Monitoring the Authenticity of Organic Grape Juice via Chemometric Analysis of Elemental Data

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Abstract Elemental determination was carried out on 36 grape juice samples (19 organic and 17 ordinary), with the goal of identifying significant differences between the two types of juice for classification purposes. Inductively coupled plasma-mass spectrometry was used for the determination of 24 elements, Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, La, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Se, Sn, Ti, V, and Zn. Ba, Ce, La, Mg, P, Pb, Rb, Sn, and Ti concentrations were found to be higher in organic versus ordinary samples, while Na and Va concentrations were higher in ordinary versus organic samples. The remaining investigated elements exhibited statistically equivalent concentration levels in both types of samples. Principal component analysis (PCA) and soft independent modeling of class analogy (SIMCA) statistical techniques of the elemental fingerprints were readily able to discriminate organic from ordinary samples and can be used as alternative methods for adulteration evaluation.

Introduction

Analytical techniques capable of providing the elemental composition of samples have been frequently combined with multivariate statistical methods for identification and classification of agricultural products according to their geographical region (Coetzee et al. 2005; Kaufmann 1997; Martinez et al. 2003) and/or authenticity (Barbosa et al. 2013, 2015; Borges et al. 2015). The successful application of such an approach depended on finding an appropriate set of elements able of providing a distinct spectral pattern for fingerprint identification of the products of interest. Among the numerous techniques that exist for elemental analysis, inductively coupled plasma mass spectrometry (ICP-MS) offers the required detection sensitivity to capture multi-elemental compositions of samples at trace levels (Coetzee et al. 2005; Gonzalvez et al. 2009; Millour et al. 2011; Nardi et al. 2009; Şahan et al. 2007). ICP-MS has been used to identify the geographical origin of samples such as honey (Batista et al. 2012; Chen et al. 2014; de Andrade et al. 2014), wine (Arvanitoyannis et al. 1999; Versari et al. 2014), meat (Schwägele 2005), fruit juices (Zielinski et al. 2014), rice (Cheajesadagul et al. 2013; Suzuki et al. 2008), beef (Zhao et al. 2013b), tea (Moreda-Piñeiro et al. 2003), and wheat (Zhao et al. 2013a).

Herein, ICP-MS was applied to investigate the authenticity of organic grape juice samples, which, to our knowledge, has not previously been applied for this purpose. Our work included juice samples from several grape varieties, harvested at

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different Brazilian locations. Principal component analysis (PCA) and soft independent modeling of class analogy (SIMCA) were used for the interpretation of the spectrometric data. We demonstrate here that the combination of ICP-MS spectral fingerprints and chemometric algorithms provide a robust approach for comparison of grape juice samples and for verifying the authenticity of organic grape juice.

Material and Methods

Instrumentation

Determination of elements in grape juice was carried out using a PerkinElmer (Waltham, MA, USA) ELAN DRCII ICP-MS instrument. High-purity argon (99.999 %, White Martins, Brazil) was used throughout the study. Detailed instrumental parameters and optimized conditions have been described in (Batista et al. 2009); they are briefly summarized in Table 1.

Table 1 Instrument settings for q-ICP-MS

Instrument	Elan DRCII (PerkinElmer SCIEX)
Nebulizer	Meinhard®
Spray chamber	Cyclonic
Torch injector	Quartz for clinical sample (2.0 mm)
Auto lens	On
RF power (W)	1100
Gas flow rates (L min^{-1})	Nebulizer 0.56–0.98; plasma 15; auxiliary 1.2
Interface	Platinum cones
Sampler	1.1 mm
Skimmer	0.9 mm
Internal standard	^{103}Rh
Scanning mode	Peak hopping
Integration time (ms)	2000
Replicates	3
Sweeps	40
Readings	1
Dwell time (ms)	50
Lens voltage (V)	6.0
Sample uptake rate (mL min^{-1})	1.0

Correction equations

Zinc$=^{64}$Zn$-(0.035247\times^{60}$Ni)

Selenium$=^{82}$Se$-(1.007833\times^{83}$Kr)

