TECHNICAL COMMUNICATIONS

Spectrophotometric Determination of Caramel Content in Spirits Aged in Oak Casks

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A new methodology was developed for determination of caramel in spirits aged in oak casks. The method is based on differences between the electronic spectra of oak aqueous alcoholic extracts and caramel solutions in the same solvent. The data were treated by 2 different approaches: the simplest one was based on the plot of caramel concentration versus the ratio of absorbance at 210 and 282 nm; the other was based on a partial least squares (PLS) calibration model using the first derivative of the spectral data. Both methodologies were applied to analysis of 159 aged spirit samples. The mean caramel content of several Brazilian sugar cane spirits (cachaça) and all United States whiskies was smaller than that of Scottish whiskies and other brandies from several countries. Correlation was good between caramel concentrations for the same sample calculated by the 2 methods. The uncertainties following PLS and the absorbance ratio method were 0.01 and 0.03 g/L, respectively, for a sample containing 0.45 g/L caramel. Treatment of UV-VIS spectra by pattern recognition using hierarchical clustering analysis and principal components analysis allowed discrimination of the samples as a function of their caramel content. It was possible to distinguish U.S. whiskies from other whiskies, but a clear differentiation among Brazilian cachaças as a function of their geographic origin was not feasible. Small caramel quantities as low as 0.08 g/L were clearly detected by these methodologies.

Spirits stored in oak casks develop an amber or golden-brown color, which is attributed to the extraction of phenolic compounds from the oak casks. In many countries, except the United States (1), oak casks are reused more than once for maturation; in some cases, with beverages like sherry, the color intensity of the final product decreases during the same period of maturation. The golden-brown color can be mimicked by addition of a suitable amount of caramel or paxarette (2), a brown syrup, into a freshly distilled spirit. However, caramel is mainly used by distillers to ensure color consistency of their aged products (3). Indeed, caramel is a factor which decreases the volatile sulfur compound concentration in spirits (4). Thus, reliable caramel determination is important not only to ascertain the beverage caramel content, but also to detect adulteration of spirits and oak extracts.

Considering the chemical composition complexity of caramel (5, 6), its quantitation is not straightforward in food product analysis. A quantitative analysis of caramel in spirits can be performed by selective extraction using Marsh reagent as indicated in the AOAC official method (7). However, this methodology (4) is subject to interference by synthetic dyes and substances liberated from noncharred oak (7).

Based on the fact that furfural (F) is extracted from oak staves (8) and 5-hydroxymethylfurfural (HMF) is the main compound of caramel (9), a liquid chromatographic (LC) method has been proposed (10, 11) to detect caramel in spirits based on the F/HMF concentration ratio. According to this method, this ratio is >1.0 for samples without caramel and <1.0 for samples containing caramel. However, this approach cannot be applied to the Brazilian sugar cane spirit (cachaça), because even in nonaged caramel-free cachaças, the F/HMF concentration ratio is <1.0 for many samples (12).

The cachaça production is around 2 billion liters per year (13), and there is a growing interest in improving product quality through consistent maturation procedures and the establishment of up-to-date chemical quality control. During our investigation of the caramel content in aged cachaças, spectral differences were noted between aqueous ethanol extract of oak and caramel solutions in the same solvent.

Thus, based on spectrophotometric measurements, 2 methodologies were developed to quantitate caramel in spirits aged in oak casks. The first uses the ratio between absorbance values for 2 different wavelengths (210 and 282 nm), and the second is based on multivariate calibration through partial least squares (PLS) using the first derivative spectra. Pattern recognition by hierarchical clustering analysis (HCA) and principal component analysis (PCA) was performed to discriminate the samples as a function of their caramel content.

