

Differentiation of sparkling wines (cava and champagne) according to their mineral content

A. Jos^a, I. Moreno^a, A.G. González^b, G. Repetto^c, A.M. Cameán^{a,*}

^a *Area de Toxicología, Facultad de Farmacia, Departamento de Bioquímica, Bromatología, Toxicología and Medicina Legal, Universidad de Sevilla, C/Profesor García González No. 2, 41012 Sevilla, Spain*

^b *Departamento de Química Analítica, Universidad de Sevilla, Sevilla, Spain*

^c *Instituto Nacional de Toxicología, Apdo. Correos 863, 41080 Sevilla, Spain*

Received 14 July 2003; received in revised form 21 October 2003; accepted 5 November 2003

Abstract

The metal content of a number of sparkling wines was determined by atomic spectrometry techniques. Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P, Sr and Zn by using inductively coupled plasma atomic emission spectrometry (ICP-AES); Cd, Ni and Pb by graphite furnace atomic absorption spectrometry (GFAAS) and As from hydride generation AAS (HGAAS). Two kinds of sparkling wines were studied with D.O. trademark: cava and champagne. 18 samples of “brut” cava and 17 samples of “brut” champagne of different brands were analyzed following the procedure described in the paper. By using the metal concentrations as chemical descriptors the two classes of samples (cava and champagne) are perfectly discriminated, when applying pattern supervised learning recognition techniques such as linear discriminant analysis (LDA) and soft independent modeling of class analogie (SIMCA). The number of false positives and negatives were zero, which indicates a remarkable authentication power of the descriptors used.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Cava; Champagne; Metal content; Atomic spectrometry; Chemometrics

1. Introduction

Data on the mineral content in wines have been extensively studied and reported due to their implications in organoleptic, hygienic and dietetic characteristics as well as their toxicological implications [1]. Moreover, it allows the characterization and the geographical differentiation of wines when reliable chemical analyses techniques in combination with modern chemometrical methods are used [2–5]. Similarly, several authors have proposed the use of the mineral content to characterise brandies [6], vinegars [7], coffees [8] and teas [9]. However, traditional sparkling wines have been scarcely studied in the chemical literature. Among the different sparkling wines there are two kinds whose consumption is increasing: Spanish cava and French champagne.

Because both sparkling wines are made following the “traditional method” process of bottle fermentation (named “champanoise method” in France), the only differences concern the different geographical locations (soil and climate) and also the types of grapes used in each region.

In the elaboration process the base wine is transformed into the final product by means of different steps, starting from the introduction of the base wine into the bottle with sugar and yeast (decanting), where the second fermentation take place. The bottles are placed horizontally in underground cellars for a minimum of nine months in case of cava wines and twelve months in champagne wines. Once the aging of the wine is finished, the remotion of the bottles is made in order to bring the yeast sediment in the neck. In this way, when the bottle is opened to expel the sediments (disgorging) the loss of wine is minimum. Finally, the initial volume is restored with dosing liqueur (a mixture made of cane sugar and old wine) and the bottle is sealed (corking). “Brut” cava and “Brut” champagne have no addition of dosing liqueur, being their sugar content between 0 and 15 g l⁻¹.

* Corresponding author. Tel.: +34-9-5455-6762; fax: +34-9-5423-3765.

E-mail address: camean@us.es (A.M. Cameán).

Due to the complexity of sparkling wines it is necessary to determine many of its constituents to obtain a good chemical characterization. For this reason, the evaluation of metal profiles of “brut” cava and “brut” champagne samples may be of great importance in order to differentiate between both of these sparkling wines.

In the present paper the content of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P, Sr and Zn have been determined in samples of two types of “brut” sparkling wines (cava and champagne) by using inductively coupled plasma atomic emission spectrometry (ICP-AES) with a previous acid digestion. Cd, Ni and Pb were measured by graphite furnace atomic absorption spectrometry (GFAAS) and As was analyzed using hydride generation atomic absorption spectrometry (HGAAS).