Antimony$=-0.125884\times^{125}$Te

Reagents and Materials

With the exception of HNO$_3$, all chemicals were of analytical reagent grade. HNO$_3$ was purchased from Synth (Diadema, Brazil) and was purified in a quartz sub-boiling still (Kürner Analysentechnik, Rosenheim, Germany) before use. High-purity deionized water (resistivity 18.2 MΩ cm) was generated using a Milli-Q water purification system (Millipore, Bedford, MA, USA). One thousand milligrams per liter of aqueous solutions of rhodium, iron, magnesium, zinc, copper, and multi-element (10 mg L^{-1}) standard aqueous mixtures were obtained from PerkinElmer. Triton® X-100 and tetramethylammonium hydroxide solution (TMAH, 25 % *w/v*) in water were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Sampling and Analytical Procedures

Certified organic (*n*=19) and ordinary grape juices (*n*=17) samples were obtained from local Brazilian retail markets. All organic samples were certified by the Brazilian IBD-Agricultural and Food Inspections and Certifications, which is accredited by the International Federation of Organic Agriculture Movements.

The ICP-MS method used in this study was based on the assay described by Batista et al. (2009) and used to determine 24 elements, namely, Al, Cr, As, Pb, Cd, Mn, Co, Se, Rb, Ni, Ba, V, Zn, Cu, Fe, Ca, Mg, Na, P, La, Ce, Mo, Ti, and Sn. A solution of rhodium at 10 μg L^{-1} was used as internal standard. A full description of the composition of the 36 grape juice samples is summarized in Table S1 (see Supplementary Material).

Data Analysis

PCA and SIMCA were performed using Pirouette (Version 3.11, Infometrix, Woodinville, WA, USA). Before applying PCA and SIMCA, all variables were "auto-scaled." This procedure gave all variables the same importance, by subtracting the average value from each variable and dividing the variable by its standard deviation. *F* test and *t* test (Miller and Miller 2005) were calculated using Microsoft Excel 2007. The dataset presented in this work is presented in Table S1 (see Supplementary Material).

SIMCA used cross-validation test; during this test, a sample was removed from the dataset. The classification model is rebuilt, and the removed sample is classified in this new model. All samples of the data set were sequentially removed and reclassified. Finally, a percentage of good classifications is also given (Frías et al. 2003).

Results and Discussion

Basic Statistics of Microchemical and Macrochemical Elements in Ordinary and Organic Grape Juices

Table 2 shows average and standard deviations obtained for the investigated macrochemical and microchemical elements in organic and ordinary grape juice samples. In addition, $P(F \leq f)$ one-tail and $P(T \leq t)$ one-tail values are given in the table.

Firstly, we applied the F test to both groups (organic and ordinary samples). The F test tells us whether two variances are "significantly" different from each other. $P(F \leq f)$ one-tail explains how to use the F test, to see whether two standard deviations are "the same" or whether they are "different." For example, comparing Al variances in organic and ordinary grape juice samples, we found a $P(F \leq f)$ one-tail value of 3.81×10^{-4}, which meant that there was a 3.81×10^{-2} % probability of observing the Al variance of organic grape juices in ordinary grape juices. Thus, assuming a 95 % confidence interval [P (0.05)], we assume that variances of Al average

concentrations in organic and ordinary grape juice samples are different.

Considering the F test at a confidence level of 95 % [P (0.05)], 14 elements had different variances (Al, Ba, Ca, Cd, Co, Cu, Fe, Mn, Na, P, Pb, Se, Ti, and V), while 10 elements exhibited equivalent variances (As, Ce, Cr, La, Mg, Mo, Ni, Rb, Sn, and Zn).

We use a t test to compare averages, to decide whether or not they are "the same." Statisticians say that the *null hypothesis* is tested, which states that the average values from two populations (organic and ordinary) are *not* different. If the F test indicates that the standard deviations are statistically equivalent at a 95 % confidence interval, a t test is carried out assuming equivalent variances. For example, there was no evidence that the As variances in ordinary and organic samples were different, because $P(F \leq f)$ one-tail had a value of 0.44. Thus, a t test was carried out assuming equivalent variances and a $P(T \leq t)$ one-tail value of 0.20 was found, which meant that there was a 20 % chance of Al averages being identical, and thus, we confirmed the null hypothesis.