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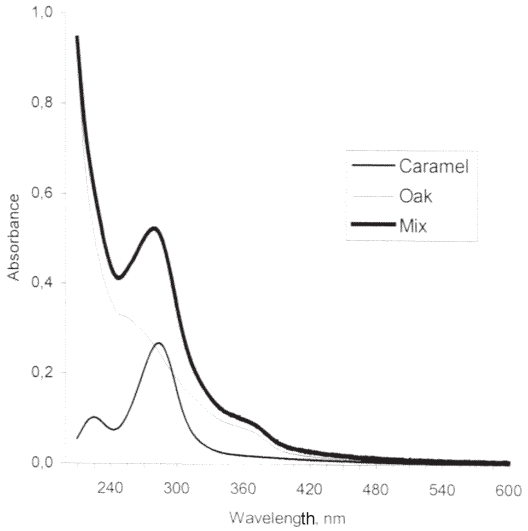

Figure 1. Electronic spectra of additive-free sucrose caramel, a cachaça aged in an oak cask for 18 months, and a mixture of both (samples diluted 10-fold with ethanol–water, 1 + 1, v/v).

Experimental

Samples

(**a**) *Aqueous ethanol solution*.—A mixture of water and ethanol (1 + 1, v/v) was used to prepare oak extracts and dilute samples.

(**b**) *Free caramel spirits*.—Samples of 16 Brazilian caramel-free cachaças were aged in 180 L oak casks to establish spectral characteristics of the oak extract. These samples were supplied and certified by Indústrias Müller de Bebidas Ltda. (Pirassununga, São Paulo, Brazil).

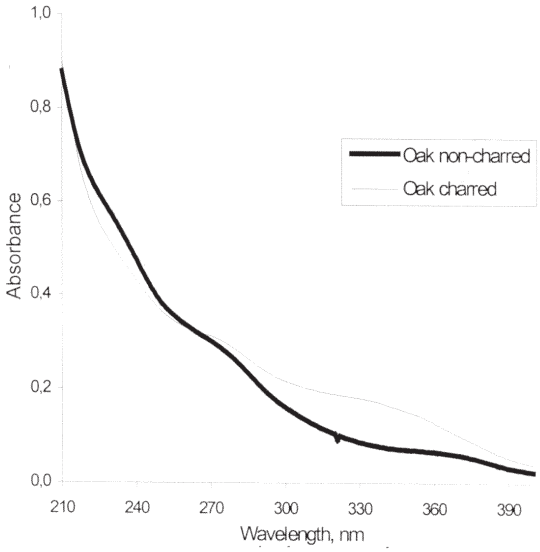

Figure 2. Electronic spectra of aqueous ethanol solutions of a charred and noncharred oak extract.

Table 1. Recovery of caramel from 5 aged cachaças spiked with caramel using the A_{210}/A_{282} ratio

	Samples					
Added caramel, g/L	1	2	3	4	5	Average
0.10	0.10	—[a]	0.15	0.19	0.11	0.14 ± 0.04
0.20	0.24	0.18	0.30	0.27	0.25	0.25 ± 0.04
0.30	0.33	0.35	0.41	0.36	0.31	0.35 ± 0.04
0.40	0.42	0.39	0.44	0.44	0.42	0.42 ± 0.02
0.50	0.55	0.47	0.56	0.57	0.50	0.53 ± 0.04
1.00	0.99	1.14	1.09	1.12	1.04	1.08 ± 0.06
1.50	1.45	1.23	1.55	1.37	1.65	1.45 ± 0.16
2.00	2.00	1.81	1.92	1.78	1.99	1.90 ± 0.10

[a] —, Missing data.

(**c**) *Commercial samples*.—A total of 159 samples were analyzed: Brazilian cachaças (São Francisco, Herr Blumenau, Jequity, Milagre de Minas, Vat 45, Parati, Paula, Ypioca, Box 32, Nega Fulo, Muller, Bocaina, Catedral, Colonial, Morretes, Sapupara, Bosco 12, Bosco 24, Bosco 36, Bosco 48, Capitão das Gerais, Velha Aroeira, Bela Vista, Terra Brasilis, Beija-Flor, Caju, Cana Verde, Dandiz, Koloniale, Salinas, Carvalheira, Mangueira, Águas Quentes, Chapéu de Palha, Cabeceira, Abaíra, Córrego Azul, Rainha, Espírito de Minas, Ancona, Moenda de Ouro, Germana, Armazém Vieira, Alambari, Guaramiranga, Coqueiro, Berro, Moribondo, Três Coronéis, Vale Verde, Serrote, Rainha da Lavoura, Bodocó, Pinga de Palmital, Curupá, Ginete, Boazinha, Setembrina, Tiquara); Scottish whiskies (Cardhu, Chivas Regal, Grant's, Laphroaig, Tiller's, Glenfiddich, Logan, Ballantine's, St. James, Bell's, Johnny Walker Green Label, Johnny Walker Red Label, Passport, Black White, Glendro, 100 Pipers, Queen Anne, Robbie Dhu, White Horse, Dalmore, White & Mackay, Glenrothes, Macallan, Balvenie); U.S. whiskies (Old Grand Dad, Jack Daniel's, Jim Beam,