Variable–variable plots were used to visualize data classes, and pattern recognition techniques, such as linear discriminant analysis (LDA) and soft independent modelling of class analogy (SIMCA) were applied.

2. Experimental

2.1. Apparatus

Elemental analyses were carried out on a A Fison-ARL 3410 inductively coupled plasma atomic emission spectrometer (Fisons Instruments, Valencia, CA). Table 1 shows the analytical lines used for each element, as well as the instrumental conditions. Moreover, a Perkin Elmer 1100B atomic absorption spectrometer attached to a PE HG-500 graphite furnace (with a PE AS-40 automatic injector, all from Perkin Elmer, Norwalk, CT, USA) was employed for quantitation

Table 1
ICP-AES operating conditions

Parameter	
RF frequency	27.12 MHz
Operating power	650 W
Coolant Ar flow	7.51 min ⁻¹
Plasma Ar flow	0.81 min ⁻¹
Carrier Ar flow	0.81 min ⁻¹
Torch type	Minitorch
Nebulizer type	Meinhard
Sample flow rate	2.3 ml min ⁻¹
Detection wavelengths (nm ⁻¹)	
Al	396.152
Ba	455.403
Ca	393.366
Fe	259.94
K	766.490
Mg	279.553
Mn	257.610
Na	589.592
P	214.914
Sr	407.771
Zn	213.856
Cu	324.754

Table 2

HG 500 graphite furnace parameters used for analysis of Cd, Pb, and Ni in cava and champagne samples

Step	Temperature (°C)		Ramptime (s)	Hold time (s)
	Ni	Cd, Pb		
1	80	80	5	15
2	100	100	5	15
3	600	1400	5	15
4	1600	2400	0	3 ^a
5	2500	2500	1	1
6	20	20	5	5

Argon flow rate: 300 ml min⁻¹; injection volume: 20 µl; spectral bandwidth 0.7 nm.

^a Gas stop for reading.

of Cd, Pb and Ni by the GFAAS technique. The graphite furnace temperature program is gathered in Table 2. This equipment was adjusted to a PE MHS-10 hydride generator (Perkin Elmer, Norwalk, CT, USA) for determining As total content by HGAAS. All the cava and champagne samples were previously degassed using an ultrasonic bath (Zarallo, Spain).

2.2. Chemical and reagents

Merck (Darmstadt, Germany) CertiPUR®. ICP-multi-element standard solutions of about 1000 mg l⁻¹ were used as stock solution for calibration. Sodium borohydride (Merck, analytical grade) 1.4% (w/v) in 1 M sodium hydroxide was used for generating the arsine in the determination of As. A mixture of hydrogen peroxide and concentrated sulfuric acid (15 + 0.5 ml both of Merck, analytical grade) was used for the mineralization of samples. Other reagents where of reagent grade or better. Milli-Q treated water was used throughout.

2.3. Samples

Eighteen samples of “brut” cava of different brands with D.O. trademark and 17 of “brut” champagne were purchased in liquor retailers and markets. The alcoholic content ranged from 11.5 to 12% (v/v) ethanol for cava samples and from 12 to 12.5% (v/v) for champagne samples. An identification code was assigned to each sample, C for catalonian cavas and F for french champagne samples. In the D.O. cava, the main varieties of grapes authorised for the elaboration of white cavas are Macabeo, Xarel-lo and Perellada, and also Chardonnay, Garnatxa and Monastrell, whereas for the production of A.O.C. champagne Pinot Noire, Pinot Meunier and Chardonnay are used. In reference to the growing areas, the zone producing cava is integrated by 160 municipalities, ubicated in seven autochtonous communities although the region of Penedés, in the south of Barcelona, produces more than 95% of total production. In fact, all the cava brands used in this work are from the Penedés region. However, in France, only the vineyards in the champagne region, located

ninety miles northeast of Paris, can be used to elaborate it. In fact, the unique mineral elements in the soil are considered as a vital factor in the distinctive characteristics and complexity of these sparkling wines (web pages <http://www.crcava.es> and <http://www.champagne-vintage-charts.com>. Last access 30/06/2003).

