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Quantitation of Twelve Metals in Tequila and Mezcal Spirits as Authenticity Parameters

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In this paper the differentiation of silver, gold, aged and extra-aged tequila and mezcal has been carried out according to their metal content. Aluminum, barium, calcium, copper, iron, magnesium, manganese, potassium, sodium, strontium, zinc, and sulfur were determined by inductively coupled plasma optical emission spectrometry. The concentrations found for each element in the samples were used as chemical descriptors for characterization purposes. Principal component analysis, linear discriminant analysis and artificial neural networks were applied to differentiate types of tequila and mezcal. Using probabilistic neural networks 100% of success in the classification was obtained for silver, gold, extra-aged tequila and mezcal. In the case of aged tequila 90% of samples were successfully classified. Sodium, potassium, calcium, sulfur, magnesium, iron, strontium, copper and zinc were the most discriminant elements.

KEYWORDS: Tequila; mezcal; mineral composition; chemometrics; artificial neural networks

INTRODUCTION

There are more than 300 species of agave plants, and from these around 200 are found in Mexico (*1*). They are cultivated to obtain the sap that in México is used for the elaboration of the beverages tequila and mezcal (*2*). *Agave tequilana* Weber var. *azul* is used for tequila production and *A. potatorum* and *A. angustifolia* for mezcal preparation (*3*). The tequila and mezcal manufacturing process involves several stages. The stem of the plant is cut and baked to obtain sugars that are fermented producing a mash, which is doubled distilled and diluted. Premium tequilas are obtained by aging in oak casks. Most mezcal uses a rudimentary fermentation and distillation process.

The elaboration of tequila is restricted by law to the blue agave from defined geographic areas, the state of Jalisco and some districts of the states of Tamaulipas, Nayarit, Michoacan and Guanajuato (*4*). Tequila production reached in 2007 well over 162 million liters, and almost half of this production was for exports (*5*). Apart from two basic categories, 100% agave and mixed tequila, there are four types, i.e. silver, gold, aged and extra-aged. Silver tequila is bottled or stored immediately after distillation. Gold type is unaged silver tequila, blended with aged or extra-aged tequilas, and often with caramel coloring, sugar-based syrup, glycerin, and/or oak extract added so as to resemble aged tequila. Aged is obtained after an aging period of a minimum of two months, but less than one year in oak barrels. Extra-aged tequila is produced with a minimum of one year, but less than 3 years in oak barrels.

Tequila is protected under the North American Free Trade Agreement (NAFTA) and an agreement between the European Union and the United Mexican States on the mutual recognition and protection of designations for spirit drinks (*6*). Due to frequent fraud, the Mexican Tequila Regulatory Council plans to tighten the regulation for exporters and overseas handlers (*7*). In food control, efficient methods are required to prevent the wrongful use of the protected name tequila as well as to check the labeled category.

The majority of the literature about chemical composition of tequila concerns the analysis of organic composition by means of chromatographic techniques. In this way, solid phase microextraction (SPME) gas chromatography−mass spectrometry has been used to characterize the volatile fraction of different types of tequila (*8*) and to determine terpenes in different *Agave* species (*3*). Gas chromatography and sensory analysis has been used to characterize the tequila flavor and to identify the odorants present (*9*). Gas chromatographic determination of volatile constituents and isotope ratio mass spectrometry (IRMS) analysis of $^{13}C/^{12}C$ ratios, as well as site-specific natural isotope fractionation nuclear magnetic resonance (SNIF-NMR) analysis of D/H ratios of ethanol, have been used to differentiate between 100% agave and mixed tequilas (*10*). Head space SPME gas chromatography IRMS was used for tequila authenticity assessment determining the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios of ethanol (*11*). Gas chromatography for higher alcohols and methanol and ion chromatography for oxalate and inorganic anions have been used to asses commercial Mexican Agave spirits (*12*). Spectroscopic techniques in combination with multivariate analysis have also been used by several authors (*13*−*15*).

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Till now the metal content has not been used for characterization purposes of different types of tequila. In the case of other beverages like cachaça, rum (*16*), sugar cane spirits (*17*), zivania (*18*) and anisette (*19*) the application of multivariate statistics to the metal content has been shown to be a powerful tool for authenticity control.