Table 2. Experimental and predicted caramel concentrations in g/L for PLS model[a], standard error of prediction (SEP), and correlation coefficient (r)

Standards	Known	Predicted	Residual
ST0	0.00	0.01	–0.01
ST1	0.08	0.07	0.01
ST2	0.45	0.44	0.01
ST3	0.80	0.80	0.00
ST4	1.18	1.19	–0.01
ST5	1.65	1.63	0.02
	SEP 0.01	R^2 0.9999[a]	

[a] One latent variable.

Table 3. Comparison of results of caramel obtained from 2 methods (partial least squares and A_{210}/A_{282} ratio)[a,b]

Sample	PLS	A_{210}/A_{282}	Sample	PLS	A_{210}/A_{282}	Sample	PLS	A_{210}/A_{282}	Sample	PLS	A_{210}/A_{282}
BC1a	0.16	0.21	BC12	0.06	0.01	BC29	0.02	–0.05	BC48	0.04	0.5
BC1b	0.05	0.03	BC13a	0.05	0.0	BC30	0.03	0.08	BC49	0.04	–0.02
BC1c	0.05	0.02	BC13b	0.05	0.00	BC31	0.04	0.03	BC50	0.06	–0.02
BC1d	0.05	0.03	BC14a	0.09	0.04	BC32	–0.03	0.11	BC51	0.07	0.28
BC1e	0.05	0.04	BC14b	0.09	0.05	BC33a	0.14	0.1	BC52	0.05	–1.04
BC2a	0.09	0.12	BC14c	0.09	0.11	BC33b	0.12	0.11	BC53	0.05	0.05
BC2b	0.08	0.05	BC15	0.14	0.11	BC33c	0.12	0.14	BC54	0.05	0.13
BC2c	0.08	0.03	BC16a	0.11	0.09	BC34a	1.04	1.19	BC55	–0.22	–0.04
BC3a	0.05	0.11	BC16b	0.12	0.07	BC34b	1.11	1.26	BC56	0.03	0.03
BC3b	0.04	–0.06	BC16c	0.13	0.12	BC35	0.14	0.17	BC57	0.03	0.04
BC4a	0.20	0.18	BC16d	0.11	0.10	BC36a	0.07	0.05	BC58	0.48	–0.02
BC4b	0.21	–0.03	BC17	0.05	0.00	BC36b	0.07	–0.01	BC59	0.03	0.07
BC4c	0.08	0.11	BC18	0.09	–0.02	BC37	0.16	0.26	BC60	0.14	0.12
BC5	0.11	0.18	BC19	0.13	0.01	BC38	0.14	0.05	BC61	0.04	0.05
BC6a	0.04	0.07	BC20	0.15	0.03	BC39a	0.07	0.15	BC62	0.16	0.04
BC6b	0.05	0.01	BC21a	0.04	0.05	BC39b	0.09	0.11	BC63	0.15	0.31
BC7	0.18	0.20	BC21b	0.03	–0.02	BC40a	0.05	0.04	BC64	0.29	0.02
BC8a	0.11	0.14	BC22a	0.04	0.07	BC40b	0.05	–0.01	BC65	0.07	0.06
BC8b	0.06	0.08	BC22b	0.04	0.00	BC41	0.07	0.03	BC66	0.04	–0.01
BC8c	0.03	–0.03	BC22c	0.04	–0.01	BC42	–0.22	–0.12	BC67	0.12	0.29
BC8d	0.10	0.08	BC23a	0.06	0.09	BC43a	1.57	1.86	BC68	0.62	0.53
BC9a	0.46	0.48	BC23b	0.07	0.26	BC43b	2.65	2.73	BC69	0.08	0.06
BC9b	0.43	0.42	BC23c	0.07	0.03	BC44	0.25	0.20	BC70	–0.34	0.4
BC9c	0.42	0.44	BC24	0.14	0.11	BC45a	0.05	0.05	BC71	0.03	–0.07
BC10a	0.07	0.01	BC25	0.02	0.00	BC45b	0.08	0.01	BC72	0.04	–0.02
BC10b	0.08	0.01	BC26	0.01	–0.01	BC45c	0.05	–0.01			
BC10c	0.07	0.02	BC27	0.02	–0.04	BC46	0.05	–0.02			
BC11	0.05	0.05	BC28	0.08	0.19	BC47	0.00	–0.05			