Once opened, cava samples were degassed and were submitted to the following digestion procedure: 50 ml of degassed sparkling wine with 15 ml of hydrogen peroxide (30%, v/v) are heated at 80 °C until a volume of about 20 ml. Then, 0.5 ml of concentrated sulfuric acid is added, and the heating is continued until a final volume of about 2 ml. This volume is mixed with Milli-Q treated water up to the starting volume. Three replicated digestions were made for each sample. Three blanks were prepared in an identical way, but omitting the sample. The average of blank ICP-AES (or GFAAS and HGAAS) signals was subtracted from analytical signals of samples before interpolation on calibration graphs.

2.4. Data analysis

The content of each mineral element was considered as chemical descriptor. Pattern recognition methods were applied to the data matrix, composed of 16 columns (the analyzed elements) and 35 rows (brut sparkling wines). LDA was used for the first level of supervised pattern recognition (PR) methods and SIMCA was employed as typical class-modeling method for the second level of PR, with the proposal of obtaining classification rules. The statistical package, STATISTICA 99, from Statsoft [10] was used for all the chemometric calculations, except SIMCA, whose calculations were performed utilizing the program SIMCA-PA from Umetrics [11].

3. Results and discussion

3.1. Mineral content in sparkling wine samples

The metal content of the different sparkling wines (cava and champagne varieties) was determined and carefully scrutinized. The results, expressed in milligram per litre, were obtained from triplicate measurements and rounded up to the last significant figure associated with random error. Table 3 shows these results. The corresponding descriptive basic statistic for both types of beverages can be seen in Table 4. Looking at these values, K was the element with a major content in all samples. The mean concentration of K was similar in cava and champagne samples, with average concentrations of 396 and 346 mg l⁻¹, respectively. Ca and Mg presented lower and similar contents, their average values being 97 and 80 mg l⁻¹, respectively, in cava samples and 83 and 84 mg l⁻¹ in champagne ones. However, P levels were higher in champagne samples, and this could be due to differences between raw materials (grapes from

different varieties and locations) used in the fermentation process. Sodium was also present with values higher than 10 mg l⁻¹. Its origin depends on the raw material; in fact, the Na content in cava samples was approximately double that in champagne ones. The other analyzed metals mostly appeared with values close to 1 mg l⁻¹, such as Al and Fe, and even lower, Cd, Ni and Pb being the metals with the lowest concentration.

3.2. Statistical procedures for classification

Using the mineral content found in the analyzed sparkling wines samples as chemical descriptors, statistical methods were applied in order to establish differences between cava and champagne samples for classification and authentication purposes. Until now, no attempts have been made on this subject. There are a number of display methods for visualizing data trends, such as principal component analysis (PCA) [12] or cluster analysis (CA) [13]. However, a very straightforward way to select optimal descriptors for visualizing data trends are the variable–variable plots [14]. Thus, if these plots are made, it can be seen that only with the descriptors Zn and Sr it is possible to differentiate between cava and champagne samples, as depicted in Fig. 1. Nevertheless, although these two variables show a fair separation of both the classes of sparkling wine, they are not sufficient for authentication purposes. Thus, other procedures building class borders and enabling the computation of false positive and negative (linked to the possibilities of type α and β errors) are needed. They are called supervised learning pattern recognition methods.

3.3. Supervised learning PR methods

With these methods, we assume an a priori knowledge of the number of classes. In this case, only two classes were considered, i.e. cava (C) and champagne (F) brut samples. A distinction can be made between discriminating (hard classification) and class-modeling (soft classification) techniques, according to the concept employed to derive the classification rules [15].