Several pattern recognition techniques can be used for authenticity purposes. Principal component analysis (PCA) (*20*) is very useful to previsualize the trends of the data and provide a first evaluation of the discriminant efficiency of the variables. Linear discriminant analysis (LDA) is a supervised pattern recognition technique that finds linear transformations, called discriminant functions, that are determined in order to best separate the samples (*21*). When the linear model does not provide a solution to the differentiation problem, a nonlinear approach such as artificial neural networks (ANN) (*22*) is very useful.

In this work, the contents of Ca, K, Mg, Na, S, Mn, Sr, Ba, Al, Zn, Cu and Fe were determined in tequila and mezcal. Samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). The metal contents were used as chemical descriptors for classification of silver, gold, aged and extra-aged tequilas and mezcal. PCA, LDA and probabilistic neural networks (PNN) (*23*) were applied to differentiate the types of tequila and mezcal.

MATERIALS AND METHODS

Chemical and Reagents. Nitric acid (65%) and vanadium pentoxide (99%) of analytical grade (Merck, Darmstadt, Germany) were used for sample mineralization. A multielement standard (1000 mg/L) of the analyzed elements was obtained from Merck. Working solutions were prepared by dilution of the standards. All aqueous solutions and dilutions were prepared with ultrapure water (Milli-Q, Millipore, Bedford, MA).

Samples. For the purposes of this work 121 bottles of tequila and 9 of mezcal from different brands were purchased in local retail shops of Mexico and Spain. Four different types of tequila were considered: silver ($n = 44$), aged ($n = 40$), extra-aged ($n = 17$) and gold ($n = 20$). According to the label all of them were 100% agave. All mezcal samples were aged.

Apparatus. A Fisons-ARL 3410 inductively coupled plasma atomic emission spectrometer (FISONS Instruments, Valencia, CA) equipped with a Minitorch burner and a Meinhard nebulizer was used for metal determinations. The instrumental conditions and wavelengths can be seen in the Supporting Information. An Ethos 900 MILESTONE Microwave Laboratory System (Sorisole, Italy) was used to mineralize the samples.

Analytical Procedure. Before analysis by ICP-OES a mineralization step of the samples is necessary. Microwave digestion using a mixture of nitric acid and vanadium pentoxide was carried out. Previously, alcohol was gently evaporated on a sand bath. 50 mL of sample was placed in a Teflon reactor, and after evaporation of the alcohol, 2.5 mL of HNO_3 and 30 μg of V_2O_5 were added. The mineralization was done in the microwave oven operated with alternating power and null periods. The program used is included in the Supporting Information. After cooling, the sample was taken to a volume of 10 mL with Milli-Q water. Finally, all the samples were filtered through disposable 0.45 μm filter units before ICP analysis. Blanks were prepared in an identical way, but omitting the sample. Concentrations were obtained by interpolation of the corresponding calibration graphs. All samples were analyzed three times.

Method Validation. Trueness, precision, detection and quantification limits and linearity ranges were considered. The accuracy was assessed by recovery assays. Known amounts of standards were added to the samples. Five concentration levels were used in order to cover the concentration ranges of metals in tequila and mezcal. Recoveries were calculated comparing the obtained amounts with those added, and their values ranged between 94 and 102%.

Table 1. Ranges of Concentration and Median Values[a] (mg/L) of the Determined Elements for Each Type of Tequila and Mezcal