Table 2 Descriptive statistical analysis of the concentrations of 24 chemical elements in ordinary and organic grape juice samples from Brazil

	Average	Average[a]	Standard deviation	Standard deviation[a]	$P(F \leq f)$ one-tail	$P(T \leq t)$ one-tail
Al	1926.5	2363.9	1038.0	2539.5	3.81E−04	2.49E−01
As	21.34	18.73	12.96	12.51	4.39E−01	2.01E−01
Ba	1818.3	5263.3	2039.3	5922.9	4.34E−05	1.29E−02
Ca	533.5	394.6	620.80	92.23	2.82E−11	1.87E−01
Cd	2.20	1.57	1.89	0.83	6.27E−04	1.08E−01
Ce	1561.3	2311.3	748.5	1004.5	1.21E−01	8.40E−03
Co	30.68	25.48	16.99	28.20	2.34E−02	2.52E−01
Cr	1130.2	1146.8	183.4	260.2	8.28E−02	4.14E−01
Cu	2328.4	2836.4	3506.8	1850.6	5.36E−03	2.99E−01
Fe	6.14	5.44	4.07	1.56	1.05E−04	2.56E−01
La	1204.0	2080.3	718.1	961.1	1.24E−01	2.10E−03
Mg	284.04	368.28	90.13	112.21	1.92E−01	9.48E−03
Mn	5758.1	6578.3	1604.5	2616.8	2.74E−02	1.30E−01
Mo	10.75	9.77	6.12	7.16	2.67E−01	3.32E−01
Na*	223.77	24.03	263.7	14.38	5.70E−19	3.30E−03
Ni	83.83	70.92	59.26	57.96	4.60E−01	2.57E−01
P	449.1	642.4	98.85	188.0	6.42E−03	2.62E−04
Pb	10.11	27.23	4.83	25.66	7.67E−09	5.10E−03
Rb	9191.5	15228.2	5488.4	7852.6	7.80E−02	6.18E−03
Se	22.22	16.32	18.24	6.45	3.35E−05	1.10E−01
Sn	18.76	45.77	18.00	22.94	1.68E−01	2.18E−04
Ti	904.9	1375.5	307.6	486.9	3.54E−02	7.09E−04
V	31.64	9.58	34.01	16.56	2.18E−03	1.18E−02
Zn	2092.1	2083.4	655.9	984.3	5.44E−02	4.88E−01

Fe, Ca, Mg, Na, and P concentrations are expressed in μg/g; all other values as ng/g

[a] Organic samples

Considering the *t* test at a confidence level of 95 % [*P* (0.05)] and assuming different variances, ordinary samples had higher Na and V concentrations than organic samples, while organic samples exhibited higher Ba, P, Pb, and Ti concentrations than ordinary samples. There was no statistical evidence that remaining elements (Al, Ca, Cd, Co, Cu, Fe, Mn, and Se) had different concentrations. Considering the *t* test at a confidence level of 95 % [*P* (0.05)] and assuming equivalent variances, organic samples exhibited higher Ce, La, Mg, Rb, and Sn concentrations than ordinary samples. There was no statistical evidence that the remaining elements (As, Cr, Mo, Ni, and Zn) had different concentrations.

Organic farming cannot use pesticides; application of certain pesticides is reflected in higher contents of Cu, Mn, and Zn in wine (Angelova et al. 1999; Komárek et al. 2010; Kristl et al. 2003; Mackie et al. 2012). Viticulturists use a Cu fungicide to combat downy mildew. The use of these Cu fungicides can increase Cu concentration in grape juice and wine (Angelova et al. 1999; Komárek et al. 2010; Kristl et al. 2003; Mackie et al. 2012). Organic samples should have lower levels of Cu, Mn, and Zn than ordinary samples, because organic farming is not supposed to use pesticides. However, there was no evidence that Cu, Mn and Zn concentrations in

organic samples were different from those in regular samples and vice versa.