3.3.1. LDA

Linear discriminant analysis is a typical discriminating method, belonging to the first level of PR, where objects are classified into either of a number of defined classes [16]. After applying standard LDA [15,17], and according to the Wilks' lambda values of each variable in the model, nine variables, namely Zn, Sr, Pb, Na, Cu, Ni, As, P and Cd seem to be optimal descriptors for distinguishing between class C and F samples. Looking at the posteriori probabilities, a recognition ability of 100% was obtained. In order to evaluate the classification performance, the leave-one-out (LOO) [18] method was used as a validation procedure, obtaining a prediction ability of 100%.

Table 3

Experimental results^a for determination of elements (mg l⁻¹) in “brut” cava and champagne samples by ICP-AES, GFAAS* and HGAAS**

Sample	Code	Zn	Mn	Fe	Cu	Al	Sr	Ba	P	Mg	Ca	Na	K	Pb*	Cd*	Ni*	As**
1	C	0.291	0.489	0.67	ND	0.59	0.283	0.056	50.1	67.8	103.6	11.37	388.5	0.0348	0.0191	0.0577	0.011
2	C	0.285	0.705	1.51	0.039	2.06	0.929	0.092	58.8	96.5	118.4	25.43	384.3	0.0111	0.0006	0.0135	0.013
3	C	0.270	0.625	1.56	0.046	1.34	0.770	0.035	84.1	58.0	82.9	29.23	404.7	0.0103	0.0006	0.0052	0.016
4	C	0.350	0.496	0.67	ND	1.12	0.328	0.031	84.2	61.2	59.2	17.04	453.4	0.0323	0.0005	0.0167	0.007
5	C	0.342	0.731	1.78	0.034	1.16	0.971	0.033	73.1	62.5	75.5	31.42	423.9	0.0018	0.0006	0.0040	0.015
6	C	0.302	0.603	1.07	0.040	1.05	0.497	0.035	80.5	65.5	78.7	32.16	408.6	0.0012	0.0004	0.0280	0.010
7	C	0.270	0.580	2.46	ND	1.75	0.349	0.043	119.7	58.5	100	23.93	352.8	0.0137	0.0001	0.0033	0.012
8	C	0.208	0.482	1.39	ND	1.75	0.292	0.052	66.0	63.4	112.3	16.07	345.0	0.0123	0.0004	0.0042	0.010
9	C	0.226	0.558	1.6	ND	2.78	0.489	0.043	65.2	77.1	95.1	21.19	349.1	0.0110	0.0003	0.0027	0.012
10	C	0.410	0.601	0.52	0.178	0.57	0.962	0.046	70.7	87.8	81.9	25.05	430.3	0.0092	0.0019	0.0555	0.012
11	C	0.275	0.821	1.83	0.145	1.20	0.659	0.065	87.9	98.8	108.2	24.67	395.4	0.0047	0.0006	ND	0.012
12	C	0.258	0.451	2.77	0.151	2.30	0.301	0.039	71.6	60.0	98.8	12.78	338.1	0.0837	0.0010	0.0032	0.014
13	C	0.372	0.753	1.38	0.044	1.16	0.903	0.044	89.8	98.6	91.6	25.13	338.1	0.0025	0.0003	0.0080	0.012