	tequila				
element	silver ($n = 44$)[b]	gold ($n = 20$)	aged ($n = 40$)	extra-aged ($n = 17$)	mezcal ($n = 9$)
Na	0.06−29.03 (2.01)	2.02−13.67 (3.83)	1.24−19.05 (3.46)	2.93−9.28 (4.06)	4.09−9.98 (8.04)
K	0.01−0.55 (0.04)	0.03−1.50 (0.50)	0.62−22.67 (3.52)	2.19−11.29 (8.17)	0.51−2.07 (0.97)
Ca	0.28−3.96 (0.76)	0.27−1.23 (0.64)	0.57−6.91 (1.36)	0.55−2.13 (1.56)	0.001−3.15 (1.94)
S	0.11−4.04 (0.33)	1.59−4.93 (3.06)	0.10−6.14 (2.23)	0.60−10.01 (1.86)	4.33−7.88 (5.87)
Mg	0.06−1.10 (0.13)	0.05−0.17 (0.12)	0.11−2.26 (0.29)	0.24−0.59 (0.44)	0.09−0.80 (0.29)
Mn	nd−0.04 (0.02)[c]	nd−0.03 (0.01)	0.02−0.05 (0.03)	0.02−0.08 (0.05)	nd−0.02 (0.01)
Fe	0.01−0.13 (0.03)	0.01−0.08 (0.04)	0.03−0.17 (0.05)	0.03−0.30 (0.07)	0.02−0.07 (0.03)
Zn	0.02−0.34 (0.06)	0.02−0.26 (0.04)	0.02−0.35 (0.07)	0.02−0.42 (0.05)	0.02−0.07 (0.05)
Sr	0.01−0.04 (0.02)	0.004−0.04 (0.02)	0.01−0.04 (0.03)	0.02−0.03 (0.02)	0.01−0.05 (0.02)
Ba	nd−0.03 (0.02)	0.01−0.02 (0.02)	0.01−0.03 (0.02)	0.01−0.02 (0.02)	0.01−0.02 (0.01)
Cu	0.02−1.79 (0.10)	nd−1.35 (0.62)	0.02−1.73 (0.32)	0.12−0.76 (0.22)	0.40−0.75 (0.65)
Al	nd−0.15 (0.04)	nd−0.10 (0.05)	nd−0.15 (0.05)	nd−0.48 (0.07)	nd−0.03 (nd)

[a] Median values are in parentheses. [b] *n*, number of samples. [c] nd, not detected.

Intermediate precision was obtained by repeating five determinations of each element along a period of two months. The precision, expressed as relative standard deviation, always remained under 5%. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as the concentration corresponding to a signal of three and ten times, respectively, the standard deviation of the blank. LOD and LOQ values ranged between 0.0008 and 0.071 mg/L and 0.0029 and 0.235 mg/L, respectively. Linearity, calculated as $(1 - (S_b/b))100$, S_b being the standard deviation of the slope and b the slope of calibration line (*24*), was >98% in all cases. Recoveries, LOD and LOQ can be seen in the Supporting Information.

Data Analysis. For the chemometric calculations a data matrix with 12 columns (the determined elements) and 130 rows (tequila and mezcal samples) was constructed. PCA was used as a visualization technique, and LDA and ANN were applied to obtain classification rules. The Statistica 7.0 software package (StatSoft Inc., 2004) was used for the statistical data analysis.

RESULTS AND DISCUSSION

Tequila and Mezcal Metal Content. The contents of the previously mentioned elements were determined in the 121 tequila and 9 mezcal samples. The results expressed in mg/L are shown in **Table 1**. According to the IUPAC recommendations values under the limit of detection have also been included (*25*). These values can provide interesting information in the chemometric study. It can be seen that the elements with a major content are sodium, potassium, calcium and sulfur. Median values of sodium in gold, aged and extra-aged tequila are around 3.8 mg/L and 8 mg/L for mezcal. Sodium concentrations in silver tequila showed a high variability in the range 0.06 to 29.03 mg/L with a median value of 2.01 mg/L. The content of potassium was lower in silver and gold tequila and in mezcal with median values of 0.04, 0.5 and 0.97 mg/L, respectively. Aged and extra-aged tequilas have higher median values, 3.52 and 8.17 mg/L, respectively. Calcium is present in similar concentrations in the majority of the samples with median values around 1.36 mg/L. Sulfur concentrations showed a higher variability. The lowest content was found in silver tequila, the median being 0.33 mg/L. Mezcal had the highest concentration with 5.87 mg/L. The rest of the determined elements, except for some individual samples, were present in concentrations under 1 mg/L. Magnesium average content was 0.34 mg/L. Copper concentrations were quite similar in all cases, the average value being 0.44 mg/L. Iron was present in concentrations lower than 0.1 mg/L. Zinc concentration was 0.1 mg/L, and aluminum was the element present in a minor concentration, the average being equal to 0.05 mg/L. Though no clear differences appear between the contents in the different types of tequila and mezcal, some trends can be inferred. The metal content in these spirits may come from the raw materials, dilution water, distillation devices and the wood casks used in the aging process. Differences between tequila and mezcal mineral content are present. Sodium, calcium, sulfur and copper concentrations are higher in mezcal, while potassium level is lower.

