

## Chemical pattern of brazilian apples. A chemometric approach based on the Fuji and Gala varieties

*Padrão químico da maçã brasileira. Uma abordagem quimiométrica baseado nas variedades Fuji e Gala*

Renato Giovanetti VIEIRA<sup>1,5\*</sup>, Rosilene Aparecida PRESTES<sup>1,4</sup>,  
Frederico DENARDI<sup>2</sup>, Alessandro NOGUEIRA<sup>1</sup>, Gilvan WOSIACKI<sup>1,3</sup>

### Abstract

The chemical composition of apple juices may be used to discriminate between the varieties for consumption and those for raw material. Fuji and Gala have a chemical pattern that can be used for this classification. Multivariate methods correlate independent continuous chemical descriptors with the categorical apple variety. Three main descriptors of apple juice were selected: malic acid, total reducing sugar and total phenolic compounds. A chemometric approach, employing PCA and SIMCA, was used to classify apple juice samples. PCA was performed with 24 juices from Fuji and Gala, and SIMCA, with 15 juices. The exploratory and predictive models recognized 88% and 64%, respectively, as belonging to a mixed domain. The apple juice from commercial fruits shows a pattern related to cv. Fuji and Gala with boundaries from 0.18 to 0.389 g.100 mL<sup>-1</sup> (malic acid), from 8.65 to 15.18 g.100 mL<sup>-1</sup> (total reducing sugar) and from 100 to 400 mg.L<sup>-1</sup> (total phenolic compounds), but such boundaries were slightly shorter in the remaining set of commercial apple juices, specifically from 0.16 to 0.36 g.100 mL<sup>-1</sup>, from 9.25 to 15.5 g.100 mL<sup>-1</sup> and from 180 to 606 mg.L<sup>-1</sup> for acidity, reducing sugar and phenolic compounds, respectively, representing the acid, sweet and bitter tastes.

**Keywords:** chemometry; chemical descriptor; pattern recognition.

### Resumo

A composição química de sucos de maçã pode ser usada para diferenciar as variedades de mesa das industriais. Fuji e Gala têm características químicas que podem ser usadas para esta classificação. Métodos multivariados relacionam descritores químicos com a categoria da variedade de maçã. Três principais descritores do suco de maçã foram selecionados: ácido málico, açúcar redutor total e compostos fenólicos. Uma abordagem quimiométrica, empregando PCA e SIMCA, foi usada para classificar amostras de sucos de maçã. PCA foi realizado com 24 amostras de suco de Fuji e Gala, e SIMCA, com 15 sucos. Os modelos exploratórios e preditivos reconheceram 88% e 64%, respectivamente, como pertencentes a um domínio misto. Os sucos de maçã de frutas comerciais mostraram um padrão com as cultivares Fuji e Gala com limites de 0,18 a 0,389 g.100 mL<sup>-1</sup> (ácido málico), de 8,65 a 15,18 g.100 mL<sup>-1</sup> (açúcar redutor total) e de 100 a 400 mg.L<sup>-1</sup> (compostos fenólicos), mas tais limites foram levemente menores no conjunto restante de sucos de maçãs comerciais, especificamente de 0,16 a 0,36 g.100 mL<sup>-1</sup>, 9,25 a 15,5 g.mL<sup>-1</sup> e 180 a 606 mg.L<sup>-1</sup> para acidez, açúcar redutor total e compostos fenólicos, respectivamente, representando os sabores ácido, doce e amargo.

**Palavras-chave:** quimiometria; descritores químicos; reconhecimento de padrões.

## 1 Introduction

The production of apples actually began in the early 1970s with cultivars adapted to the highland locations in the Southern States of Brazil. The economic viability was then explained to the people involved with investments in the apple business, focusing on the technological intensification on the Fuji and Gala varieties, which represent 93% of the apple production (KREUTZ et al., 2002). The remaining 7% of apple production comprises many precocious varieties, most of them with a very low chilling requirement and harvesting time much earlier than cv. Gala, which currently represents good options to small fruit growers and attractive prices. In a world-wide perspective, Gala

and Fuji have been ranked as the 3<sup>rd</sup> and 4<sup>th</sup> apples produced, in metric ton, only behind Golden Delicious (1<sup>st</sup>) and Delicious (2<sup>nd</sup>) (WORLD APPLE REVIEW, 2008).

Fuji and Gala apples were brought to Brazil in the 1960s, the former from Japan and the latter from New Zealand (WOSIACKI et al., 2002). Even in the colder regions of Southern Brazil, the chilling requirement for these apples is not satisfied in areas below an altitude of 1.300 m, where chemical treatments are needed to break bud dormancy. For cv. Fuji, even with good flowering, cropping and a non-biannual bearing, the fruit quality is better above an altitude of 1.300 m. In contrast, Gala has good

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<sup>1</sup> Departamento de Engenharia de Alimentos, Universidade Estadual de Ponta Grossa - UEPG, Av. Carlos Cavalcanti, 4748, CEP 84030-900, Ponta Grossa, PR, Brasil

E-mail: gilvan.wosiacki@pesquisador.cnpq.br; alessandro.nogueira@pesquisador.cnpq.br; raprestes@yahoo.com.br; renatogiovanetti@gmail.com

