Food Research International 54 (2013) 1343–1350

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Effect of dehydration process on mineral content, phenolic compounds and antioxidant activity of Cabernet Sauvignon and Merlot grapes

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ARTICLE INFO

Article history:
Received 29 July 2013
Accepted 8 October 2013

Keywords:
Phenolic compounds
Grape
Minerals
Dehydration process
Antioxidant activity

ABSTRACT

Cabernet Sauvignon and Merlot grapes were dehydrated under controlled conditions (7 °C and 35% relative humidity) and the effect of this process on the mineral composition, phenolic profile and antioxidant capacity was investigated. The grapes were analysed at the moment of harvest and then every 7 days until reaching 30% and 40% weight loss. A significant difference was observed between the chemical compositions of the control and dehydrated grapes. The dehydration process increased the soluble solids content, total acidity, total polyphenols, total monomeric anthocyanin content, colour intensity, individual phenolic compounds, antioxidant activity and elemental composition. Principal components analysis demonstrated the separation of the samples according to the different dehydration percentages, indicating that changes which occurred in the composition of the grapes are correlated with the percentage of water loss, which influences the final characteristics of the musts.

1. Introduction

Brazilian viticulture is based mainly on the cultivation of American and hybrid grape cultivars for the production of table wines, grape juice and other derivatives such as grappa, vinegar and jams (Protas, 2011). The production of *Vitis vinifera* varieties in Brazil is concentrated in the south of the country, a region where over-ripening techniques have been used to improve the quality of grapes.

The dehydration of grapes for winemaking is carried out in various wine-making regions in order to concentrate the soluble solids and produce wines rich in sugars, phenolic compounds and flavour (Moreno et al., 2008). Dehydration can be accomplished by various techniques, such as exposure to sunlight after harvesting (Pedro Ximenez, Passito), dehydration in closed chambers with warm or cool air (Amarone, Vin Santo, Recioto), or leaving the grapes to dehydrate in the vineyard, under freezing conditions (Ice wine, Eiswein) (Barbanti, Mora, Ferrarini, Tornielli, & Cipriani, 2008; Bellincontro, De Santis, Botondi, Villa, & Mencarelli, 2004; López de Lerma, Moreno, & Peinado, 2013; Setkova, Risticevic, & Pawliszyn, 2007). Dehydration carried out in the natural environment is strongly dependent on the climatic features of a particular year and serious problems may affect the grapes, for instance, the growth of fungi which produces toxins, such as ochratoxin A (Serratosa, Lopez-Toledano, Merida, & Medina, 2008). To improve the quality of grapes, traditional drying techniques should be replaced by industrial dryers which are far more rapid, providing uniformity and hygienic grape drying process conditions (Doymaz, 2006).

Grapes and wine are comprised of numerous compounds, most notably sugars, alcohols, organic acids, polyphenols and minerals. The phenolic compounds play a very important role in the composition of grapes and wines, owing to their contribution to the sensory properties of wine, mainly colour, astringency and bitterness (Puértolas, Saldaña, Condón, Álvarez, & Raso, 2010). Grape and wine polyphenols are mainly flavonoids, stilbenes and phenolic acids, all of which are well known for their involvement in the reactions of polymerisation, condensation and copigmentation, besides their strong biological action (Puértolas et al., 2010). Phenolic compounds have been reported to be capable of reducing the risk of chronic diseases, eliminating free radicals that induce vascular relaxation, and they also exhibit anti-inflammatory, anti-cancer, antiviral and antibacterial properties (Gris et al., 2011).

The concentrations of different minerals in grapes principally derive from their absorption by the vines from the soil, and thus they provide information regarding the wine origin and authenticity (Galgano, Favati, Caruso, Scarpa, & Palma, 2008; Paneque, Álvarez-Sotomayor, Clavijo, & Gómez, 2010). However, factors such as climate, grape variety, use of fungicides in the vineyards and winemaking processes also influence the elemental composition of grapes and wines (Castiñeira, Brandt, Jakubowski, & Andersson, 2004). Most studies on the mineral composition have focused on characterizing and classifying grapes and wine according to the

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http://dx.doi.org/10.1016/j.foodres.2013.10.016

production area (Arcari, Chaves, Vanderlinde, Rosier, & Bordignon-Luiz, 2013; Burin et al., 2010).