[a] Letters are different samples of the same product. Only caramel concentrations >0.07 g/L were considered as reliable data. The order of samples is not the same as that in the text.

[b] BC = Brazilian cachaça.

Four Roses, Early Times, Evan Williams, Maker's Mark); Canadian whisky (Canadian Club); Irish whiskies (Jamaison, Tullamore Dew). More than one sample of the same product was analyzed in some cases. The number of cachaças samples by region was proportional to region participation in Brazilian cachaça production.

(**d**) *Oak wood samples*.—Powdered oak woods of Scottish origin (Seagrams), both charred and noncharred, were used to prepare aqueous ethanol extracts and to record absorption spectra. In a typical experiment, 1.0 g oak powder was added to 100.0 mL aqueous ethanol solution at 60.0°C, and stirred for 45 min. The mixture was then filtered, and the filtrate was diluted to the desired volume with the aqueous alcoholic solution. As a self-consistency test, 15 aqueous alcoholic extracts of noncharred oak from the United States, Poland, Spain, Czechoslovakia, France, and Scotland were also used for standard recognition analysis.

(**e**) *Caramels*.—Caramel solutions were prepared with 7 commercially available sugars (sucrose). In a typical preparation, 20.0 g sugar was heated above the melting point for 10 min to obtain a dark-colored paste. The caramel (10.0 g) was transferred to a 100.0 mL volumetric flask containing the aqueous alcoholic solution, and the volume was adjusted to 100.0 mL. The absorptivity was calculated for each sample from a plot of the caramel concentration vs the respective absorbance.

Spectrophotometric Measurements

The samples were diluted with aqueous ethanol solution prior to analysis: 1 + 10 for the cachaças; 1 + 20 for other beverages. To calculate the sample caramel concentration, the absorbance

Table 4. Comparison between results of caramel obtained from 2 methods (partial least squares and A_{210}/A_{282} ratio)[a]

Sample[b]	PLS	A_{210}/A_{282}	Sample[b]	PLS	A_{210}/A_{282}
USW1	0.01	0.09	SW16b	0.21	0.55
USW2	–0.11	–0.01	SW17a	0.07	0.08
USW3	–0.08	–0.03	SW17b	0.17	0.49
USW4	0.03	0.24	SW17c	0.05	0.01
USW5	–0.07	–0.11	SW18	0.27	0.49
USW6	0.17	0.58	SW19a	0.28	0.55
USW7	–1.49	–1.25	SW19b	0.18	0.49
SW1	0.34	0.49	SW20	0.37	0.64
SW2	0.16	0.20	SW21a	0.38	0.70
SW3	0.14	0.18	SW21b	0.24	0.68
SW4	0.22	0.25	SW22	0.30	0.58
SW5	0.97	1.10	SW23a	0.26	0.39
SW6	0.22	0.19	SW24	0.54	0.79
SW7	0.23	0.31	SW25a	0.30	0.45
SW8	0.29	0.30	SW25b	0.19	0.43
SW9	0.11	0.32	SW26	0.23	0.39
SW10	0.78	0.85	SW27a	0.18	0.67
SW11	0.34	0.57	SW27b	0.33	0.75
SW12	0.29	0.45	CW1	0.14	0.34
SW13	0.32	0.32	CW2a	0.12	0.32
SW14	0.14	0.22	CW2b	0.16	0.30
SW15a	0.21	0.31	IW1a	0.28	0.49
SW15b	0.12	0.67	IW1b	0.21	0.39
SW15c	0.35	0.90	IW2a	0.39	0.52
SW16a	0.23	0.35	IW2b	0.17	0.44

[a] Letters are different samples of the same product. Only caramel concentrations >0.07 g/L were considered as reliable data. The order of the samples is not the same as that in the text.