<sup>2</sup> Empresa de Pesquisa Agropecuária e Extensão Rural de Santa Catarina, Rua Alcides Tombini, 33, CEP 89500-000, Paraíso, Caçador, SC, Brasil

<sup>3</sup> CNPq-PQ1, Departamento de Engenharia de Alimentos, Universidade Estadual de Ponta Grossa, Av. Carlos Cavalcanti, 4748, CEP 84030-900, Ponta Grossa, PR, Brasil

<sup>4</sup> CNPq-PDJ, Departamento de Engenharia de Alimentos, Universidade Estadual de Ponta Grossa, Av. Carlos Cavalcanti, 4748, CEP 84030-900, Ponta Grossa, PR, Brasil

<sup>5</sup> CNPq-AT, Departamento de Engenharia de Alimentos, Universidade Estadual de Ponta Grossa, Av. Carlos Cavalcanti, 4748, CEP 84030-900, Ponta Grossa, PR, Brasil

\*Corresponding author

performance even at lower elevations. According to Henschke (1994), more studies must be conducted to improve the main varieties concerning appearance, amount of juice, size, shape, storage capacity and to reach a yield of 25 ton.ha<sup>-1</sup> of high quality apples aiming to export them to other places, within Brazilian borders or overseas. Harvested commercial apples are driven through a complex selection and physical classification system where 70% are classified as table fruit and, of the remaining fruit, 10% is classified to be waste (negative costs) and 20% is damaged but healthy fruit, which constitutes the actual Brazilian industrial raw material. The classification of apples for commercialization was made by taking into consideration sensorial aspects such as acid, sweet and bitter tastes. The amounts of malic acid and total phenolic compounds have been used for the commercial classification of apples, usually as bitter sweet, but such *praxis* does not include the total reducing sugar content.

The use of multivariate methods to establish the relationship between the independent continuous variable and the categorical variable is becoming widespread (BARROS NETO; SCARMÍNIO; BRUNS, 2006; BLANCO-GOMIS et al., 1998).

Exploratory techniques such as Principal Component Analysis (PCA) may be used to select the main continuous descriptors of a categorical variable and, with the auto-scaled data, may provide an exploratory model. Classificatory techniques such as Soft Independent Modeling of Class Analogy (SIMCA) may be used to classify similar categorical variables (BARROS NETO; SCARMÍNIO; BRUNS, 2006). Alonso-Salces et al. (2005) used the pattern recognition analysis of the apple polyphenolics to classify them by their maturity state. Blanco-Gomis et al. (1998) discriminated apple juices clarified by micro-filtration or by ultra-filtration by an exploratory HCA to select the best descriptor, using PCA to quantify the components, and LDA (Linear Discriminant Analysis) and KNN to classify the juices with 100% correctness. González, Peña-Mendez (2000) were able to differentiate must and wine through chemometric analysis such as Discriminant Analysis (DA), PCA, Biplot (BA) and Factor Analysis (FA). Molfetta et al. (2005) studied the structure – activity relationship (SAR) of quinone compounds with biological activity by employing PCA, HCA, SIMCA and KNN.

A multivariate analyses approach may be useful to classify apple varieties according to a few independent chemical descriptors of apple juices. The main purpose of this article was to establish the chemical pattern of Brazilian commercial apples according to the selected chemical descriptors of the Fuji and Gala varieties by employing multivariate methods.

## 2 Materials and methods

### 2.1 Materials

Samples of commercial and experimental varieties of apple were collected during many seasons, since 1992 to the present, from many places in the Southern States of Brazil. Their juices were analyzed and the results stored in the GTM database. From

this database, the chemical descriptors of many samples from Fuji and Gala juices were recovered for an initial screening to select the main descriptors for juice classification. Then, the chemical descriptors of 12 samples from both varieties, as well from 15 authentic apple juices obtained from commercial varieties, were recovered in order to test the capacity of the predicting model. Usually, 5-10 kg of sample were processed to obtain depectinized juice. Stabilized apple juices were used for further analyses after a qualitative paper filtration, when necessary. Pectinolytic enzymes samples (Pectinex 3 XL – NOVO Nordisk do Brazil) used for apple juice clarification were donated by LNF Ltd., Bento Gonçalves, RS. Chemical products used in the analyses or in the experiments were also from quality *pro analysis*.

### 2.2 Methods

#### Processing

Apple juice was obtained by mechanical pressure according to the protocol described by Wosiacki et al. (1989), depectinized in a hot step in a water bath (2 hours, 45 °C), filtered through paper, bottled, closed and stabilized through freezing.