Winemaking techniques play an important role in the extraction of minerals and polyphenols from grapes and consequently in the future stability of the wine properties (Arcari et al., 2013; Puértolas et al., 2010). Pre-fermentation processes, such as dehydration, alter the phenolic compounds content of grapes and wines. Studies on the metabolic levels have demonstrated that the dehydration process results in a high degree of expression of the genes involved in stress protection mechanisms, as well as genes involved in hexose metabolism and transport, cell wall composition, and secondary metabolism, particularly the phenolic and terpene pathways (Zamboni et al., 2008). Although the changes in the phenolic composition of grapes resulting from the dehydration process are extensively described in the literature, little is known about the influence of this process on the elemental composition of the grapes.

Changes in the chemical composition of the grapes during the dehydration process are influenced mainly by the temperature, relative humidity and air flow of the chamber–dryer. Temperature plays the most important role because it affects the water evaporation rate and also the main metabolic pathway, and the reduction in the relative humidity associated with the air flow in the dehydration process accelerates the water loss. Low temperatures during the dehydration process causes slow withering and reduces the oxidation of volatile compounds (Barbanti et al., 2008; Bellincontro et al., 2004; Cirilli et al., 2012; Mencarelli et al., 2010).

The objective of this research was to study the effect of the dehydration process on the mineral composition, phenolic profile and antioxidant activity of Cabernet Sauvignon and Merlot grapes. This paper reports the first detailed research study on the changes in the mineral composition of grapes dehydrated applying a controlled process. Knowledge of these transformations provides an improvement in winemaking techniques and may also provide an insight into the relationship between different dehydration percentages and the mineral composition, phenolic profile and antioxidant activity of the grapes.

2. Material and methods

2.1. Chemicals

All chromatographic solvents (HPLC grade) and 65% (v/v) concentrated nitric acid were purchased from Merck (Darmstadt, Germany). Standards of (+)catechin, gallic acid, ellagic acid, *p*-coumaric acid, myricetin, tyrosol, quercetin, (−)epicatechin, protocatechuic acid, caffeic acid, caftaric acid, kaempferol, *trans*-resveratrol, syringic acid, L(−)malic acid, L(+)tartaric acid, lactic acid, citric acid, succinic acid and a stock solution of 1000 mg L^{-1} Rh, as well as the Folin–Ciocalteu reagent and the DPPH (1,1-diphenyl-2-picrylhydrazyl) and ABTS [2,2-azino-bis(3 ethylbenzothiazoline-6-sulphonic acid)] radicals were purchased from Sigma-Aldrich (St. Louis, USA). Ferulic acid and vanillic acid were obtained from Fluka (Steinheim, Germany). The standard multielement solution ICP III was purchased from PerkinElmer (Norwalk, USA). Ultrapure water was generated using a Milli-Q Millipore system (Massachusetts, USA).

2.2. Samples

Cabernet Sauvignon and Merlot grapes from the Tangará region of Santa Catarina State (SC), Brazil were harvested in 2012 when the soluble solids content (SSC) reached 19 ± 1°Brix. The grapes (180 kg) of both varieties were harvested and placed to dehydrate, according to a patented process (BRPI0804728), in a commercial chamber (515 m^3) at a constant temperature of 7 °C, relative humidity of 35% and volumetric air flow of 12 m^3/s. The patented dehydration process is based on the loss of water from the berry to the outside due to the low relative humidity of the air that circulates around the grape, generating a vapour pressure deficit.

To verify the changes in the chemical composition of the grapes during the dehydration process, samples were taken at harvest (control samples) and every seven days until the grapes reached the final drying percentages of 40% (w/w). To investigate the effect of the different dehydration percentages on the mineral composition, phenolic compounds and antioxidant activity grapes samples were collected at the time of harvest (control samples) and when the fixed dehydration percentages of 30% and 40% (w/w) were reached. These were identified as CST0, CST30 and CST40 for the Cabernet Sauvignon control and 30% and 40% dehydrated samples, respectively, and as MT0, MT30 and MT40 for the Merlot control and 30% and 40% dehydrated samples, respectively.

