentration of congeners, trace elements, ethanol, and compared with the set values according to the source and current standards. However, these parameters depending of the factors which difficult the assessment food is genuine. It is obvious then that these methods are not sufficient to achieve safe product identification. (Aylott and Mac Kenzie 2004).

Therefore, standardization, quality monitoring and recognition of adulteration in beverages are concerning features to the industries.

Whisky is a beverage widely targeted by counterfeiters. Generally, adulteration processes are performed by adding a mixture of alcohol (non-drinking or cereal alcohol), water, caramel, dyes and flavours to beverages of lower commercial value or by diluting whisky with water, alcohol or a less expensive whisky.

Whisky is one of the most commonly consumed alcoholic beverages. It is originally from Scotland, and the "Scotch" is among the world the most valued whiskies, being the single malt one of the most exclusive. Although the market share of industrially produced whiskies has been progressively worn by similar products coming from emerging markets, the position market for single malt Scotch whisky has been increasingly booming, apparently defying global economic uncertainty. Indeed, it reached a 19% increase in export in June 2011 (The Scotch Whisky Association 2013).

In accordance with the ancient name "uisge beatha" – water of life – given to them by the Celts, malt whiskys are essentially aqueous-ethanol micro-emulsions that include volatile phenolic compounds and a range of congeners, which are responsible for the sensory profile of whisky. In fact, the phenolic compounds are derived from the burning of peat during the kilning of the malted barley, while the congeners depend on the wood lignin–ethanol interaction that occurs during the maturation processes in casks (Harrison and Priest 2009; Mosedale and Puech 1998). Plain spirited caramel of a specific grade is added simply in order to adjust the consistency of the color (The Scotch Whisky Regulations 2009).

The complex and diverse aromas and flavors of Scotch whisky reflect their place of origin (Jackson 2010).

Each distinctive taste is fundamentally the taste of its own "terroir", that is of the geology, soil, vegetation, climate, water, and vapors of the sea and seaweeds – a sort of story to narrate. While globalization has standardized most drinks, a new generation of consumers is emerging, made up of people who are increasingly looking for drinks that come from somewhere that reflects their place of origin, instead of from nowhere. Traditionally, whiskies can be classified according to their sensory profiles. Panels of trained assessors employing a consensus vocabulary (pungent, smoky, peaty, smooth, woody, sulfury, rancid, etc.) can distinguish Scotch whisky of different product categories (Lee et al. 2001; Jack and Steele 2002).

For an instrumental assessment, authenticity analyses are carried out in specialized laboratories, where use is made of gas chromatography, mass spectrometry, headspace solid-phase micro-extraction, and capillary electrophoresis (González-Arjona et al. 2006; Câmara et al. 2007; Heller et al. 2011). Other olfactory and tasting classifications can be attained by means of innovative e-noses and e-tongues (Wang et al. 2011; Novakowski et al. 2011). Optical spectroscopy is progressively gaining momentum for whisky quality assessment and for product authentication, and is starting to compete with conventional analytical techniques. The ultraviolet spectral range has been successfully exploited for verifying the authenticity of commercial brands (Aylott and MacKenzie 2004), while chromatic analyses extending to the visible have also been experimented (Jones, Deakin and Spencer 2009; Jones, Deakin and Brookes 2009).

More recently, the mid-infrared spectral range has provided a means for detecting counterfeit samples (McIntyre et al. 2011), and Raman spectroscopy excited in the near-

infrared has demonstrated its effectiveness in quality monitoring, especially with regard to aging and ethanol content (Gallignani et al. 1993; Tipparat et al. 2001; Mendes et al. 2003; Nordon et al. 2005; Ashok et al. 2011). Fluorescence spectroscopy, which has been found to be successful in both ethanol determination and spirit classification (Tòthovà et al. 2008; Bozkurt et al. 2010).

In this work, an inexpensive method for the classification of whiskies according to their trademark is proposed, with the additional advantage of being able to discriminate per years of aging for whiskies of high commercial value by using of modern chemometric techniques of pattern recognition and UV-vis spectroscopy.