#### Analysis

Total Soluble Solids (TSS) were determined in a refractometer adjusted to 20 °C (INSTITUTO..., 1985). The content of glucose (GLC) was determined with a glucose oxidase kit assay and the amount of fructose (FRU) was then calculated as the remnant from reducing sugar. The amount of sucrose (SAC) was determined as the difference between total reducing sugar and reducing sugar (SOMOGYI, 1945; NELSON, 1944). The total titrable acidity (TTA) was determined with 0.1 M NaOH and expressed as malic acid (MAL) in g.100 mL<sup>-1</sup>. The total phenolic compounds (TPC) were determined through the Folin-Ciocalteu reagent (TANNER; BRUNNER, 1979) and expressed as (+) catechin, in mg.L<sup>-1</sup>. The *ratio* was calculated by total reducing sugar/total titrable acidity as an adimensional figure. The Descriptive Statistic Analysis of the chemical descriptors was made by employing the *Statistic*® 7.0 software. The Principal Component (PCA) was employed in the exploratory analysis and the pattern recognition method Soft Independent Modeling of Class Analogy (SIMCA) was used to classify the apple varieties (categorical) according to their relationship with selected chemical descriptors (continuous variable). The auto scaled processing allowed the results to be compared to each other at the same scale (BARROS NETO; SCARMÍNIO; BRUNS, 2006). PCA and SIMCA were performed with *Pirouette*® software, version 4.1 (Infometrix).

## 3 Results and discussion

Table 1 shows the main chemical attributes of ‘Fuji’ and ‘Gala’ apple juice samples, recovered from the database maintained by the GTM (Apple Working Team) at Ponta Grossa State University. All the independent chemical attributes were

tested aiming to select the most interesting ones to be used as a discriminative attribute, or chemical descriptor.

All attributes were submitted to exploratory analyses and those with greater statistic potential, for further pattern recognition methods, were selected as chemical descriptors. The main independent descriptors were total malic acid (MAL), total reducing sugar (TRS) and total phenolic compound (TPC) contents. These descriptors represent the acid taste, the sweetness or sweet taste and bitterness or bitter mouth feeling. A relative descriptor, namely *ratio*, a function of the total reducing sugar and total malic acid contents,  $ratio [r = f(\text{TRS}, \text{MAL})]$ , was left together due to its utilization in the first step of apple characterization.

A group of 24 authentic 'Fuji' and 'Gala' apple juices, whose descriptors are shown in Table 2, was used in the exploratory experiments with multivariate methods. The values found for both fruit cultivars were close, but they suggest that Fuji ( $\text{MAL} = 0.275 \pm 0.045 \text{ g.100 mL}^{-1}$ ;  $\text{TRS} = 12.52 \pm 1.44 \text{ g.100 mL}^{-1}$ ;  $\text{TPC} = 255 \pm 77 \text{ mg.L}^{-1}$ ) is sweeter than Gala ( $\text{MAL} = 0.278 \pm 0.056 \text{ g.100 mL}^{-1}$ ;  $\text{TRS} = 11.30 \pm 1.64 \text{ g.100 mL}^{-1}$ ;  $\text{TPC} = 317 \pm 116 \text{ mg.L}^{-1}$ ), which has a higher acidity and bitterness.

Although the results of total phenolic compounds from samples Gala 13 and Gala 21 seem to be quite different from the Gala set, these samples were not excluded by the Q-test (SHUGAR; BALLINGER, 1996).

**Table 1.** Main physical-chemical attributes of apple juices.

Analysis	Fuji						Gala					
	N*	Min	Mean	Max	Std. Dev.	Var	N	Min	Mean	Max	Std. Dev.	Var
Malic acid, g.100 mL <sup>-1</sup>	40	0.136	0.249	0.434	0.082	0.007	55	0.123	0.285	0.401	0.058	0.003
Reducing Sugar, g.100 mL <sup>-1</sup>	40	6.46	10.36	15.31	2.09	4.37	55	6.30	8.70	14.65	1.90	3.60
Total reducing sugar, g.100 mL <sup>-1</sup>	39	10.17	12.75	16.29	1.56	2.44	54	9.00	11.06	15.04	1.51	2.28
Ratio	24	24.82	67.10	113.92	28.62	819.22	33	25.52	40.52	56.54	8.60	73.89
Total phenolic compounds, mg.L <sup>-1</sup>	37	130	254	404	69	4,716	52	124	297	544	98	9,578
Fructose, g.100 mL <sup>-1</sup>	33	3.33	7.36	9.84	1.63	2.64	48	4.87	6.99	9.99	1.54	2.36
Glucose, g.100 mL <sup>-1</sup>	34	0.99	2.98	5.20	1.11	1.23	49	0.82	1.46	2.29	0.29	0.08
Sucrose, g.100 mL <sup>-1</sup>	38	0.52	2.62	5.62	1.22	1.50	53	0.55	2.52	5.95	0.96	0.92