14	C	0.427	0.759	0.94	0.112	1.01	0.990	0.040	82.2	90.6	96.5	24.66	490.2	0.0011	ND	0.0838	0.013
15	C	0.234	0.559	1.28	0.194	1.78	0.655	0.050	130.7	99.5	116.1	23.49	458.7	0.0032	0.0014	0.0109	0.015
16	C	0.575	0.749	1.08	ND	0.62	1.061	0.034	89.5	99.0	95.3	24.94	391.7	0.0079	0.0010	ND	0.009
17	C	0.248	0.940	2.41	0.152	1.90	0.999	0.069	85.5	104.9	122.2	20.20	414.7	0.0062	0.0007	0.0201	0.013
18	C	0.247	0.668	1.29	ND	2.39	0.989	0.059	72.3	100.3	106.2	23.60	365.7	0.0104	0.0006	0.0024	0.011
19	F	0.668	0.734	1.53	0.043	0.65	0.223	0.028	91.7	83.5	86.1	10.14	367.2	0.0123	ND	0.0047	0.013
20	F	0.601	0.639	0.808	0.043	0.66	0.262	0.027	169.7	81.1	72.9	9.22	336.1	0.0057	ND	0.0101	0.013
21	F	0.524	0.700	1.668	0.049	0.63	0.262	0.029	75.5	72.5	80.9	9.56	353.3	0.0118	0.0003	0.0052	0.013
22	F	0.557	0.715	1.583	0.038	0.72	0.256	0.025	81.2	77.5	89.3	10.19	337.6	0.0100	0.0006	ND	0.012
23	F	0.630	0.812	1.038	0.048	0.80	0.277	0.039	125.7	87.56	79.3	13.04	426.3	0.0077	0.0011	0.0014	0.013
24	F	0.444	0.632	1.521	ND	1.01	0.270	0.025	120.7	73.5	91.0	10.42	319.1	0.0088	0.0016	ND	0.010
25	F	0.589	0.66	1.895	0.054	0.86	0.273	0.040	127.3	78.9	91.6	10.90	391.7	0.0111	0.0011	0.0088	0.016
26	F	0.728	0.857	2.356	0.049	0.78	0.322	0.028	113.5	95.8	87.9	11.04	378.6	0.0220	0.0017	0.0023	0.015
27	F	0.651	0.943	1.003	0.039	0.73	0.225	0.038	128.6	93.8	93.3	9.77	264.8	0.0226	0.0017	0.0032	0.012
28	F	0.742	0.856	1.401	0.055	0.67	0.291	0.055	142.6	91.3	81.5	11.78	334.2	0.0130	0.0007	0.0187	0.012
29	F	0.697	0.838	1.354	0.044	1.27	0.293	0.037	107.3	82.2	76.5	12.39	379.0	0.0157	0.0018	0.0061	0.013
30	F	0.508	0.851	1.439	0.483	0.57	0.301	0.034	103.8	82.9	86.2	17.73	311.8	0.0095	0.0004	ND	0.014
31	F	0.707	0.835	1.332	0.034	0.56	0.271	0.029	138.7	89.8	64.6	9.38	332.7	0.0131	0.0003	ND	0.014
32	F	0.639	0.926	2.512	0.059	0.78	0.273	0.030	117.9	85.2	82.2	9.78	339.2	0.0130	0.0012	0.0046	0.013
33	F	0.681	0.851	1.738	0.092	0.59	0.372	0.039	121.8	82.9	86.2	7.70	339.0	0.0106	0.0014	0.0522	0.017
34	F	0.694	0.964	2.169	0.039	0.80	0.305	0.047	105.4	89.4	86.2	14.55	308.2	0.0127	0.0006	0.0099	0.016
35	F	0.664	0.786	2.188	0.071	0.76	0.261	0.031	117.4	78.9	80.8	11.05	358.3	0.0122	0.0016	ND	0.015