MATERIALS AND METHODS

Whisky Samples

Fifteen samples whisky were considered: 5 samples were single malts produced in superior distilleries: "*Jhonny Walker" Label Red* (6 years of aging), "*Jhonny Walker" Label Black* (12 years of aging), "*J&B"* (8 years of aging), *"J&B"* (12 years of aging) and "*J&B"* (15 years of aging) – while the 10 remaining samples were utilized for made multivariate models, besides being used for classification to according trademark, in addition to providing higher robustness to multivariate models obtained. Six bottles of each whisky was available, and the samples to measure were extracted from these.

The diversities in whisky characteristics are related to both the geographic origin and the production method. In fact, the quality of malt and water reflects the geographic origin, and the different drying methods and cask types for aging are related to the production method. In addition, the production method itself is strongly linked to the geographic area due to the own traditions.

Sample preparation

All reagents were of analytical grade. Ultrapure water (Millipore UV Synergy System, Billerica, MA, USA) resistivity of 18.2 MΩ cm was used to prepare all solutions. For method development, each whisky sample was submitted to the following treatment: 2 mL of whisky and 10 mL of Clark and Lubs´s buffer pH 12 (Meites 1982) were diluted to 25 mL. Clark and Lubs´s buffer was prepared with solution 0.2 mol L^{-1} KCl (Merck, Darmstadt, Germany) and solution 0.2 mol L^{-1} NaOH (Merck, Darmstadt, Germany).

All dilutions were prepared and tested immediately after the whisky bottles were opened in order to prevent oxidation reactions.

Instrumentation

UV-Vis spectral measurements were taken using an Ocean Optics Model CHEMUSB4000 UV-vis spectrophotometer with a linear CCD array detector (Duiven, The

Netherlands). The pH measurements were taken with a pH meter HORIBA F42 (Tokyo, Japan). The absorbance spectra were obtained from six different bottles of each sample of whisky, with a working range from 200 to 600 nm.

Data analysis

In order to classify the samples whisky according to trademark and discriminate whiskies of high commercial value according to the degree of aging, we made use of principal components analysis (PCA), linear discriminant analysis (LDA), and partial least square discriminant analysis (PLS-DA). These multivariate statistical methods allowed verification of the contribution of each variable to the model and its capacity to discriminate one category from another. The Unscrambler 6.11 software (CAMO-ASA, Trondheim, Norway) was used for the PCA and PLS-DA modeling and LDA was calculated using the Infostat software (Córdoba, Argentina).

RESULTS AND DISCUSSION

Optimal dilutions, pH buffer and curves spectral of the samples of whisky studied

Previous to obtain the multivariate models, a study of spectral behavior of whisky at eight different pH values: 1, 3, 4, 5, 7, 9, 10 and 12 was performed. This study assesses the pH value with the best spectral condition for further use in multivariate models.

Fig. 1 A) show the results obtained from the molecular absorption spectra at different dilutions and Fig. 1 B) for different pH for one sample of whisky. Evaluation allowed to select the 1/10 dilution and pH 12 as appropriate for proceeding with the rest of the beverage, in order to obtain spectra with absorbance values appropriate. For the selection of optimal pH, the different spectral curves were analyzed, which show two peak between 200 and 300 nm to a pH 10 and 12 ; this peak does not appear in the curves to lower pH and could be used for classification and discrimination. The spectral curve at pH 12 is too different from the rest of the curves, besides possessing adequate sensitivity and absorbance values, for this reason; we preferred to select the pH 12 for following analysis.

In Fig. 2 A) shows the absorption spectra for samples overlapped different degrees of aging whisky brand "*Johnny Walker"*, it can be noted that, although the bands are the same in both cases, there is a clear increase in absorbance sample of 12 years of aging with respect to aging than 6 years of aging. Absorption bands present in the spectra arise because the beverage components (congeners such as sugars, esters, higher alcohols and aldehydes; colorants compounds barrels from the save). Whisky major components, water and ethanol have no absorption in the working wavelengths so that one can not determine the water / ethanol from the measurements carried out.

Similarly, the Fig. 2 B) show curves of molecular absorption for samples 8, 12 and 15 years of aging of whisky brand "*J&B"*, absorption increases with increasing years of maturation. This may be because the longer the time the beverage remains in the barrel, the higher will be the concentration of the compounds that are formed during the aging process.