**Table 2.** Chemical descriptors of 24 apple juices from cvs. Fuji and Gala.

Code	Variety	Crop	Malic acid (g.100 mL <sup>-1</sup> )	Total reducing sugar (g.100 mL <sup>-1</sup> )	Total phenolic compounds (mg.L <sup>-1</sup> )	Ratio
1	Fuji	1986-1987	0.287	15.80	404	55.052
2	Fuji	1990-1991	0.250	12.04	200	48.14
3	Fuji	1991-1992	0.330	13.37	200	40.52
4	Fuji	1993-1994	0.220	12.08	130	54.91
5	Fuji	1994-1995	0.265	12.29	195	46.38
6	Fuji	1995-1996	0.310	12.50	261	40.32
7	Fuji	2000-2001	0.290	12.04	260	41.52
8	Fuji	2001-2002	0.310	11.46	259	36.97
9	Fuji	2002-2003	0.346	10.17	374	29.39
10	Fuji	2004-2005	0.196	13.59	309	69.60
11	Fuji	2005-2006	0.238	13.65	228	80.05
12	Fuji	2006-2007	0.259	11.33	240	43.92
13	Gala	1986-1987	0.317	15.04	544	47.45
14	Gala	1990-1991	0.315	12.70	200	40.32
15	Gala	1991-1992	0.330	12.00	200	36.36
16	Gala	1993-1994	0.200	10.62	222	53.10
17	Gala	1994-1995	0.162	10.62	222	65.76
18	Gala	1999-2000	0.320	11.11	403	34.72
19	Gala	2000-2001	0.312	10.33	309	33.15
20	Gala	2001-2002	0.313	10.56	293	33.78
21	Gala	2002-2003	0.250	9.32	493	37.28
22	Gala	2004-2005	0.249	12.86	392	51.60
23	Gala	2005-2006	0.329	11.21	238	35.19
24	Gala	2006-2007	0.240	9.20	291	38.33

The chemical descriptors of a set with 15 authentic commercial varieties of apple juices, selected to verify the effectiveness of the model, are shown in Table 3. Average figures of the selected descriptors (malic acid =  $0.295 \pm 0.087$  g.100 mL<sup>-1</sup> [29.7%], total reducing sugar =  $12.12 \pm 1.52$  g.100 mL<sup>-1</sup> [12.57%], total phenolic compounds =  $349 \pm 131$  mg.L<sup>-1</sup> [37.59%]) reflect a more acid and bitter set, although intermediate in sweetness.

According to Lea (1995) and Lea and Drilleau (2003), the scatter plot of the amount of malic acid and total phenolic content (Table 2) may define four groups as the former separate the sweet ( $< 0.45$  g.100 mL<sup>-1</sup>) from the sharp ( $> 0.45$  g.100 mL<sup>-1</sup>) and the latter, the bitter ( $> 200$  mg.L<sup>-1</sup>) from the sweet ( $< 200$  mg.L<sup>-1</sup>). The four apple groups are named sweet, sharp, bitter sweet and bitter sharp by these criteria. Schobinger (1995) used the central criterion but stretched the boundaries, creating domains with expressions such as “very low acid – flat”, “very high acid – sour”, for instance, and proposed a circular area inside the diagram where the combination was harmonious. It must be considered that the enzyme-treated apple juices do have lower amounts of phenolic compounds and so the process should be kept the same (SCHOBINGER, 1995; NOGUEIRA et al., 2003).

Figure 1a shows the position of each of the 24 samples of apple juice from the set of authentic Fuji and Gala varieties concerning the malic acid and phenolic compound coordinates. The chemical domain of these commercial apples is defined within the limits from 0.15 to 0.35 g.100 mL<sup>-1</sup> of malic acid and from 100 to 600 mg.L<sup>-1</sup> of total phenolic compounds, and so they can be classified as sweet and bittersweet apples. However, neither the ‘Fuji’ nor the ‘Gala’ domains can be discriminated in such a classification procedure. Likewise, Figure 1b shows the position of each of the 15 authentic samples of commercial apple juices, and it was confirmed that they fall in the same area, with the exception of Royal Gala [47], Princesa [21] and Imperial Gala [46], which are slightly more acidic than 0.35 g.100 mL<sup>-1</sup>.

Czelusniak et al. (2003) analyzed fruits harvested in a commercial orchard including fruits from producer and pollinator trees during the 2001/2002 season. Among 27 apple juices, one was classified as sweet; 14 as bittersweet within the boundaries of this experiment; three were found to contain more phenolic compounds; and ten were categorized as bitter sharp. The first 15 samples were apples with commercial appeal. Table apples are usually qualified as bittersweet (SCHOBINGER et al., 1995). According to these criteria, Paganini et al. (2004), qualified five apples as bittersweet and two as sweet from seven commercial apple varieties harvested in the 2003/2004 season. Fertoni et al. (2006) reported that the samples of ‘Gala’, ‘Fuji’ and ‘Joaquina’ they used to extract pectin from *pomaceae* were indeed qualified as bitter. Nogueira et al. (2006) reported that from 14 samples of apple juices, comprising four commercial and ten advanced selections, five were qualified as bitter sharp and could be used as raw material and the others as bittersweet, obviously table apples.

The ratio between total reducing sugar and malic acid provides a descriptor for the quality of apple and the adimensional value of 20 separates the industrial from the commercial (LEA, 1995). Figures 2a and 2b show that all apples listed in Tables 2 and 4 are table fruits and do not fit any technological utilization. This experiment states that none of the samples tested falls in the domain of industrial set of apples, considering their own profile of quality, completely clustered in the domain of commercial apples. This can be extended to the conclusion that the apples used for juice processing in Brazil are, indeed, of commercial quality and they do not fit any industrial pattern. But, while working with 27 samples of apple varieties (including three producers and pollinizers), Czelusniak et al. (2003) proved that, although many components of this set belong to the commercial category, they have been classified as industrial. The highest is ‘Einshemer’, with a high malic acid content – around 1.0 g.100 mL<sup>-1</sup>, and Rainha,