Principal Component Analysis

PCA was used to achieve reduction of dimensions and to observe a primary evaluation of between-class similarity. PCA is a projection method that allows easy visualization of all the information contained in a dataset. In addition, PCA helps to elucidate how one sample is different from another and which variables contribute most to this difference. PCA was used to observe similarities among different grape juice samples, reducing dimensions from 24 variables to two principal components (Moreda-Piñeiro et al. 2003). For example, a dataset was obtained that consisted of 36 grape juice samples (19 organic and 17 ordinary) and 24 elements: Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, La, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Se, Sn, Ti, V, and Zn. The actual measurements can be arranged in a table or a matrix of size 36 × 24; this table is shown in Table S1 in the Supplementary Material (Bro and Smilde 2014)

With 36 lines and 24 columns, obtaining a proper overview of the available information within the dataset was difficult. PCA is a convenient statistical technique for this purpose,

Fig. 1 Principal component analysis of elemental concentration levels based on 24 chemical element levels in 36 grape juice samples. **a** score plot, **b** loading plot. Organic samples are *gray* and marked with the prefix "#"
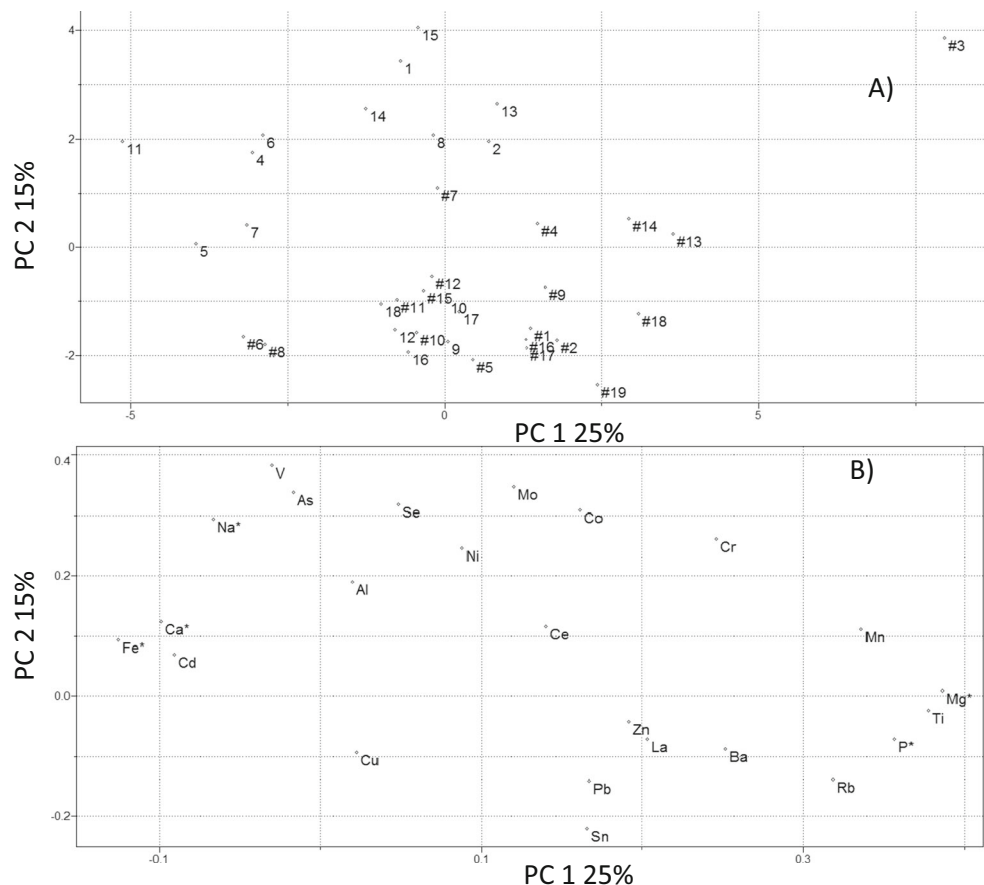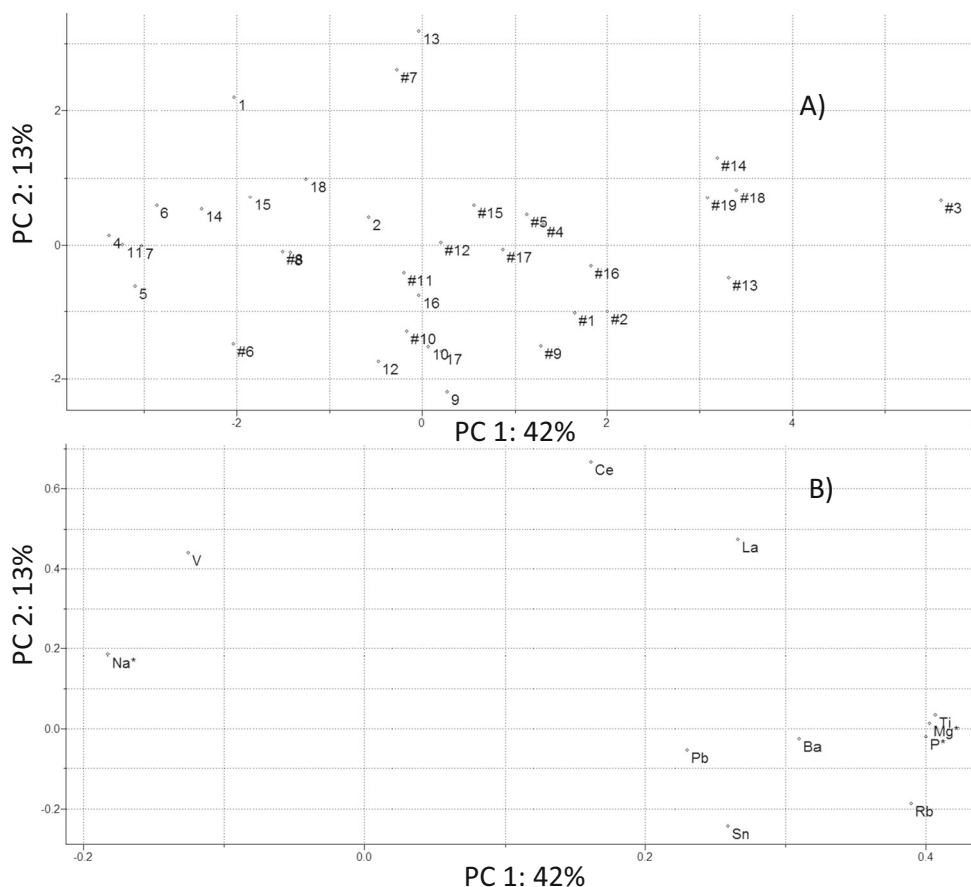
however, providing new variables, which better describe the variation in the entire dataset (Bro and Smilde 2014).