For the spectrophotometric analysis and to determine the classic oenological parameters, *in vitro* antioxidant activity, individual phenolic compounds content and elemental composition a must was obtained for each grape sample. For the preparation of the musts, 100 g of randomly selected berries were crushed manually for 7 min and then macerated for 24 h with agitation (100 rpm) in a dark room (17 ± 1 °C). The must obtained was filtered through a Whatman n°1 filter paper. For all samples the must yield from 100 g was calculated and the results are expressed in g/100 g grape berries.

2.3. Drying analysis

For the drying curves, the moisture content was determined by gravimetry at 105 °C. The water activity was determined at 25 °C, using an AQUA-LAB Decagon hygrometer (Pulman, USA) for six berries cut into four parts, in triplicate, for the samples collected every seven days during the dehydration period.

Four semi-theoretical mathematical models were tested for the drying of the Cabernet Sauvignon and Merlot grapes: Handerson and Pabis ($MR = a \exp(-kt)$), Newton ($MR = \exp(-kt)$), Page ($MR = \exp(-ktn)$) and Logarithmic ($MR = a \exp(-kt) + b$), where a, b = drying constant; n = drying constant, positive integer; k = drying rate constant; t = the time of dehydration (days). In these models, the moisture ratio (MR) during the drying process was calculated by the equation: $MR = M/M_0$, where M is the moisture content at time t (kg moisture/kg dry matter) and M_0 is the initial moisture content (kg moisture/kg dry matter). The selection of the best model to describe the drying behaviour of the grapes was based on the highest coefficient of determination R^2 and lowest reduced chi-square χ^2 values (Doymaz, 2006).

2.4. Oenological parameters

The classic oenological parameters, soluble solids content (SSC; °Brix), titratable acidity (meq/L) and pH, were determined according to the methods described in OIV (2012). The results were obtained, in triplicate, for the samples collected every seven days during the dehydration process until a sample dehydration of 40% (w/w).

2.5. Spectrophotometric analysis

Samples were analysed to determine the total polyphenols (TP) (mg gallic acid/100 g of grape berries) using the Folin–Ciocalteu reagent according to Singleton and Rossi (1965). Colour intensity (CI) was determined in the grape musts through the sum of absorbance measurements at 420, 520 and 620 nm (Glories, 1984). Total monomeric anthocyanin (TMA) content was determined according to the method described by Giusti and Wrolstad (2001) and expressed as mg malvidin-3-glucoside/100 g grape berries. Measurements were taken for the samples collected every seven days during the dehydration

process, in triplicate, using a UV–vis spectrophotometer (Hitachi U 2010, CA, USA).

2.6. HPLC analysis

Chromatographic analysis was performed using a Shimadzu (Kyoto, Japan) liquid chromatograph, equipped with a vacuum degasser (DGU-14A), quaternary pump LC-10AT, UV–vis detector ((DAD) SPD-M20A) and a manual injector (Rheodyne) with a 20 μL loop, employing LC-Solution software (CBM-20A). The column (4.6 mm × 250 mm, 5 μm particle size — Shimadzu CLC-ODS(M), Kyoto, Japan) and guard column (4.6 mm × 12.5 mm — Shimadzu G-ODS(4), Kyoto, Japan) were of the type C18 reversed-phase.

For the organic acids determination, the must was diluted and filtered through a modified 0.45 mm PTFE membrane filter with 13 mm of diameter (Millipore, USA) and injected into the system. HPLC separation of the organic acids was carried out according to the method described by Escobal, Iriondo, Laborra, Elejalde, and Gonzalez (1998) with modifications. The mobile phase was water acidified (0.1%) with phosphoric acid (A) and methanol (B). The elution gradient used was: 0–5% B in 10 min, 5–30% B in 10 min, 30–50% B in 10 min, 50–0% B in 5 min, and the last 5 min was used to recondition the column. The flow rate was 1.0 mL/min, with detection at 212 nm.