**Table 3.** Chemical descriptor of 15 apple juices from commercial varieties

Code	Variety	Malic acid (g.100 mL <sup>-1</sup> )	Total reducing sugar (g.100 mL <sup>-1</sup> )	Total phenolic compounds (mg.L <sup>-1</sup> )	Ratio
25	Catarina	0.265	14	250.417	52.819
26	Condessa	0.177	11.264	447.495	63.746
27	Daiane	0.286	13.788	397.934	48.151
28	Eva	0.403	10.217	244.937	26.214
29	Golden delicious	0.312	10.533	535.082	33.757
30	Imperatriz	0.250	14.711	460.566	58.767
31	Joaquina	0.194	13.044	250.545	67.776
32	Kiko 8	0.227	12.944	257.8	57.001
33	Mollie's Delicious	0.260	11.267	523.312	43.799
34	NF Golden	0.324	10.236	381.281	31.607
35	Red Delicious	0.206	13.522	518.689	66.071
36	Royal Gala	0.270	10.356	318.033	38.372
37	Sansa	0.337	12.889	364.204	38.207
38	Princesa	0.456	11.06	114	10.307
39	Eva	0.454	11.982	183.5	26.897

Primicia, and Princesa, with malic acid contents of 0.64, 0.46 and 0.42, respectively.

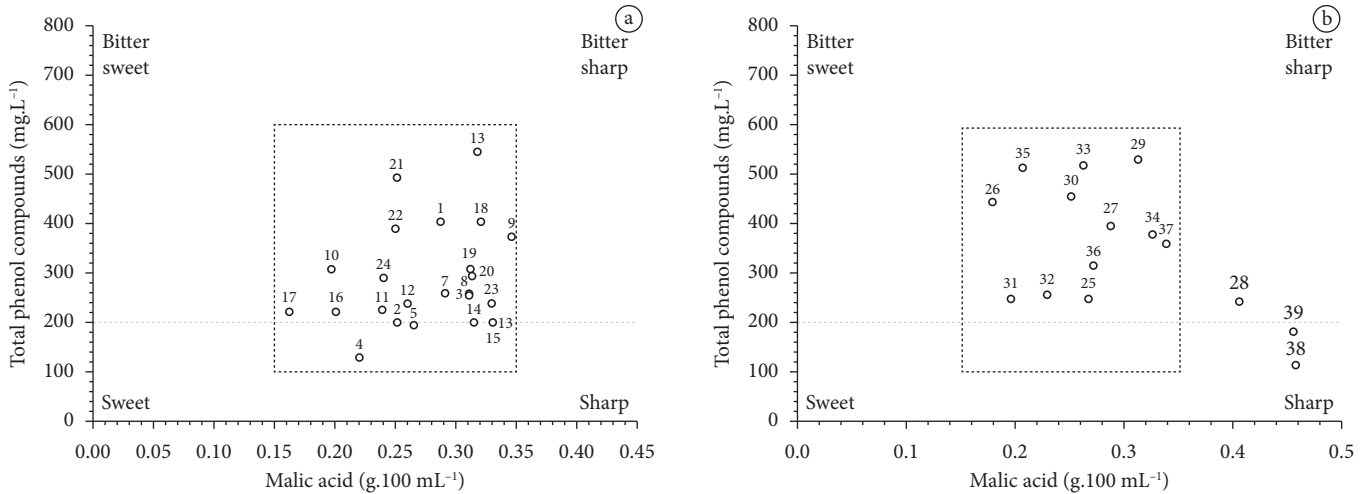
These approaches to classify apples do not give any direct information concerning the total reducing sugar and both plots in Figure 2 are not quite correct, since a high ratio (TRS/MAL) may be achieved either by acid-poor or by sugar-poor apples

In this experiment, it was shown that the main commercial Brazilian apples have an intrinsic profile of quality, and so, chemometric methods may be used to recognize this pattern in their juices. It seems reasonable to look for techniques of pattern recognition to classify apples for definitive commercial and industrial purposes.

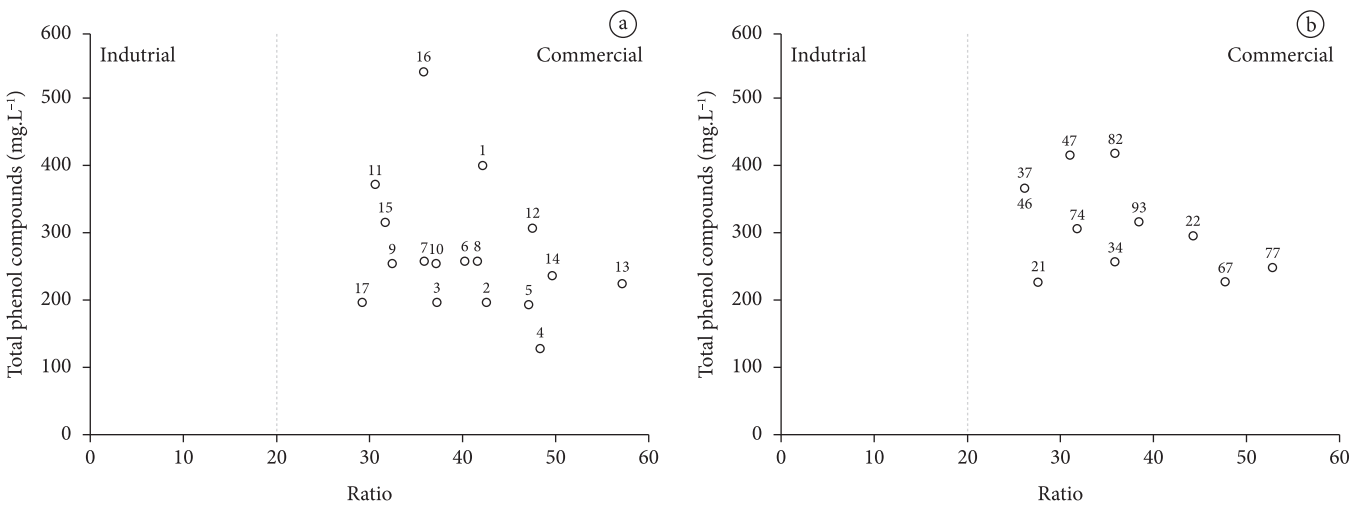
The Principal Component Analysis (PCA) aims to group the chemical descriptors generating a new set of variables called Principal Components (PCs), which are linear combinations of