It is most likely that metals present in tequila and mezcal come from dilution water, distillation devices and wood casks. The presence of sulfur may be due to the agave plants used in the elaboration process. Compounds like 4-methylthiazole, 4-methyl-5-vinylthiazole, 2,3-dimethylthiophene and 4-methylthiazole (*26*) have been detected in agave juice. Also, dimethyl sulfide has been detected in tequila (*9*). Furthermore, SO_2 used to prepare the oak casks can be present. The sulfur content determined in this study corresponds to the total concentration. An oxidizing treatment with nitric acid was used to mineralize the samples before measuring, and under these conditions all sulfur compounds are oxidized to sulfate. As the higher content appears in aged and extra-aged tequila and mezcal, the main origin of sulfur containing compounds can be associated with the contact with the wood of the casks during the aging period. The metal content could depend on the alcoholic strength. In order to check this dependence Pearson correlation coefficients were calculated, but no significant correlation was found for any of the metals. One of the main sources of the metals, such as Ca, Mg and Na, present in spirits can be the dilution water (*27*). It could be expected that water from different areas shows different mineral content. Then, differences in the metal content in samples of the same type but from different production areas should be expected. A Spearman correlation study was carried out to find possible relationships between the metal content and the origin of samples. To avoid the influence of the aging process only silver tequila was considered. Tequila samples elaborated in different production areas of the State of Jalisco were used. Variables with a significant correlation were sodium, potassium and copper. These elements could be related to the dilution water, though copper may also come from the stills used in the distillation (*27, 28*). The higher contents of sodium, potassium and calcium in aged and extra-aged tequila can be due to the contact with the wood of the casks during the aging.

Differentiation of Tequilas and Mezcal. The four types of tequila and mezcal were five classes considered in the chemometric study. The classes were labeled as silver (44 samples), gold (20 samples), aged (40 samples), extra-aged (17 samples) and mezcal (9 samples). Different pattern recognition procedures, PCA, LDA and PNN were applied to the data set trying to differentiate the four types of tequila and mezcal. Data were previously autoscaled.

PCA. By applying this method, the three first PCs were extracted, explaining up to 60.9% of the total variance. **Figure 1** shows the corresponding scores plot obtained from eigenanalysis of the covariance matrix of autoscaled data in the plane

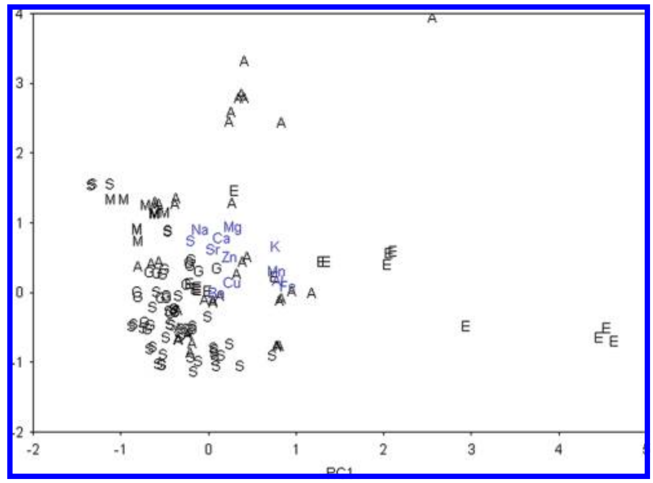

Figure 1. Biplot of the samples and loadings of the variables for the two first PCs. Tequila: S, silver; G gold; A, aged; E, extra-aged; M, mezcal.