Principal component analysis (PCA)

Principal component analysis (PCA) is a projection method, and dimension reduction of the data can be achieved using a smaller number of principal components than original variables. The principal components are often called underlying components, and their values are the scores. The principal components are, in fact, linear combinations of the original variables. The linear coefficients of the inverse relation of linear combinations are called the component loadings, that is, the correlation coefficients between the original variables and the principal components. PCA is an unsupervised method of pattern recognition in the sense that no grouping of the data has to be known before the analysis. Still, the data structure can be revealed easily and class membership is easy to assign.

The principal components are uncorrelated and account for the total variance of the original variables. The first principal component (PC1) accounts for the maximum of the total variance, the second (PC2) is uncorrelated with the first one and accounts for the maximum of the residual variance, and so on, until the total variance is accounted for.

For practical reasons, it is sufficient to retain only those components that account for a large percentage of the total variance.

In summary, PCA decomposes the original matrix into multiplication of loading and score matrices. The algorithm of PCA can be found in chemometric articles and textbooks (Forina et al. 1986, Wold et al. 1987, Otto 1999). PCA was applied to the matrix formed by the UV-vis spectra corresponding to samples of whisky.

The PCA model was built using 200 variables, corresponding to the absorbance values, from 200 to 400 nm. Using the selected variables, the model was obtained using only 3 Principal Components (PC), which explain the 99.85% of the original information. Fig. 3 shows the classification obtained by PCA, through the scores plot of samples in the bi-dimensional space formed by the first and second PCs.

As can be seen, there are five incipient groups corresponding to the five samples de whisky of high commercial value studied ("*Johnny Walker"*: 6 and 12 years of aging and "*J&B"*: 8, 12 and 15 years of aging). The classification was possible because of the different concentration of several compounds which varies depending on regions (Urbano et al. 2005). UV-Vis spectra contain information regarding to the absorbing moieties, basically, acetaldehyde, methanol, ethyl acetate, n-propanol, isobutanol, 2-methylbutanol, 3-methylbutano (Aylott and MacKenzie 2010). The ultraviolet–visible band, which represents the congener information, is the same one used by multivariate models for classification and discrimination. Other more complex molecules (e.g., vanillic acid, syringic acid, vanillin, syringaldehyde, gallic acid, coniferaldehyde, ellagic acid, escopoletin and 5-hydroxymethyl furfural, a congener mainly associated with caramel) also show moderate or strong interaction in the visible range. The composition of these compounds is therefore the principal factor modulating the color of whiskies and some taste characteristics, and therefore, in the absorbance values in the visible range (Aylott and MacKenzie 2004).

Linear discriminant analysis (LDA)

LDA, similarly to PCA, can be considered as a dimension reduction method. For feature reduction, we need to determine a smaller dimensión hyperplane on which the points will be projected from the higher dimension space. Where as PCA selects a direction that retains maximal structure in a lower dimension among the data, LDA selects a direction that achieves maximum separation among the given classes. The latent variable obtained in this way is a linear combination of the original variables.

This function is called the canonical variate, and its values are the roots. If we have *k* classes, *k* - 1 canonical variates can be determined. In the method of LDA a linear function of the variables is to be sought, which maximizes the ratio of between-class variance and minimizes the ratio of within-class variance. Finally, a percentage of correct classification is given. A variant of this method is the stepwise discriminant analysis that permits the variables with a major discriminant capacity to be selected. The description of the LDA algorithm can be found in references (Vandeginste et al. 1998, Otto 1999).

LDA is a supervised learning method, in which a discrimination model is constructed using the data of the objects pre-categorized into known categories (the training data set) and the calculation algorithm is trained to discriminate the objects (e.g. whisky samples) into the given categories (classes) (Sharma 1996; Otto 1999).

The goal is to find the allocation rule which gives the highest percentage of correct discrimination. The LDA procedure maximizes the variances between categories and minimizes the variances within categories (Adams 1995).

In order to measure the discrimination power of the analytical data, the number of individuals correctly predicted to belong to the assigned group is calculated; this number is expressed as a percentage of the group population: *Classification power = (number of correctly classified individuals/sample population) · 100* (Sperková and Suchánek 2005).