[b] Abbreviations: USW, U.S. whisky; SW, Scottish whisky; CW, Canadian whisky; IW, Irish whisky.

values were corrected considering the corresponding dilution factor. A Hitachi (San Jose, CA) U-3501 spectrophotometer, equipped with a 1.00 cm long quartz cell, was used for spectral data acquisition. The spectra were recorded from 210 to 400 nm.

Data Analysis

PCA (14) is widely used to simplify large data sets so that patterns and relationships can be readily recognized and understood. The underlying purpose of the technique is dimension reduction. The samples are mapped through scores and the wavelengths are mapped by the loadings in a new low dimensional vector space defined by the principal components. HCA is also an exploratory tool used to confirm the grouping previously identified by PCA. Its primary purpose is to display the data so as to emphasize its natural clusters and patterns in a 2-dimensional space. The results, qualitative in nature, usually are presented in a form of dendograms, making it possible to visualize similarities among samples or variables. In HCA, the distances between samples or variables are calculated, transformed into a similarity matrix, S, and then compared. For any 2 samples, k and l, the similarity index is defined as

$$S_{kl} = 1000 - \frac{d_{kl}}{d_{\max}}$$

where S_{kl} is an element of S, $d_{\max}$ is the largest distance among each pair of samples in the data, and d_{kl} is the Euclidean distance among the samples k and l.

The PLS regression was used for caramel quantitation (15) in the first derivative of spectral data. The advantage of using a multivariate method is that an estimate of more than one regression coefficient is made possible for the property being modeled. The PLS method calculates a new set of variables, called latent variables, that are generated as a linear combination of the originals and then used as predictors of concentration. The latent variables are computed, taking into account both the spectral data and the respective caramel content, and making use of more information at the modeling step. The predictability of the resulting model can be assessed by the "leave-one-out" cross-validation procedure given by the lowest standard error of prediction (SEP), defined as

$$\mathrm{SEP} = \sqrt{\frac{\sum_{i=1}^{n} (c_i - \hat{c}_i)^2}{n}}$$

where c is the experimental value, is the predicted value, and n is the number of samples used for model building.

Once the model was validated, real samples were tested for their caramel content. The data were analyzed with Pirouette statistical software by Infometrix (Seattle, WA).

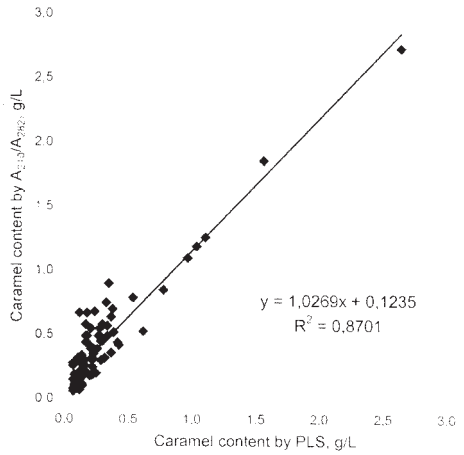

Figure 3. Correlation between the A_{210}/A_{282} ratio and PLS calibration methodologies to determine caramel content in aged spirits.

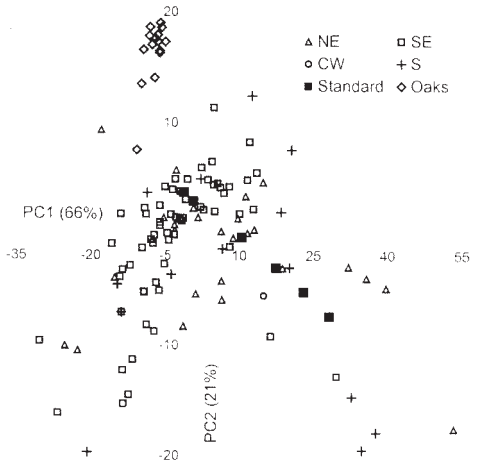

Figure 4. PCA scores plot of aqueous ethanol oak extract, standards of caramel-free cachaça with successive additions of caramel (0.0, 0.1, 0.4, 0.8, 1.2, and 1.7 g/L) and 109 commercial cachaças from different Brazilian regions: (NE) northeast, (SE) southeast, (CW) central west, and (S) south. Data processing: mean-centered.