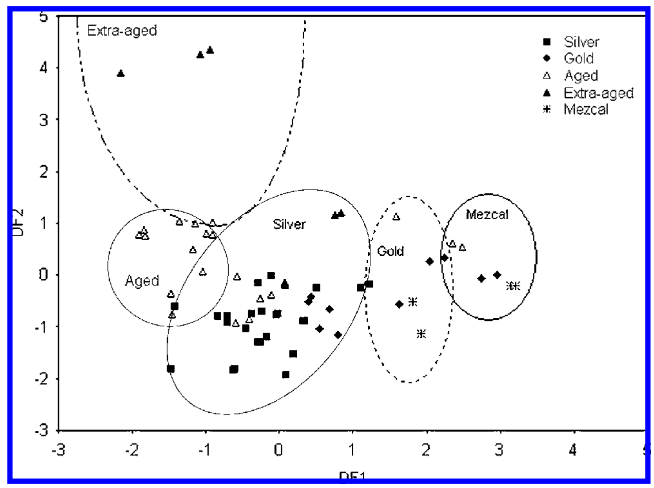

Figure 2. LDA. Scatter plot of the samples in DF1 and DF2 plane.

of the two first PCs. Loadings of the variables are also included in this figure. As can be seen, mezcal samples appear in a scattered group at the negative scores of PC1 and positive scores of PC2, but mixed with some aged and silver tequilas. Most of the silver tequila samples appear grouped at negative values of PC1 and PC2, except some of them that are close to the mezcal group of samples. Gold samples can be located at negative values of PC1, but close to zero in PC2. Extra-aged tequilas are located at positive values of PC1. The variables with higher contribution to PC1 were K, Mn and Fe and for PC2 Na and Mg. Although there is no clear separation between the samples, some trends can be observed. Mezcal appear completely separated from gold and extra-aged tequilas, but only partially separated from aged and silver. Gold tequila is closer to silver and aged ones. This could be explained because gold tequila is elaborated as a mixture of silver and aged tequilas. Extra-aged tequilas appear clearly separated from silver ones, but some overlapping with aged tequilas can be observed.

LDA. To apply LDA a random division of the samples into training ($N = 64$) and test ($N = 66$) sets was performed. As we are considering five classes, four discriminant functions (DF) were calculated. DFs were obtained using forward stepwise analysis, and the variables included in the model were S, Mn, Sr, K, Al, Fe, Zn and Cu. After the model was constructed the test set was used to evaluate its prediction ability. **Figure 2** shows the plot of the test samples in the plane defined by DF1

Table 2. Confusion Matrix LDA Corresponding to Test Set[a]

	silver		gold		aged		extra-aged		mezcal	
	+	−	+	−	+	−	+	−	+	−
+	23	10	3	4	14	0	5	1	2	4
−	1	32	7	52	6	46	3	57	2	58

[a] Test set includes 66 samples from silver, gold, aged and extra-aged tequila and mezcal.

Table 3. Confusion Matrix PNN Corresponding to Test Set[a]

	silver		gold		aged		extra-aged		mezcal	
	+	−	+	−	+	−	+	−	+	−
+	24	2	10	0	18	0	8	0	4	0
−	0	40	0	56	2	46	0	58	0	62

[a] Test set includes 66 samples from silver, gold, aged and extra-aged tequila and mezcal.

and DF2. As can be seen, a complete separation of mezcal from silver and extra-aged tequilas was accomplished. No complete separation between gold and silver tequilas was attained. Aged and silver classes appear overlapped, and some extra-aged samples are considered as silver. The confusion matrix obtained for the samples included in the test set is shown in **Table 2**. According to this, the sensitivity (SENS) and specificity (SPEC) of the constructed model were calculated (*29*). SENS of a class is referred to the number of objects belonging to this class that are correctly classified. SPEC of a class corresponds to the number of objects not belonging to this class that are correctly considered as belonging to different classes. SENS for silver, aged and extra-aged classes were 95.8, 70 and 62%, respectively. In the case of mezcal, SENS was 50%. A higher number of misclassified cases correspond to the gold class with SENS equal to 30%. SPEC of aged, gold and extra-aged tequilas and mezcal were 100, 96.3, 98.3 and 93.5%, respectively. The majority of the misclassified samples were considered as belonging to the silver class, with a SPEC value of 76.2%. This model can differentiate completely mezcal from extra-aged and silver tequilas. Also, gold and extra-aged can be differentiated.