The LDA model was constructed using the original variables that were used in PCA. The samples were organized into categories according to trademark and years of aging. Fifteen random samples were used to build the model by cross validation. Table 1 shows the results of the LDA model, evidencing good fitting, which wear obtained two discriminant functions that correctly classifies 99.15% to according trademark and 100% of the samples analyzed by years of aging.

Partial least square discriminant analysis (PLS-DA)

Partial least squares (PLS) was originally designed as a tool for statistical regression and nowadays is one of the most commonly used regression techniques in chemistry (Wold 2001). It is a biased method and its algorithm can be considered as an evolution of the non-linear iterative partial least squares (NIPALS) algorithm.

The PLS algorithm has been modified for classification purposes and widely applied in several fields, such as medical, environmental, social, and food sciences. In this order (Barker and Rayens 2003), showed that partial least squares-discriminant analysis (PLS-DA) corresponds to the inverse-least-squares approach to LDA and produces essentially the

same results but with the noise reduction and variable selection advantages of PLS. Therefore, if PLS is somehow related to LDA, it should be applied for dimensión reduction aimed at discrimination of classes, instead of PCA.

The theory of PLS algorithms (PLS1 when dealing with one dependent *Y* variable and PLS2 in presence of several dependent *Y* variables) has been extensively studied and explained in the literature: PLS-DA is essentially based on the PLS2 algorithm that searches for latent variables with a maximum covariance with the *Y* variables. The main difference is related to the dependent variables, since these represent qualitative (and not quantitative) values, when dealing with classification. In PLS-DA the *Y* -block describes which objects are in the classes of interest.

The solution to this is to unfold the class vector and apply the PLS2 algorithm for multivariate qualitative responses (PLS-DA). For each object, PLS-DA will return the prediction as a vector of size G, with values in-between 1 and 5: a g-th value closer to one indicates that the object does not belong to the g-th class, while a value closer to five the opposite. The object can be assigned to the class with the maximum value in the Y vector or, alternatively, a threshold between one and five can be determined for each class.

In this technique, each sample in the calibration set is assigned a dummy variable as a reference value set as "*J&B"* = 1 (8 years of aging), "*J&B"* = 2 (12 years of aging), "*J&B"* = 3 (15 years of aging), "*Jhonny Walker"* (6 years of aging) = 4 and "*Jhonny Walker"* = 5 (12 years of aging).

The PLS-DA model was developed using the same variables than PCA, which served as a variable preselecting tool (Hernandez et al. 2005; Louw et al. 2009).

The PLS-DA model was obtained using 3 Principal Components Discriminant (PCD), which explained a 99.5% of information from the original spectral variables. Fig. 4 shows the score plot of the first three PCDs of the PLS-DA model. It is similar to the PCA score plot; however, separation of years of aging more obvious.

This might be explained from the fact that the PLS-DA algorithm maximizes the variance between groups rather than within the group (Kemsley 1996). With this 3 PLS components discriminants for the model, the observed-predicted discrimination plot for whiskies was obtained, showing an r^2 coefficient = 0.998, abscise=0.012 and slope=0.994, which suggest a good fit of the model (ideal values of r^2 = 1, abscise = 0 and slope = 1).

Then the percentage of discrimination was obtained according to years of aging (Table 2) obtaining the same results as LDA.

CONCLUSIONS

The combination of molecular absorption spectroscopic data, suitably merged and processed by means of multivariate data analyses, demonstrated the possibility of classification whiskies for trademark and discriminate according at years of aging for whiskies of high commercial value.

The results of this work show that the combinations of full-spectra spectrophotometric methods with chemometric data analysis for the quality control of whiskies of high commercial value can be implemented immediately in the routine analysis.

Also this method can be used without previous chemical separations using only a UV spectrophotometer: for this reason it is simple, rapid and inexpensive, can be used as an alternative procedure for laboratories of routine analysis and quality control laboratories of minor complexity.

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Conflict of Interest Miguel Ángel Cantarelli declares that he has no conflict of interest. Silvana Mariela Azcarate declares that she has no conflict of interest. Marianela Savio declares that she has no conflict of interest. Eduardo Jorge Marchevsky declares that he has no conflict of interest. José Manuel Camiña declares that he has no conflict of interest.

This article does not contain any studies with human or animal subjects.

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FIGURES CAPTIONS

Figure 1- A) Spectral curves of whisky sample at different dilutions and B) spectral curves at eight different pH values.