Results and Discussion

Nonaged, caramel-free cachaças do not present any significant absorption in the UV-VIS region of the spectrum; this is in contrast to aqueous alcoholic caramel solutions, aqueous alcoholic oak extracts, and a mixture of both, as shown in Figure 1. The HMF content of sucrose caramelization process was followed by LC (12) and, at the same time, the UV-VIS spectrum of the sample was recorded. These experimental data indicate that HMF is responsible for at least 60% of the absorbance values at 282 nm, which corresponds to the λmax for HMF. The sucrose absorptivity at 282 nm, calculated as an average value of 7 different samples, is 8.0 ± 0.9 L/g·cm. As a matter of fact, the oak wood contains furanic compounds such as furfural, 5H-furanone, 2-furyl-1-propanona, 2-furoic acid, methyl furoate, and HMF (16), among other classes of compounds, which contribute to the typical spectral characteristic of oak extract solution.

The band at 282 nm is absent in caramels with additives such as sulfites and ammonium salts because HMF is absent in caramels containing such additives (6). Therefore, caramels containing sulfites and ammonium in aged spirits cannot be detected by LC based on the F/HMF ratio or spectrophotometrically, as they will not show any significant spectrum difference from the oak extract. Thus, if the AOAC method (7) detects the presence of caramel that was not detected by spectrophotometric measurements, a caramel with sulfite or ammonium was likely used to darken the aged spirit.

A detailed analysis of the spectral features of 16 caramel-free cachaças aged in oak casks and of aqueous ethanol oak extracts showed that the ratio of absorbance values at 210 and 282 nm (A_{210}/A_{282}) was 4.2 ± 0.5. Charred and noncharred oaks of the same origin do not show any significant absorbance ratio differences at 210 and 282 nm from what occurs in another region of the spectrum (Figure 2).

The addition of caramel to an aqueous alcoholic oak extract leads to some modification in the absorption spectrum (Figure 1), resulting in a change in the A_{210}/A_{282} ratio. This feature was used to calculate the caramel content in aged spirits. The contribution of substances extracted from oak cask to the absorbance at 282 nm can be estimated by dividing the absorbance at 210 nm by 4.2. Thus, the caramel content can be estimated by the difference between the experimentally determined absorbance at 282 nm and that calculated by the following equation:

$$CC = DF\,[A_{282} - (A_{210}/4.2)]/CA_{282}$$

where CC is the caramel content, DF is the dilution factor (10 for cachaças and 20 for other beverages), A_{282} is the absorbance at 282 nm, A_{210} is the absorbance at 210 nm, and CA_{282} is the caramel absorptivity at 282 nm (8.0 L/g·cm).

The accuracy of the method was evaluated by analyzing samples prepared by adding different amounts of caramel to 5 different cachaças aged in oak casks (Table 1). These results show that the uncertainty decreases when the caramel concentration increases, which is probably due to a better definition of the absorption band at 282 nm. Consequently, when caramel concentrations fall to <0.2 g/L, the method is indicated for

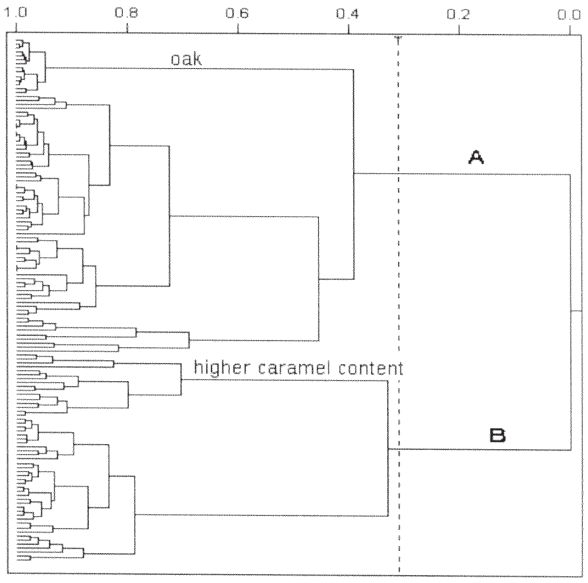

Figure 5. HCA dendogram plot of aqueous ethanol oak extract, standards of caramel-free cachaça with successive additions of caramel (0.0, 0.1, 0.4, 0.8, 1.2, and 1.7 g/L) and 109 commercial cachaças using normalized spectral absorbance as variables. Similarity measurement: Euclidean distance; data processing: mean-centered; clustering technique: incremental.