From the data, it was obvious that some variables were measured at much larger quantities than others. For example, Fe, Ca, Mg, Na and P were present at µg/g levels, whereas all remaining elements were seen in the ng/g range. If these scale differences are not properly handled, then PCA will only focus on high concentration numbers (Bro and Smilde 2014; Moreda-Piñeiro et al. 2001). It is always desired to model all variables; there is a preprocessing tool called auto-scaling, which adjusts all columns to the same "size," giving them an equal opportunity of being modeled (Bro and Smilde 2014). Auto-scaling means that from each variable, the mean value is subtracted and then the variable is divided by its standard deviation. Thus, our data was auto-scaled before the PCA model was build.

Initially, PCA analysis was carried out using 24 element concentrations as shown in Fig. 1, where Fig. 1a is the scores plot and Fig. 1b is the loadings plot. The variables were reduced by a projection of the 36 grape juice samples onto two new variables termed principal components (PCs). These were orientated and the first PC (PC1) described as much original variation as possible between the objects. In Fig. 1, the PC1 accounted for 25 % of total variance and the second principal component PC2 accounted for 15 % of total variance.

The importance of each variable to the original variables included in the PC is described by the loadings. By plotting the loadings for the two PCs, it is possible to assess the relative importance of each of the variables. In the loadings plot, the farther the distance of a chemical element is from the origin, the higher is its importance to the PC. For examples, in Fig. 1b, Ca, Cd, Fe, and Na are placed far from the origin in the left hand side and Mg, Mn, P, Rb, and Ti are placed far from the origin in the right hand side, which means that these concentrations have high importance in PC1. This observation could be extended to the description of the importance of each variable to PC2. Cr, Pb, and Sn are placed far from the origin in the bottom and As, Co, Mn, Mo, Na, Ni, and Se are placed far from the origin in the top, which indicates that these variables have high contributions to PC2. Elements placed close to the origin, such as Cu and Al, have lower importance to both PCs. The importance of each original variable in the distribution of samples (grape juice) is shown in the scores plot. For example, samples, which are placed at the right hand side, have higher Mg, Mn, P, Rb, and Ti concentrations and lower Ca, Cd, Fe, and Na concentrations.