Figure 2- A) Absorption spectrum overlapping of "*Jhonny Walker" Red Label* whiskies: (6 years of aging) and *Black Label* (12 years of aging) and B) Absorption spectrum overlapping of "*J&B"* whiskies (8, 12 and 15 years of aging).

Figure 3- Score plot for the classification of whiskies according to years of aging.

Figure 4- PLS-DA 3D score plot for 5 samples of whisky of high value commercial to according years of aging: "*Jhonny Walker*" Red Label whiskies: (6 years of aging), Black Label (12 years of aging) and "J&B" whiskies (8, 12 and 15 years of aging).

TABLES

Table 1. Results of the discrimination ability of the LDA model according to years of aging for "*Jhonny Walker*" and "*J&B*" brands.

Table 2. Results of the discrimination ability of the PLS-DA model for samples of whiskies of high value commercial to according to years of aging.

Figure

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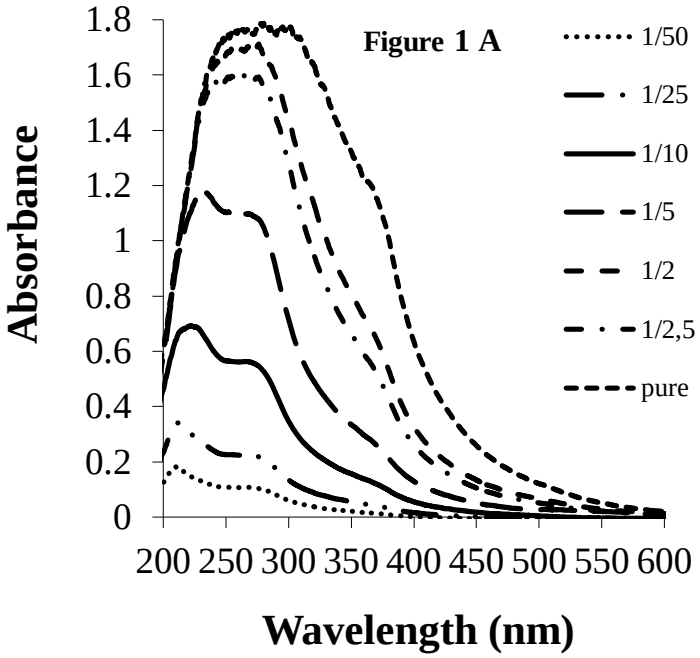

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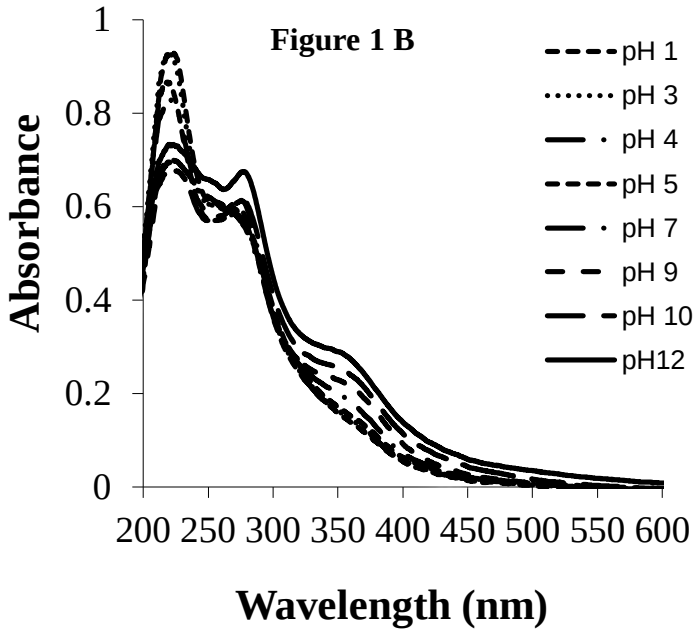