the original continuous variables, completely independent. After several attempts to obtain a good classification for the categorical variables (apple varieties), the best results were found with three independent and continuous variables (Table 2). The first three principal components explain 100% of the total variance as follows: PC1 = 42.50%, PC2 = 31.00%, PC3 = 26.50%. The plots of scores were examined and the most informative one is presented in Figure 3, which shows the PC1 against PC2, corresponding to a total of 73.50%. Such a plot revealed that sample discrimination is related to the first principal component (PC1).

Figure 3a shows the separation of the sweeter Fuji juices from the more acidic and bitter Gala juices, according to the loadings of the continuous variables, shown in Figure 3b. The samples Gala 14 and Fuji 10 lay down in a mixed domain, because their descriptors are so close that the model could not



**Figure 1.** Scatter plot (malic acid vs. total phenolic compounds) of the samples of standard commercial Fuji and Gala apples a) discriminates their domain, and the group of authentic samples of selected commercial apples is included in such domain, b) except for three varieties, which are more acidic.



**Figure 2.** Scatter plot (ratio vs. total phenolic compounds) of the samples of Fuji and Gala apples a) and of the samples of commercial apple varieties b), showing that none of them have an industrial profile.

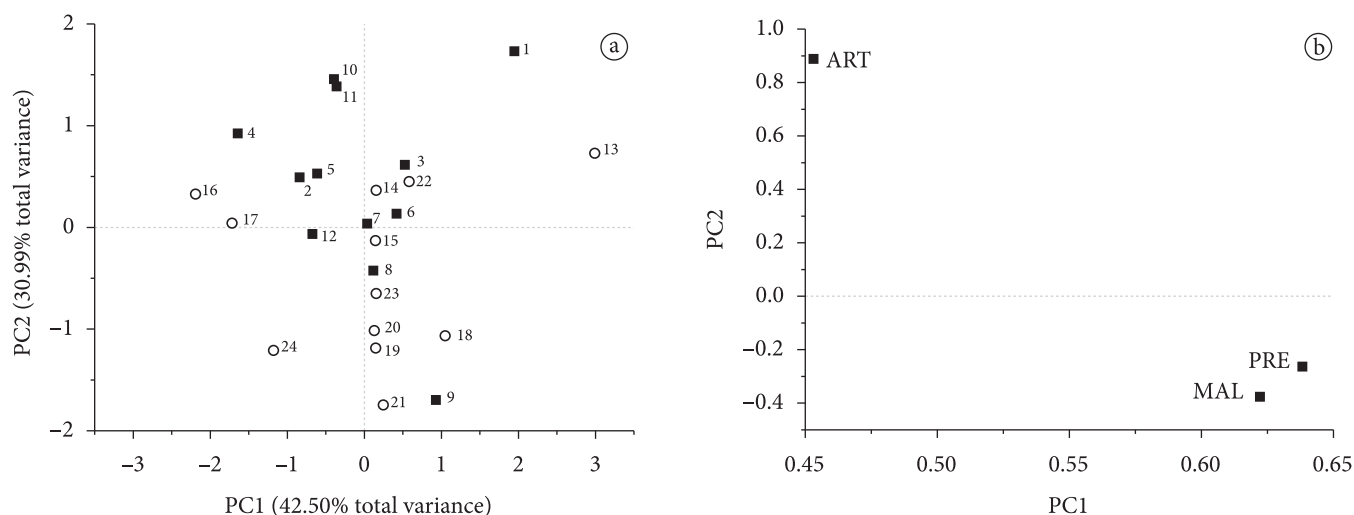
discriminate them. The samples of Fuji juice have a descriptor with less dispersion, so its cluster is more homogeneous, once it occupies a smaller space than that of Gala juices. As there are spatial domains where 'Fuji' and 'Gala' may fit due to their similarity, the test apple juices can be qualified either as Fuji or/and as Gala.

SIMCA, related to PCA because both are based on the generation of new variables that are a linear combination of the original, may also be used for pattern recognition and classification of apple varieties. The 3D plot of PC1, PC2 and PC3 factor 3 is shown in Figure 4.