PNN. Considering that the linear model did not provide a complete solution to the differentiation problem, a nonlinear approach such as ANN was used (*22*). A probabilistic neural network was applied to construct a classification model to differentiate mezcal and tequila types. The data set was divided into two subsets, training ($N = 64$) and test ($N = 66$). Best results were obtained when the input variables were Na, K, Ca, S, Mg, Fe, Sr, Cu and Zn. The architecture of the network was 9:64:5:1 and the smoothing factor was finally optimized at 0.3. Once the model was constructed, the test set of samples was used to validate the classification procedure. **Table 3** shows the corresponding confusion matrix. As can be seen, all cases were correctly classified for silver, gold, extra-aged tequilas and mezcal, their SENS being 100%. Only aged tequilas presented misclassified samples, and the SENS for this class was 90%. The misclassified samples were included in the silver class. Consequently, SPEC of this class was 95.24%. This fact can be explained because aged tequilas are matured during a period of time between two months and one year and the misclassified samples could be those of the shorter aging period. There is also the possibility of mislabeling giving as a result an erroneous classification. A SPEC value of 100% was obtained for the other considered classes. Due to the high efficiency of the PNN model it could be applied for forensic purposes, though studies with a higher number of samples of certified origin should be necessary to confirm this tendency.

ABBREVIATIONS USED

ANN, artificial neural networks; ICP-OES, inductively coupled plasma optical emission spectrometry; IRMS, isotope ratio mass spectrometry; LDA, linear discriminant analysis; NAFTA, North American Free Trade Agreement; PCA, principal component analysis; PNN, probabilistic neural networks; SENS, sensitivity; SNIF-MNR, site-specific natural isotope fractionation nuclear magnetic resonance; SPEC, specificity; SPME, solid phase microextraction.

Supporting Information Available: ICP-OES conditions, microwave program, method validation and calibration parameters and metal content data matrix. This material is available free of charge via the Internet at http://pubs.acs.org.

LITERATURE CITED

(1) Cedeño, M. C. Tequila production. *Crit. Rev. Biotechnol.* **1995**, *15*, 1–11.

(2) Gentry, H. S. *The Agaves of Continental North America*; University of Arizona Press: Tucson, AZ, 1982; p 670.

(3) Peña-Alvarez, A.; Díaz, L.; Medina, A.; Labastida, C.; Capella, S.; Vera, L. E. Characterization of three Agave species by gas chromatography and solid-phase microextraction-gas chromatography - mass spectrometry. *J. Chromatogr. A* **2004**, *1027*, 131–136.

(4) Mexican Ministry of Commerce and Industry. *Regulation NOM-006 SCFI 2005. Alcoholic drinks -Tequila specifications*. Diario Oficial de la Federación: Mexico, 2006.

(5) Consejo Regulador del Tequila. http://www.crt.org.mx.

(6) Agreement between de European Community and the United Mexican States on the mutual recognition and protection of designations for spirit drinks. *Off. J. Eur. Communities* **1997**, *L152*, 16−26.

(7) Guthrie, A. Mexico relents on tequila crackdown. *San Diego Union Tribune* 2004 (April 7).

(8) Vallejo-Córdoba, B.; González-Córdova, A. F.; Estrada-Montoya, M. C. Tequila volatile characterization and ethyl ester determination by solid phase microextraction gas chromatography/mass spectrometry analysis. *J. Agric. Food Chem.* **2004**, *52*, 5567–5571.

(9) Benn, S. M.; Peppard, T. L. Characterization of tequila flavor by instrumental and sensory analysis. *J. Agric. Food Chem.* **1996**, *44*, 557–566.

(10) Bauer-Christoph, C.; Christoph, N.; Aguilar-Cisneros, B. O.; López, M. G.; Richling, E.; Rossmann, A.; Schreier, P. Authentication of tequila by gas chromatography and stable isotope ratio analyses. *Eur. Food Res. Technol.* **2003**, *217*, 438–443.

(11) Aguilar-Cisneros, B. O.; López, M. G.; Richling, E.; Heckel, F.; Scheier, P. Tequila authenticity assessment by headspace SPME-HRGC-IRMS analysis of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios of ethanol. *J. Agric. Food Chem.* **2002**, *50*, 7520–7523.

(12) Lachenmeier, D. W.; Sohnius, E. M.; Attig, R.; López, M. G. Quantification of selected volatile constituents and anions in Mexican Agave spirits (tequila, mezcal, sotol, bacanora). *J. Agric. Food Chem.* **2006**, *54*, 3911–3915.