Figure

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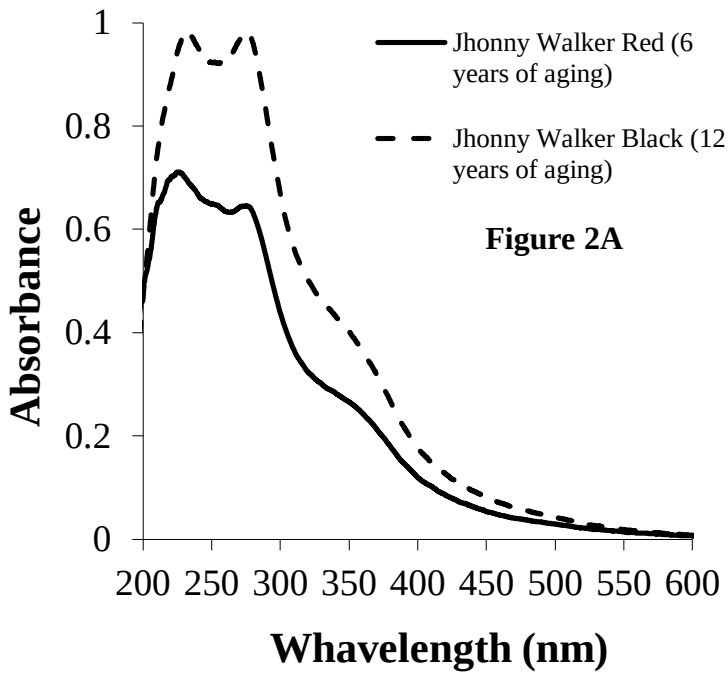

Figure 2A

Figure

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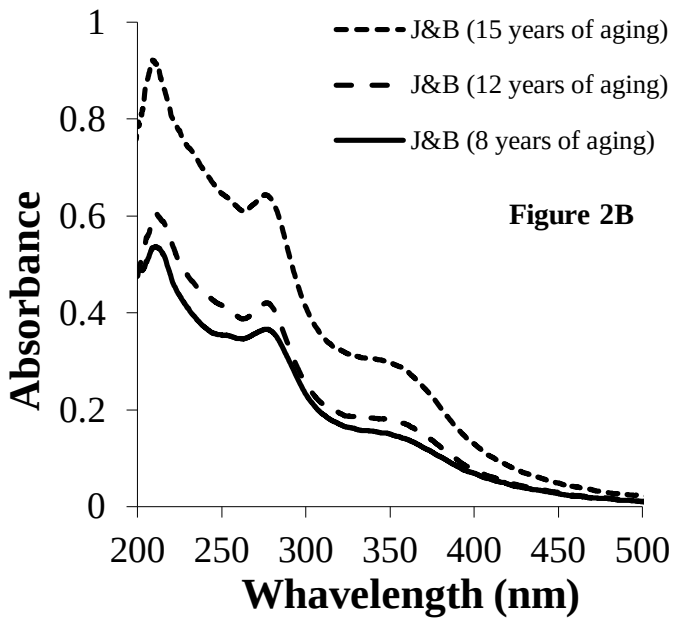