Figure 1a shows that organic and ordinary grape samples were separated into two classes. Organic samples fell into the right hand side, while ordinary samples were located at the left hand side. Thus, the discrimination power was based on PC1.

Fig. 2 Principal component analysis of elemental concentration levels based on 11 chemical element levels in 36 grape juice samples. **a** score plot, **b** loading plot. Organic samples are *gray* and marked with the prefix "#"

Fig. 3 Coomans plot of the SIMCA model carried out for 24 chemical element concentrations. CS2@4 (*y*-axis) are ordinary samples. CS1@3 (*x*-axis) are organic samples. Organic samples have the prefix #; continuous lines are the critical SIMCA distances for each category
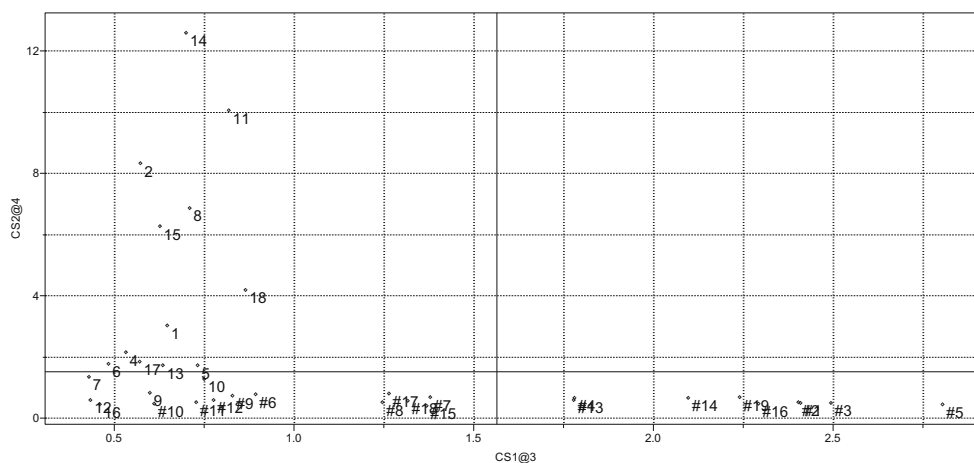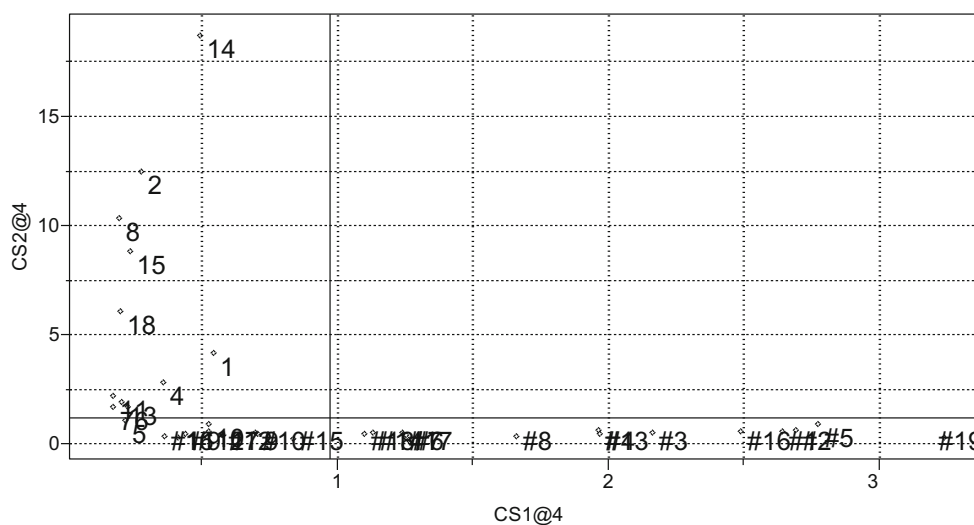