For the individual polyphenol compounds the samples CST0, CST30, CST40, MT0, MT30 and MT40 were subjected to liquid–liquid extraction according to the method described by Malovaná, Montelongo, Pérez, and Rodríguez-Delgado (2001) and the phenolic compounds were determined according to the procedure detailed in Ferreira-Lima, Burin, and Bordignon-Luiz (2013). The mobile phase consisted of water:acetic acid (98:2 v/v) (A) and water:acetonitrile:acetic acid (58:40:2 v/v/v) (B). The elution gradient used was: 0–80% B for 55 min, 80–100% B for 15 min and 100–0% B for 5 min. The flow rate was 0.9 mL/min. The detection was carried out at 280 nm for (+) catechin, (−)epicatechin and tyrosol, 320 nm for *p*-coumaric, caffeic, caftaric and ferulic acids, 306 nm for *trans*-resveratrol and 360 nm for myricetin, quercetin and kaempferol. The hydroxybenzoic acids were determined according to Burin, Arcari, Costa, and Bordignon-Luiz (2011), with detection at 280 nm.

The identification of all compounds was carried out through comparison of their retention times and UV–vis spectra with those obtained by injection of the standard solutions under the same conditions and the quantification were carried out by external standard method.

2.7. Antioxidant activity

The antioxidant activity of the grape must was determined by ABTS and DPPH methods. The ABTS method was performed as described by Re, Pellegrini, Proteggemnte, Pannala, Yang, and Rice-Evans (1999), and the DPPH method was carried out as described by Kim, Guo, and Packer (2002). Total antioxidant activity of the grape must was measured on a UV–vis spectrophotometer (Hitachi U 2010, CA, USA), in triplicate, and was expressed in μmol of Trolox equivalent antioxidant capacity/100 g grape berries (μmol TEAC/100 g grape berries).

2.8. ICP-MS analysis

Elemental analysis was carried out using an inductively coupled plasma mass spectrometer (ICP-MS), PerkinElmer SCIEX, model ELAN 6000 (Thornhill, Canada) coupled to a cross-flow nebulizer and a Scott spray chamber. Argon (99.996%) (White Martins, Brazil) was used as the plasma and aerosol carrier gas. The operational parameters were: auto-lens mode on, main gas flow rate of 1.5 L min^{-1}, nebulizer 1.0 L min^{-1}, peak-hopping measurement mode, detector voltage of 1250 V (pulse) and −2287 V (analogic), dwell time of 50 ms, dead time of 55 ns, 50 sweeps per reading, 1 reading per replicate and 3 replicates. Platinum sampler and skimmer cones, and an alumina injector of 1.5 mm i.d. were used.

The elemental analysis of grape juices was conducted according to Millour et al. (2011). The samples CST0, CST30, CST40, MT0, MT30, were pretreated by microwave-assisted digestion using a MLS 1200 Mega station with closed PTFE vessels (Milestone, Italy). To correct non-spectral interferences, 10 μg L^{-1} Rh was used as the internal standard. The method accuracy was assessed through the analysis of two certified reference materials SRM n° 1643e (trace elements in water) from NIST (Gaithersburg, EUA) and DOLT-4 (Dogfish liver) from NRC (Ottawa, Canada), as well as recovery tests carried out directly on the digested samples.

The chemical elements in all grape must samples were determined, in triplicate, monitoring the isotopes ^{39}K, ^{24}Mg, ^{43}Ca, ^{23}Na, ^{85}Rb, ^{55}Mn, ^{57}Fe, ^{66}Zn, ^{63}Cu, ^{27}Al, ^{88}Sr, ^{138}Ba, ^{52}Cr, ^{60}Ni, ^{208}Pb and expressed in μg/100 g grape berries for each element.

2.9. Statistical analysis

Analysis of variance (ANOVA), the Tukey test ($p \leq 0.05$), non-linear regression analysis of mathematical drying models, correlation matrix and principal component analysis (PCA) were performed using the STATISTICA v. 6.0 (2001) (StatSoft Inc., Tulsa, OK, USA) programme. All analyses were carried out in triplicate and results expressed as mean values ± standard deviation.

3. Results and discussion

3.1. Drying analysis

The time required for the grapes to dehydrate 40% (w/w) was differed according to the variety: Cabernet Sauvignon grapes took 42 days and Merlot required 45 days. The difference observed is due to the initial moisture content of the grapes of each variety and the moisture loss rate determined from the moisture ratio ($MR = M/M_0$), which was 0.66 for Cabernet Sauvignon and 0.60 for Merlot. The variations in the physical properties of the berries of the two grape varieties (intercellular spaces, epicarp thickness) and in the chemical composition (membrane lipid contents) can explain the need for a longer dehydration time for the Merlot compared with the Cabernet Sauvignon grapes. The texture of the grape berry is one of the physical parameters associated with the rate of dehydration and anthocyanin extractability, is evaluated based on parameters such as hardness and berry skin break force, and each grape variety has a texture characteristic (Hernández-Hierro, Quijada-Morín, Rivas-Gonzalo, & Escribano-Bailón, 2012; Rolle, Siret, Río Segade, Maury, Gerbi & Jourjon, 2012). As noted by Rolle, Caudana, Giacosa, Gerbi, and Río Segade (2011) the grape variety that has low berry skin break force values dehydrates quickly.