Figure 2B

Figure

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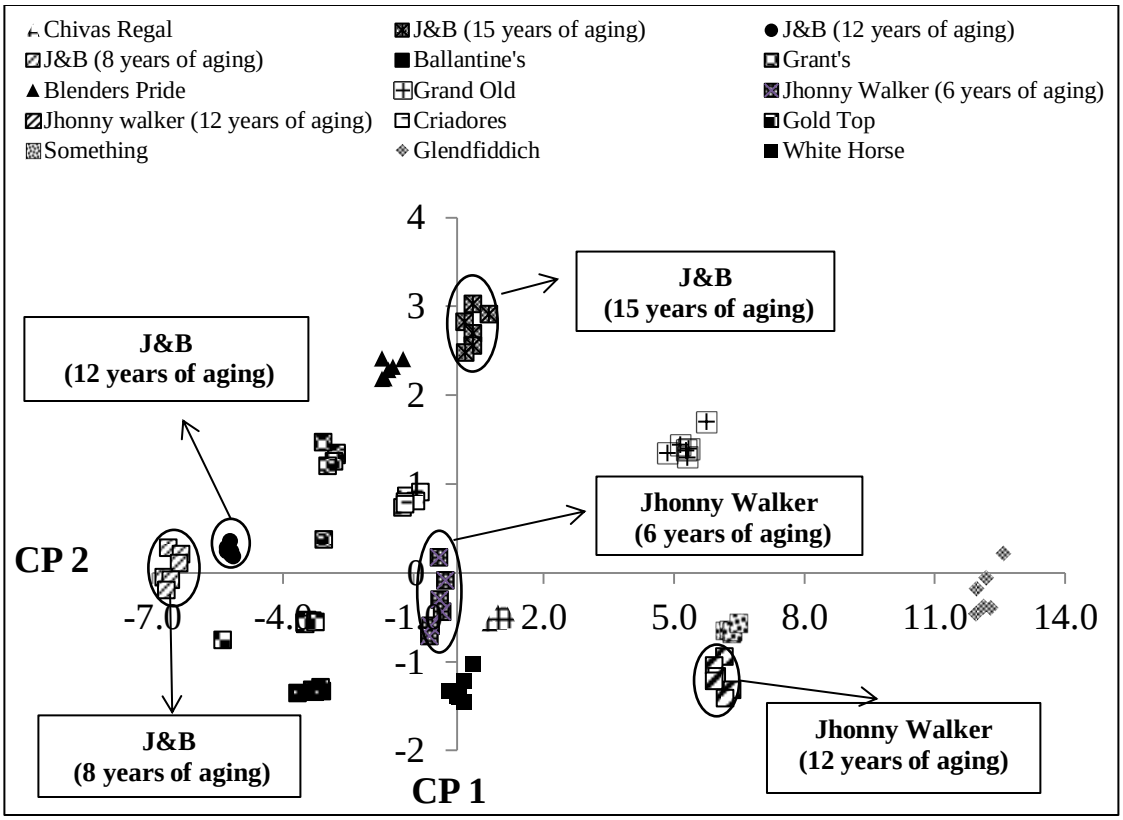

Figure
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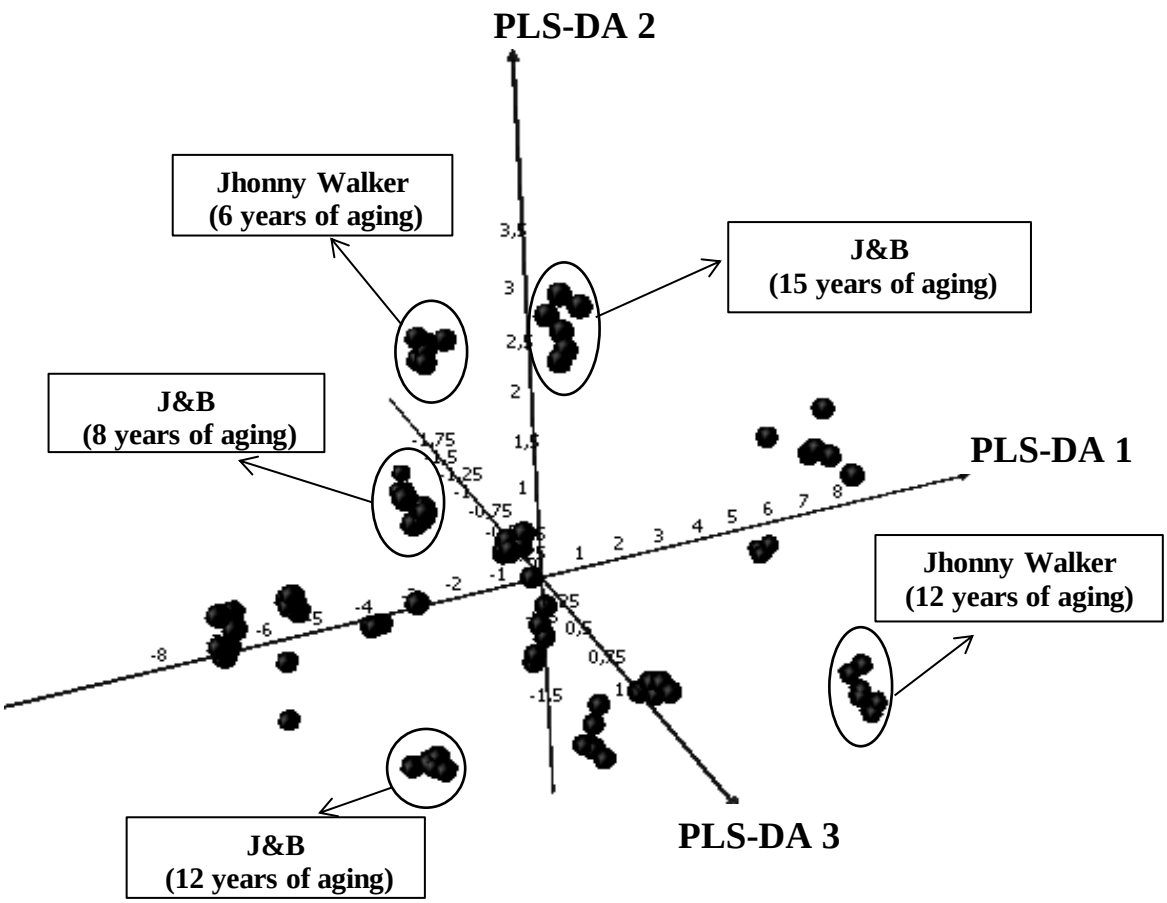