(13) Barbosa-García, O.; Ramos-Ortiz, G.; Maldonado, J. L.; Pichardo-Molina, J. L.; Meneses-Nava, M. A.; Landgrave, J. E. A.; Cervantes-Martínez, J. UV-vis absorption spectroscopy and multivariate analysis as a method to discriminate tequila. *Spectrochim. Acta, Part A* **2007**, *66*, 129–134.

(14) Frausto-Reyes, C.; Medina-Gutierrez, C.; Sato-Berrú, R.; Sahagún, L. R. Qualitative study of ethanol content in tequilas by Raman spectroscopy and principal component analysis. *Spectrochim. Acta, Part A* **2005**, *61*, 2657–2662.

(15) Lachenmeier, D. W.; Richling, E.; López, M. G.; Frank, W.; Schreier, P. Multivariate analysis of FTIR and ion chromato-

graphic data for the quality control of tequila. *J. Agric. Food Chem*. **2005**, *53*, 2151–2157.
(16) Cardoso, D. R.; Andrade, L. G.; Leite, A. F.; Reche, R. V.; Isique, W. D.; Ferreira, N. M. C.; Lima, B. S.; Franco, D. W. Comparison between cachaça and rum using pattern recognition methods. *J. Agric. Food Chem*. **2004**, *52*, 3429–3433.
(17) Fernández, A. P.; Santos, M. C.; Lemos, S. G.; Ferreira, M. M. C.; Nogueria, A. R.; Nobrega, J. A. Pattern recognition applied to mineral characterization of Brazilian coffees and sugar-cane spirits. *Spectrochim. Acta, Part B* **2005**, *60*, 717–724.
(18) Kokkinofta, R.; Petrakis, P. V.; Mavromoustakos, T.; Theocharis, C. R. Authenticity of the traditional Cypriot spirit Zivania on the basis of metal content using a combination of coupled plasma spectroscopy and statistical analysis. *J. Agric. Food Chem*. **2003**, *51*, 6233–6239.
(19) Jurado, J. M.; Alcázar, A.; Pablos, F.; Martin, M. J.; González, A. G. Determination of Zn, B, Fe, Mg, Ca, Na and Si in anisette samples by inductively coupled plasma atomic emission spectrometry. *Talanta* **2004**, *63*, 297–302.
(20) Jolliffe, I. T. *Principal Component Analysis*; Springer: New York, 2002; pp 78−108.
(21) Gardiner, W. P. *Statistical Analysis Methods for Chemists*; Royal Society of Chemistry: Cambridge, United Kingdom, 1997; pp 313−314.
(22) Zupan, J.; Gasteiger, J. *Neural Networks for Chemists: An Introduction*; VCH: Weinheim, Germany, 1993; pp 167−181.
(23) Specht, D. F. Probabilistic Neural Networks. *Neural Networks* **1990**, *3*, 109–118.
(24) Cuadros-Rodríguez, L.; Campaña, A. M.; Sendra, J. M. B. Statistical estimation of linear calibration range. *Anal. Lett.* **1996**, *29*, 1231–1239.
(25) Inczedy, J.; Lengyel, T.; Ure, A. M. *Compendium of Analytical Nomenclature. Definitive Rules. Section 18.4.3.7 Detection and quantification capabilities*, 3rd ed.;IUPAC. Available from www.iupac.org.
(26) Mancilla-Margalli, N. A.; López, M. G. Generation of Maillard compounds from inulin during the thermal processing of Agave tequilana Weber var. azul. *J. Agric. Food Chem*. **2002**, *50*, 806–812.
(27) Ibañez, J. G.; Carreon-Alvarez, A.; Barcena-Soto, M.; Norberto Casillas, N. Metals in alcoholic beverages: A review of sources, effects, concentrations, removal, speciation and analysis. *J. Food Compos. Anal*. **2008**, *21*, 672–683.
(28) Moutsatsou, A.; Chalarakis, E.; Zarangas, G. Influence of raw materials and distillation equipment on the heavy metal content of waste from alcoholic beverage. *J. Hazard. Mater*. **2003**, *B96*, 53–64.
(29) Forina, M.; Armanino, C.; Leardi, R.; Drava, G. A class modeling technique based on potential functions. *J. Chemom*. **1991**, *5*, 435–453.

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