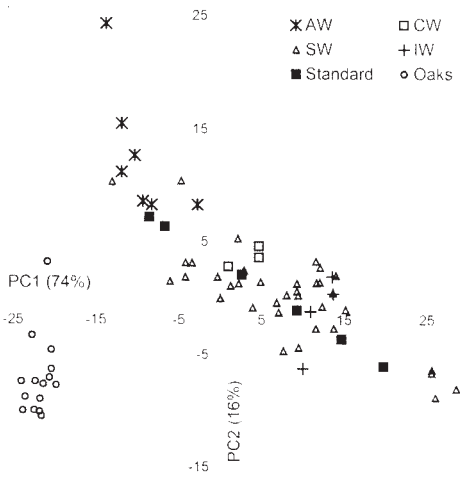

Figure 6. PCA scores plot of aqueous ethanol oak extract, standards of caramel-free cachaça with successive additions of caramel (0.0, 0.1, 0.4, 0.8, 1.2, and 1.7 g/L) and 50 commercial whiskies from United States (USW), Ireland (IW), Canada (CW), and Scotland (SW).

semiquantitative or qualitative purposes only. However, in the concentration range of 0.4–2.0 g/L, the uncertainty was <10%. Due to the complexity of the caramel chemical composition, we recommend that a calibration plot be prepared using caramel standards from the same supplier of the sample whenever possible.

A set of 6 additive-free caramel solutions with known concentration was used to build the PLS calibration model. Table 2 shows the experimental and estimated caramel concentrations obtained by leave-one-out cross-validation. Experimentally, through successive caramel additions to an oak extract solution, it is possible to verify that concentrations >0.08 g/L can be detected by this methodology. The A_{210}/A_{282} ratio and the PLS calibration model were used to predict the caramel content in 109 cachaças samples and 50 imported spirits (Tables 3 and 4).

The negative values indicate the total absence of caramel, and probably reflect small variations in oak wood composition and, thus, in the spectra. The averages for the caramel content in cachaças by PLS and A_{210}/A_{282} ratio were 0.044 ± 0.165 and 0.057 ± 0.204, respectively. The higher value for the same sample was about 2.65 g/L (PLS) and 2.73 g/L (A_{210}/A_{282}). Only 12% of the samples had a mean value for both methodologies >0.20 g/L. This result can be explained by the fact that traditionally aged cachaças generally have a light color and do not require caramel to darken them.

The caramel concentration data for U.S. whiskies (5 Bourbons and 1 Tennessee whiskey) are below the detection limit of the proposed method. Only in one Bourbon (sample USW6) was the calculated caramel content higher than the detection limit. This was expected, because caramel addition is forbidden for straight whiskies. The averages of caramel content in whiskies calculated by PLS and A_{210}/A_{282} ratio were 0.199 ± 0.305 and 0.389 ± 0.305, respectively. The higher values for the same sample were about 0.97 g/L (PLS) and 1.10 g/L (A_{210}/A_{282}). The PLS calibration method gave mean values smaller than those obtained with A_{210}/A_{282} methodology. For whiskies with higher values, these differences were around 100% as a function of unknown factors. About 74% of the whisky samples showed a mean value >0.20 g/L for both methodologies. Figure 3 shows good correlation between values obtained by the 2 methods for the same samples ($y = 1.11x + 0.11$; $R^2 = 0.87$).

From the exploratory analysis by PCA and HCA, we classified 159 samples of spirits into groups as a function of spectral similarities. The PCA results for Brazilian cachaças (Figure 4) indicated that the 2 first principal components explain 87% of the total variance in the data. The wavelengths in the region of 282 nm are dominant in PC1, whereas the wavelengths of 240 nm are dominant for PC2. As caramel addition increased in the standards of oak aqueous ethanol solutions, the PC1 scores became more positive. Thus, samples with high positive scores in PC1 were expected to have high caramel concentrations, whereas those with negative scores probably had no caramel added. The standards and 15 samples of pure oak extracts are included in data analysis for comparison. Note that these oak samples are separated, making a distinct group with negative scores in PC2.