ND: not detected.

^a Mean of triplicate determinations.

Table 4

Metal concentrations in “Brut” cava samples ($n = 18$) and “Brut” champagne samples ($n = 17$)

Element	“Cava samples”			“Champagne” samples		
	Mean \pm S.D. (mg l ⁻¹)	Median (mg l ⁻¹)	Range of quantified values (mg l ⁻¹)	Mean \pm S.D. (mg l ⁻¹)	Median (mg l ⁻¹)	Range of quantified values (mg l ⁻¹)
Al	1.5 \pm 0.6	1.271	0.6–2.8	0.75 \pm 0.17	0.73	0.56–1.27
As	0.012 \pm 0.002	0.012	0.007–0.016	0.014 \pm 0.002	0.013	0.010–0.017
Ba	0.048 \pm 0.016	0.043	0.031–0.092	0.340 \pm 0.008	0.031	0.025–0.055
Ca	97 \pm 16	98	59–122	83 \pm 7	86	65–93
Cd	0.0010 \pm 0.0030	0.0070	0.0001–0.0190	0.0090 \pm 0.0006	0.0011	0.0003–0.0018
Cu	0.1 \pm 0.06	0.1	0.03–0.2	0.07 \pm 0.11	0.048	0.034–0.48
Fe	1.5 \pm 0.6	1.4	0.5–2.7	1.6 \pm 0.5	1.5	0.8–2.5
K	396 \pm 44	394	338–490	346 \pm 37	339	265–426
Mg	80 \pm 18	82	58–105	84 \pm 7	83	72–96
Mn	0.6 \pm 0.1	0.6	0.4–0.9	0.8 \pm 0.1	0.8	0.6–1
Na	23 \pm 6	24	11–32	11 \pm 2	10	8–18
Ni	0.015 \pm 0.021	0.006	0.001–0.084	0.075 \pm 0.012	0.005	0.001–0.052
P	81 \pm 19	81	50–131	117 \pm 23	118	75–170
Pb	0.014 \pm 0.014	0.011	0.001–0.084	0.013 \pm 0.004	0.012	0.006–0.023
Sr	0.7 \pm 0.3	0.04	0.03–1.06	0.28 \pm 0.03	0.27	0.22–0.37
Zn	0.31 \pm 0.09	0.28	0.21–0.57	0.63 \pm 0.08	0.65	0.44–0.74

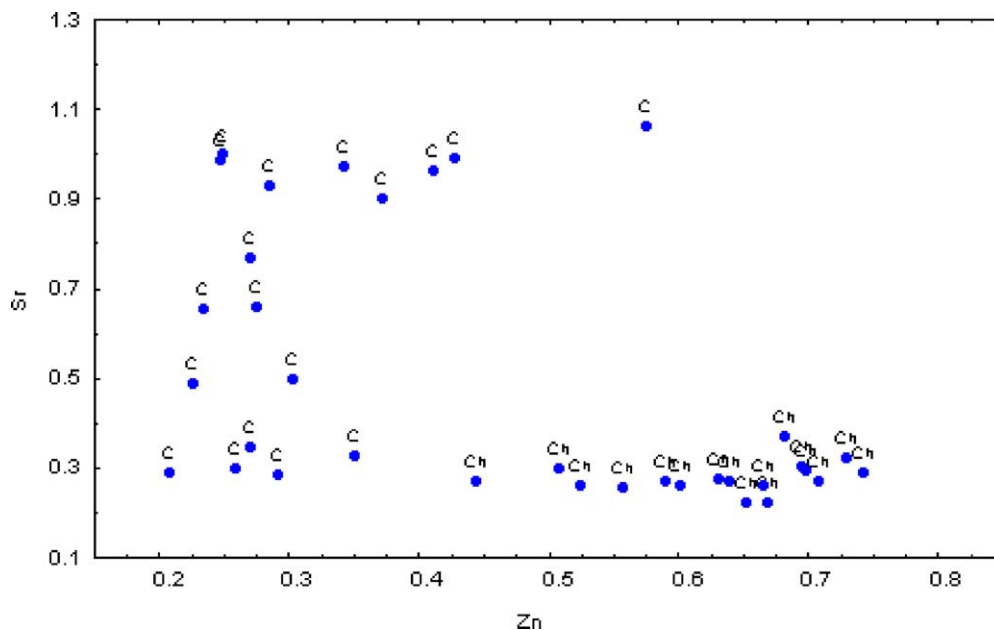
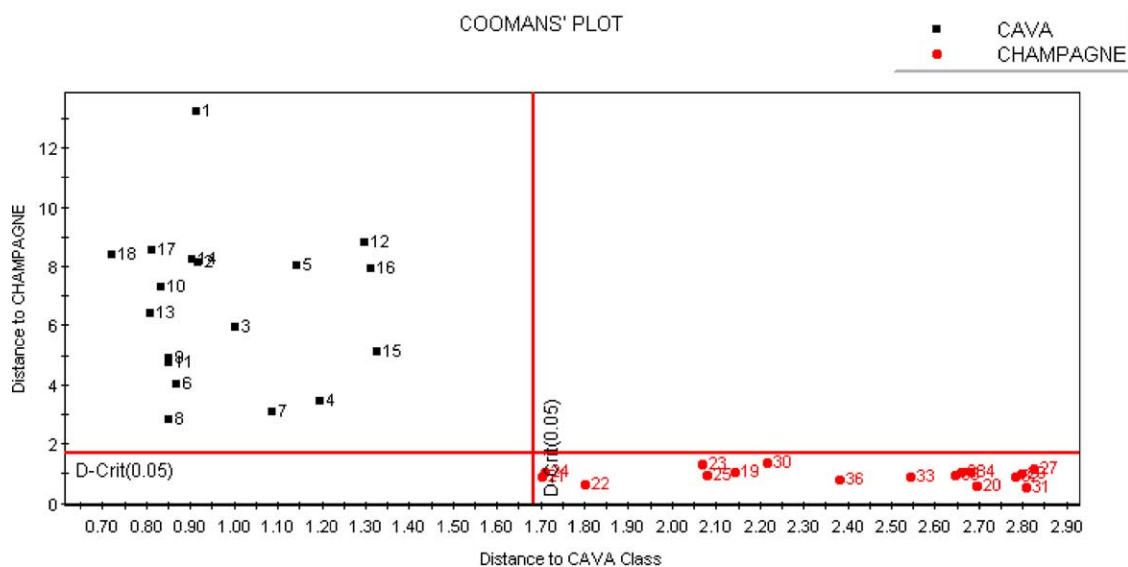