The distribution of the samples in Fig. 1a was in accordance with basic statistical analysis, where ordinary samples, with higher Na concentrations, were placed at the left hand side, while ordinary samples, with higher Mg, Mn, P, Rb, and Ti levels, were placed at the right hand side

Our first PCA model was unable to differentiate all organic samples from ordinary samples. Thus, a new PCA model was built using variables, which were statistically different. The new PCA model was carried out using Ba, Ce, La, Mg, Na, P, Pb, Rb, Sn, Ti, and Va concentrations, and is shown in Fig. 2, where Fig. 2a shows the scores plot and Fig. 2b the loadings plot. The model has a higher discrimination power in PC1 than the previous PCA model; it readily separated ordinary from organic samples, as is obvious from comparing both score plots (Figs. 1a and 2a).

In the new PCA model, the elements with high importance were Na and V, at the left hand side, and Mg, P, Rb, and Ti at the right hand side. Organic samples, which were placed at the right hand side, had lower Na and V and higher Mg, P, Rb, and Ti concentrations than ordinary samples, which were placed in the left hand side. However, this model was still unable to separate all organic samples from ordinary samples.

Classifications of Results via Soft Independent Modeling of Class Analogy

SIMCA is a modeling statistical technique that uses a box for each category. The center of the box is the mean value of the objects, and the orientation is defined by principal components; a range for each component is built on the basis of the distribution of the scores. Initially, the SIMCA model was carried out using 24 chemical element concentrations; three components were used for ordinary grape samples and four components for organic grape juice samples.

The recognition of the two classes (organic and regular) was highly satisfactory and SIMCA recognition only misclassified regular sample no. 16 as an organic sample, giving 94 % prediction ability for regular and 100 % for organic grape juice samples. Coomans plot (Fig. 3) showed that none of the built models admitted samples from the other category; thus, specificity was 100 % in all cases.

The SIMCA model was also carried out using only chemical element concentrations, which are statically different, as in our second PCA model. This SIMCA model was carried out using four components for ordinary and organic grape juice samples.

Fig. 4 Coomans plot of the SIMCA model carried out for 11 chemical element concentrations (Ba, Ce, La, Mg, Na, P, Pb, Rb, Sn, Ti, and Va). CS2@4 (*y*-axis) are ordinary samples. CS1@4 (*x*-axis) are organic samples. Organic samples have the prefix #; continuous lines are the critical SIMCA distances for each category

The recognition of the two classes (organic and regular) was highly satisfactory and SIMCA recognition misclassified four samples; three regular samples were misclassified as organic and one organic sample as ordinary, giving 82 % prediction ability for regular and 95 % for organic grape juice samples. Coomans plot (Fig. 4) showed that none of the built models admitted samples from the other category; thus, specificity was 100 % in all cases.

The threshold lines divide the plot into four quadrants. A sample in the fourth quadrant is a member only of the *x*-axis class; its distance to that class is small enough for it to be considered a member of the class. A sample falling in the second quadrant is a member only of the *y*-axis class. A sample in the third quadrant could belong to either category and one in the first quadrant belongs to neither. These plots can be thought of as decision diagrams, as described by Coomans (Frías et al. 2003).

In the Coomans plot, samples placed in the third quadrant could reduce SIMCA's prediction ability for samples placed outside of the calibration dataset. The first SIMCA model, which was carried out with 24 concentrations, had higher prediction ability than the second model, which was carried out using 11 chemical element concentrations. However, the second SIMCA model contained fewer samples in the third quadrant than the first SIMCA model, which indicates that the second SIMCA model afforded a better prediction ability of samples that were outside the training dataset.

Conclusion

This paper describes the first application of ICP-MS to the discrimination of organic and regular grape juices. The concentration levels of 24 chemical elements (both macroelements and microelements) were interpreted using techniques such as PCA and SIMCA, which provided a robust approach for evaluation of authenticity of organic grape juice samples. In addition, the SIMCA model, which was carried out with 11 chemical element concentrations, may provide a better prediction ability for samples that are outside of the calibration dataset than the SIMCA model, which was carried out with 24 chemical element levels. In Brazil, organic grape juices are 2–5 times more expensive than ordinary grape juices, and the approach presented here is therefore expected to be very useful for the verification of the organic authenticity.

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