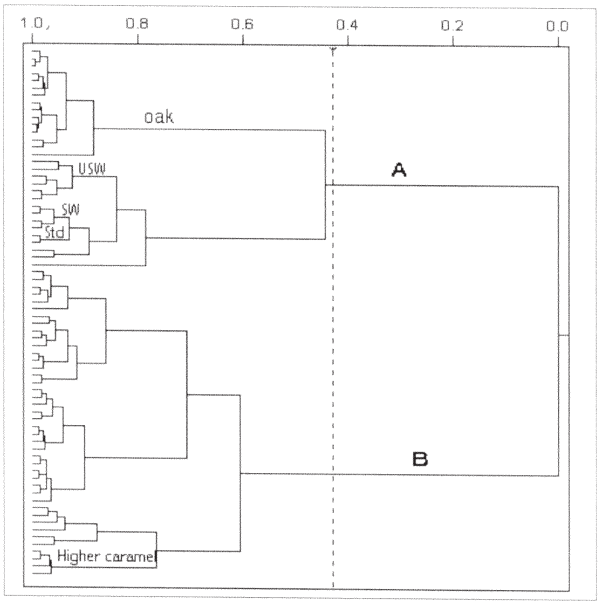

Figure 7. HCA dendogram plot of aqueous ethanol oak extract, standards of caramel-free cachaça with successive additions of caramel (0.0, 0.1, 0.4, 0.8, 1.2, and 1.7 g/L) and 50 commercial whiskies from United States (USW), Ireland (IW), Canada (CW), and Scotland (SW), using normalized spectral absorbance as variables. Similarity measurement: Euclidean distance; data preprocessing: mean-centered; clustering technique: incremental.

It was not possible to distinguish the cachaças through their geographic regions based on caramel content. This fact suggests no regional practices on caramel use to color the cachaças. However, HCA analysis (Figure 5) shows a similarity index of 0.32, indicating that Brazilian cachaças are separated into 2 main groups. The first (group A) is more correlated to oak extracts, whereas the second (group B) is less correlated to oak extracts and more to sucrose caramel added. The samples with negative PC1 scores in Figure 4 are included in group A, indicating that both standard recognition methodologies are suitable for discriminating the samples as a function of the caramel added to the beverage and to their extract characteristics.

Figure 6 shows the results of exploratory analysis for whiskies. The first 2 principal components can explain 90% of the total variance in the data. All U.S. whiskies analyzed were close to the oak standards, which do not have caramel added (negative scores in PC1). In Brazil and in other countries, distillers reuse casks already used for maturation of other beverages such as sherry and U.S. whiskies (14), thereby decreasing the amount of available oak extracts to color the beverages. Of the 50 whisky samples analyzed, all 7 U.S. whiskies and 6 Scottish whiskies had negative PC1 scores, indicating the absence of caramel use. The 15 samples of oak extract were also included in the analysis as comparison. Again, they appear in a separate group having negative scores in PC1, which means absence of caramel.

For HCA analysis (Figure 7), as with the cachaça samples, the whiskies were separated into 2 clusters with a similarity index of 0.43. Those with negative PC1 scores are in the same group as the oak standards (group A), suggesting the absence or low concentration of caramel. Group B contains samples with positive PC1 scores (Figure 6) and the highest caramel contents.

Conclusions

The proposed methodologies can be used for forensic purposes. The results have demonstrated that it is possible to identify and quantitate sucrose caramel in spirits aged in oak casks by UV-VIS spectroscopy. Combining this methodology with the AOAC method for caramel determination, it thus becomes possible to discriminate between the addition of sucrose caramel and starch caramel prepared with sulfite additives. Many renowned distillates were found to have a relatively high caramel content, suggesting that the use of caramel is more frequent than expected. Caramel itself does not disqualify the products, if local laws allow it. However, the customer should be aware of the use of caramel through an indication on the bottle label.

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