Fig. 1. Variable-variable plot using the descriptors Zn and Sr. Key: C, cava samples; Ch, champagne samples.

3.3.2. SIMCA

Soft independence modeling of class analogies, was proposed by Wold et al. [18,19]. It is a typical class-modeling method which can be used for the second level of PR. Class-modeling techniques build frontiers between each class and the rest of the universe and the decision rule for a given class is a class-box that envelopes the position of the class in the pattern space [20]. SIMCA is based on the evaluation of the principal components derived for each category separately. Model functions for each class are cal-

culated using a specified number of principal components and a critical distance with probabilistic meaning [21]. Every considered sample is assigned to one class according to its distance from the class model [22]. In our case, each class was suitably modeled by using five PCs (explaining about 80% of class variance). Fig. 2 shows the Cooman’s plot for the square SIMCA distances obtained for C and F classes. Cava samples are completely separated from the champagne ones, without any overlapping between the two classes.



M2-D-Crit[4] = 1.706 M1-D-Crit[4] = 1.685

Fig. 2. Cooman’s plot for the square SIMCA distances obtained for C and F classes.

SIMCA, being a soft modeling procedure, enables us to detect the number of false positive/negative for each class. Therefore, two parameters to validate the classification procedure may arise: sensitivity (SENS) and specificity (SPEC) [23]. The SENS of a class corresponds to the rate of validation objects belonging to this class (n_A) that are correctly classified ($\langle n_A \rangle$). The SPEC of a class corresponds to the rate of validation objects not belonging to this class (\bar{n}_A) that are correctly considered as belonging to different classes ($\langle \bar{n}_A \rangle$). This may be explained in terms of the first and second kind of risk associated with the prediction. The first kind of error (α) refers to the probability of rejecting erroneously a member of the class as a non-member (false negative). The second kind of error (β) is the probability of classifying erroneously a non-member of the class as a member (false positive). Thus, for an ideal class A, we have

$$\text{SENS} = \frac{\langle n_A \rangle}{n_A} = 1 - \alpha$$

$$\text{SPEC} = \frac{\langle \bar{n}_A \rangle}{\bar{n}_A} = 1 - \beta$$

In our case, both SENS and SPEC are unity (or 100%) and, consequently the probabilities for false negatives and false positive can be taken as negligible. As a result, a neat differentiation between brut cava and brut champagne classes was achieved. Both are fermented beverages, but commercialised as different products. These results shows that an authentication of these different products can be established using some mineral variables as descriptors.