Table 4 shows the pattern recognition of the standard and of some authentic samples of apple cultivars stating its similarity for 'Fuji', for 'Gala', for both, or for none of them. In the set of authentic 'Fuji' and 'Gala' samples, none of the samples were recognized as 'Fuji', but three samples belong to Gala's domain and 21 (88%) belong to the mixed domain. As expected, none of the samples became ungrouped. In the set of 15 authentic commercial samples to be modeled, none were predicted to be 'Fuji', and four were found in the 'Gala' domain, nine (60%) were found in the mixed domain and three were excluded by the model. These results confirmed the pattern recognition of the model, and the possibility to qualify any commercial apple as Fuji and/or Gala.

Figure 4a shows the SIMCA model for authentic Fuji and Gala samples and Figure 4b shows the qualification of authentic commercial apple samples. The chemical pattern established by the chemical descriptors of 'Fuji' and 'Gala' was recognized until the 3<sup>rd</sup> level by multivariate statistic methods (SIMCA). Curiously, none of the commercial authentic samples was qualified as 'Fuji', but four (Rainha, Imperatriz, Mollie's Delicious and Red Delicious) were categorized as 'Gala' alone. All other test samples belonged to the mixed domain, except for Princesa and Eva, which were ungrouped. It seems reasonable to quantify the selected descriptors in order to restrict the chemical pattern as that based in the Fuji and Gala domain, and to respect the borders defining the model. Table 5 shows such values, including the borders of the model.

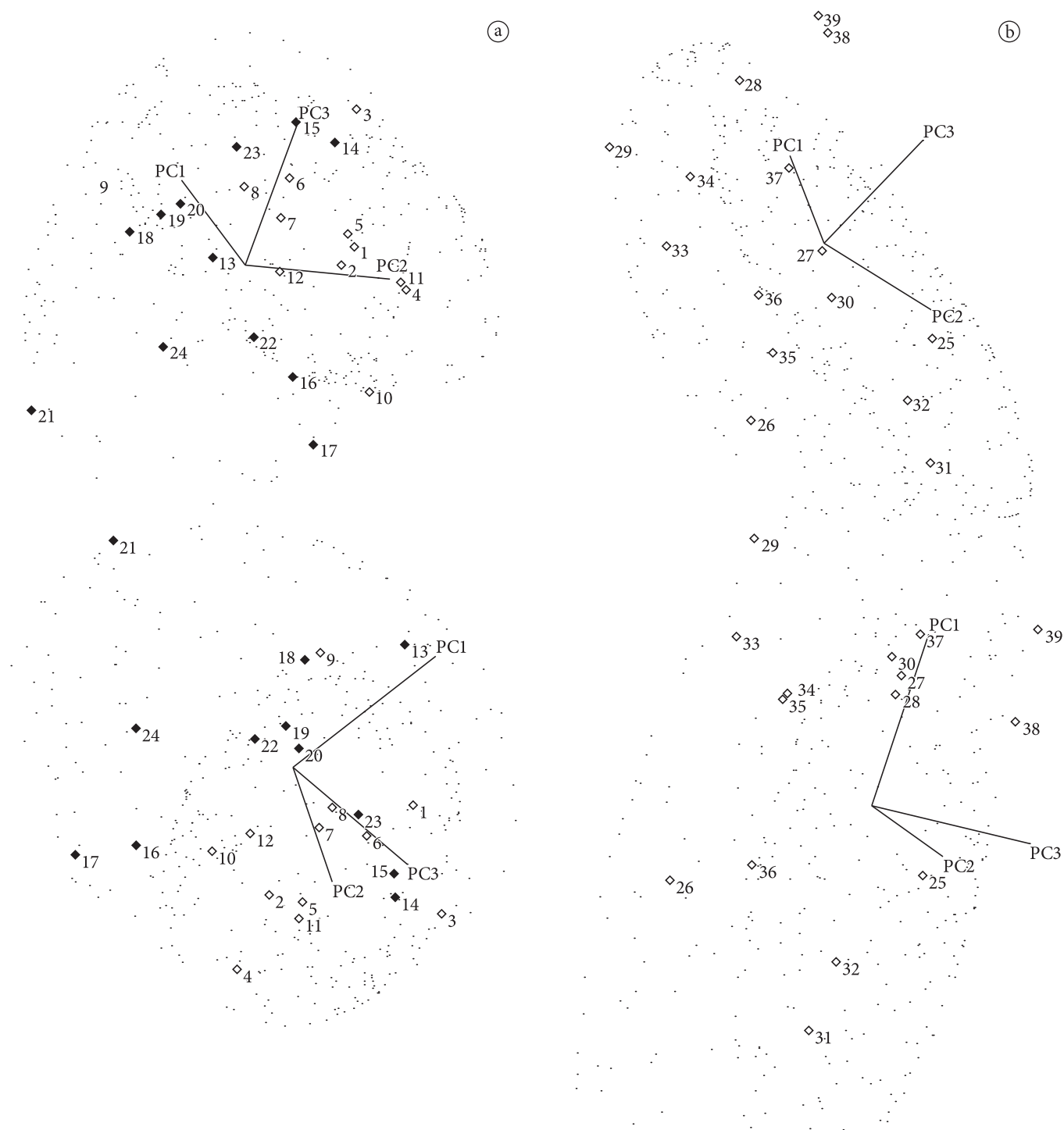
Those values were not comparable to those reported by Czelusniak et al. (2003) on the chemical classification of samples from apples of 27 varieties, because there are not any internal reference varieties. However, if one takes into account only the fruits fitting the commercial frontier in this article, based on Fuji and Gala apples, their results are similar because  $MAL = 0.274 \pm 0.068 \text{ g} \cdot 100 \text{ mL}^{-1}$  with a minimum of 0.150 and a maximum 0.340,  $TRS = 10.65 \pm 1.4 \text{ g} \cdot 100 \text{ mL}^{-1}$ , from 8.25 to 12.70, and  $TPC = 286 \pm 97 \text{ mg} \cdot \text{L}^{-1}$ , from 222 to 403.