Tables

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Table 1. Results of the discrimination ability of the LDA model according to their trademark and for the years of aging for Johnnie Walker and J&B brands.

Date set	Ballantine's	Blenders Pride	Chivas Regal	Criadores	Glendfiddich	Gold Top	Grand old	Grand's	Johnny W. (6 years)	Johnny W. (12 years)	J&B (6 years)	J&B (12 years)	J&B (15 years)	Something	White Horse	Total	% correct
Ballantine's	6	0	0	0	0	0	0	**0**	**0**	**0**	**0**	**0**	**0**	0	0	6	100.00
Blenders Pride	0	6	0	0	0	0	0	**0**	**0**	**0**	**0**	**0**	**0**	0	0	6	100.00
Chivas Regal	0	0	6	0	0	0	0	**0**	**0**	**0**	**0**	**0**	**0**	0	0	6	100.00
Criadores	0	0	0	6	0	0	0	**0**	**0**	**0**	**0**	**0**	**0**	0	0	6	100.00
Glendfiddich	0	0	0	0	5	0	0	**0**	**0**	**0**	**0**	**0**	**0**	0	0	5	83.33
Gold Top	0	0	0	0	0	0	0	**0**	**0**	**0**	**0**	**0**	**0**	0	0	6	100.00
Grand old	0	0	0	0	0	6	0	**0**	**0**	**0**	**0**	**0**	**0**	0	0	6	100.00
Grant's	0	0	0	0	0	0	6	**0**	**0**	**0**	**0**	**0**	**0**	0	0	6	100.00
Jhonny W. (6 years)	0	0	0	0	0	0	0	**6**	**6**	**0**	**0**	**0**	**0**	0	0	6	100.00
Jhonny W. (12 years)	0	0	0	0	0	0	0	**0**	**0**	**6**	**0**	**0**	**0**	0	0	6	100.00
J&B (6 years)	0	0	0	0	0	0	0	**0**	**0**	**0**	**6**	**0**	**0**	0	0	6	100.00
J&B (12years)	0	0	0	0	0	0	0	**0**	**0**	**0**	**0**	**6**	**0**	0	0	6	100.00
J&B (15 years)	0	0	0	0	0	0	0	**0**	**0**	**0**	**0**	**0**	**6**	0	0	6	100.00
Something	0	0	0	0	0	0	0	**0**	**0**	**0**	**0**	**0**	**0**	6	0	6	100.00
White Horse	0	0	0	0	0	0	0	**0**	**0**	**0**	**0**	**0**	**0**	0	6	6	100.00
Total	6	6	6	6	5	6	6	**6**	**6**	**6**	**6**	**6**	**6**	6	6	90	**99.15**

Table 2. Results of the discrimination ability of the PLS-DA model for samples of whiskies of high value commercial to according to years of aging.

Data set	**J&B (6)[a]**	**J&B (12)[a]**	**J&B (15)[a]**	**Jhonny W.(6)[a]**	**Jhonny W.(12)[a]**	% correct
J&B (6)	6	0	0	0	0	100
J&B (12)	0	6	0	0	0	100
J&B (15)	0	0	6	0	0	100
Jhonny W.(6)	0	0	0	6	0	100
Jhonny W.(12)	0	0	0	0	6	100
Total	6	6	6	6	6	100

[a]years of aging