4. Conclusion

Using a chemometric approach, the mineral content provides a suitable method to differentiate two classes of sparkling wines, brut cava and brut champagne samples, both with D.O. trademark. The difference between both classes arises mainly from the descriptors Zn, Sr, Pb, Na, Cu, Ni, As, P and Cd. Standard LDA and SIMCA procedures led to excellent classifications with a percentage of hits in both recalling and prediction of 100%. SIMCA method permits the net separation of class envelopes, with maximum sensitivity and specificity.

Acknowledgements

This work has been mainly supported by a grant from the Andalusia Government (CTS-358, II Plan Andaluz de Investigación). We are also grateful to G. Peña for his technical assistance.

References

- [1] M. López-Artíguez, A.M. Cameán, M. Repetto, J. AOAC Int. 79 (1996) 1191–1197.
- [2] G. Thiel, K. Danzer, Fresenius J. Anal. Chem. 357 (1997) 553–557.
- [3] L. Sun, K. Danzer, G. Thiel, Fresenius J. Anal. Chem. 359 (1997) 143–149.
- [4] K. Danzer, D. García, G. Thiel, M. Reichenbacher, Am. Lab. (1999) 26–34.
- [5] W.U. Kwan, B.R. Kowalski, J. Food Sci. 43 (1978) 1320–1323.
- [6] A.M. Cameán, I. Moreno, M. López-Artíguez, M. Repetto, A.G. González, Talanta 54 (2001) 53–59.
- [7] M.I. Guerrero, C. Herce-Pagliai, A.M. Cameán, A.M. Troncoso, A.G. González, Talanta 45 (1997) 379–386.
- [8] M.J. Martín, F. Pablos, A.G. González, Food Chem. 66 (1999) 365–370.
- [9] A. Marcos, A. Fisher, G. Rea, S.J. Hill, J. Anal. At. Spectrom. 13 (1998) 521–525.
- [10] Statsoft, Inc., STATISTICA for Windows (computer program manual), Tulsa, OK, 1999 (<http://www.statsoft.com>).
- [11] SIMCA P-9 Multivariate Data Analysis Package 2001, Umetrics, Umea, Sweden.
- [12] J. Jolliffe, Principal Component Analysis, Springer-Verlag, Berlin, 1986.
- [13] N. Bratchell, Chemom. Int. Lab. Sys. 6 (1989) 105–125.
- [14] L.A. Wilson, J.H. Ding, A.E. Woods, J. AOAC 74 (1991) 248–256.
- [15] D. González-Arjona, A.G. González, Anal. Chim. Acta 363 (1998) 89–95.
- [16] C. Albano, W. Dunn, U. Edlund, E. Johansson, B. Nordén, M. Sjöström, S. Wold, Anal. Chim. Acta 103 (1978) 429.
- [17] A. Alcázar, F. Pablos, M.J. Martín, A.G. González, Talanta 57 (2002) 45–52.
- [18] S. Wold, Pattern Recogn. 8 (1976) 127.
- [19] S. Wold, M. Sjöström, ACS Symposium Series 52 (1977) 243.
- [20] M.P. Derde, D.L. Massart, Anal. Chim. Acta 191 (1986) 1–16.
- [21] P.L. Fernández, A. López, F. Pablos, A.G. González, M.J. Martín, Microchim. Acta (2003) 1–6.
- [22] S. Wold, C. Albano, W.J. Dunn, U. Edlund, K. Esbensen, P. Geladi, S. Hellberg, E. Johansson, W. Lindberg, M. Sjöström, in: B.R. Kowalski (Ed.), Chemometrics, Mathematics and Statistics in Chemistry, Reidel, Dordrecht, 1984, p. 17.
- [23] D. González-Arjona, G. López-Pérez, A.G. González, Chemomet. Intelligent Lab. Syst. 57 (2001) 133–137.