**Figure 3.** Score a) and loading b) plots of data concerning samples of Fuji (■) and Gala (○) apple juice.

**Table 4** Results of SIMCA concerning similarity to 'Fuji' or to 'Gala' apples.

Domain	Exploratory model	Predictive model
Only Fuji	None	None
Only Gala	1, 13, 21	26, 30, 33, 35
Either Fuji or Gala	2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, 16, 17, 18, 19, 20, 22, 23, 24	25, 27, 28, 29, 31, 32, 34, 36, 37
Neither Fuji nor Gala	None	38, 39

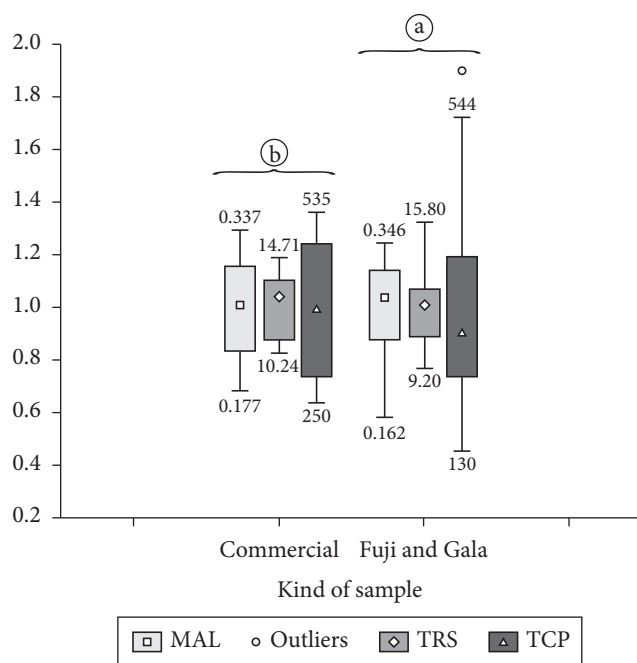


**Figure 4.** SIMCA model obtained with the a) descriptors of Fuji and Gala and the b) predictive classification of authentic commercial apples, from two different points of view.

**Table 5.** Descriptor values of the Fuji and Gala domain.

Descriptors	Average	Borders
Malic acid (g.100 mL <sup>-1</sup> )	0.259 ± 0,051	0.156-0.361
Total Reducing Sugars (g.100 mL <sup>-1</sup> )	11.38 ± 1.574	9.24-15.51
Total Phenolic Compounds (mg.L <sup>-1</sup> )	392 ± 107	178-606

To illustrate such a chemical pattern, Figure 5 shows a box and whisker plot with a broader amplitude of the 'Fuji' and 'Gala' descriptor than that of the commercial apple juice samples and a slight exception in what concerns malic acid – the apple juices used to test the model are slightly more acidic than the standard juices.



**Figure 5.** a) Representation of the inferior and superior normalized values of the chemical descriptors from 17 authentic commercial Fuji and Gala apples. b) Representation of the inferior and superior borders of ten authentic commercial apples that are clearly inside the volume of the Fuji and Gala borders.

#### 4 Conclusions

The chemical descriptors malic acid and total phenolic compounds state the chemical pattern based on the main commercial varieties in Brazil, namely Fuji and Gala, in the domain  $0.15\text{--}0.35\text{ g}\cdot 100\text{ mL}^{-1}$  (malic acid) and  $100\text{--}500\text{ mg}\cdot\text{L}^{-1}$  (total phenolic compounds), qualified as sweet and bittersweet apples, respectively. None of the authentic samples of apple fit the condition to be considered as industrial, with a ratio TRS/MAL below 20.

The exploratory PCA screened and auto-scaled the best malic acid, total reducing sugar and total phenolic compound chemical descriptors to be used in the classificatory SIMCA, whose model discriminates all commercial varieties as Fuji, as Gala or as both Fuji and Gala, with 100% correctness.

The chemical pattern of commercial apple varieties could be conventionally established and, based on Fuji and Gala apple juice, be included within the borders of malic acid ( $\text{MAL} = 0.16\text{--}0.33\text{ g}\cdot 100\text{ mL}^{-1}$ ), total reducing sugar ( $\text{TRS} = 9.32\text{--}13.33\text{ g}\cdot\text{mL}^{-1}$ ) and total phenolic compounds ( $\text{TPC} = 130\text{--}418\text{ mg}\cdot\text{L}^{-1}$ ).

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