The time required to dehydrate the grapes by 40% in this study was shorter than the times observed in other studies on white and red grapes, confirming that a low relative humidity reduces the dehydration time required (Barbanti et al., 2008; Bellincontro et al., 2004; De Sanctis et al., 2012). The curves of the weight loss (kg water/kg dry weight) versus dehydration time decreased linearly (Fig. 1) with good determination coefficients of $R^2 = 0.9346$ for Cabernet Sauvignon variety and $R^2 = 0.9505$ for Merlot being obtained.

Based on the data for the moisture rate versus time for the dehydration of the Cabernet Sauvignon and Merlot grapes, four mathematical drying models were fitted and in all cases the R^2 values for the four models were greater than $R^2 = 0.90$, (data not shown) indicating a good fit of the models. The model that provided the highest R^2 value (0.95 for Cabernet Sauvignon and Merlot) and the lowest χ^2 value (0.001 for Cabernet Sauvignon and 0.0008 for Merlot) was the Henderson and Pabis model, suggesting that this

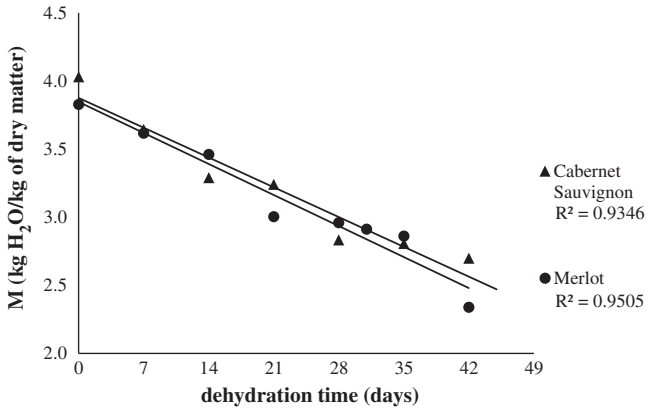

Fig. 1. Drying curves for Cabernet Sauvignon and Merlot grapes.

model is most suitable for describing the kinetics of Cabernet Sauvignon and Merlot grape dehydration. To validate the selected model, a curve comparing the observed values for the moisture rate with those predicted by the Henderson and Pabis model was constructed (Fig. 2). The results predicted by the model and the values observed during the experiment were close, indicating that an acceptable fit was achieved on applying the Henderson and Pabis model to describe the dehydration of the grapes under the controlled conditions. This model has also been found to be appropriate to describe the dehydration process of other vegetal products (Koua, Fassinou, Gbaha, & Toure, 2009; Panchariya, Popovic, & Sharma, 2002).

3.2. Oenological parameters

During the dehydration process, a significant decrease in the water activity (Aw) and increase in the soluble solids content (SSC) were observed, as can be seen in Table 1. For the control Cabernet Sauvignon sample Aw = 0.98 and SSC = 19.92°Brix and after 40% (w/w) dehydration the values for Aw and SSC were 0.96 and 24.92°Brix, respectively, which indicate an increase of 25% in the SSC. In the case of the control Merlot grapes Aw = 0.98 and SSC = 19.92°Brix, and after 40% (w/w) dehydration the values for Aw and SSC were 0.95 and 27.83°Brix, respectively, which indicate an increase of 39.6% in the SSC. This increase in the SSC is in agreement with the findings of other studies on dehydration at low temperatures (Mencarelli et al., 2010).

The water loss during the dehydration period modified the titratable acidity (meq/L), pH and organic acids (mg/100 g grape berries) of the Cabernet Sauvignon and Merlot grapes (Table 1). This increase in the titratable acidity was the result of the water removal from the berries, since the concentration of tartaric and malic acids did not increase,

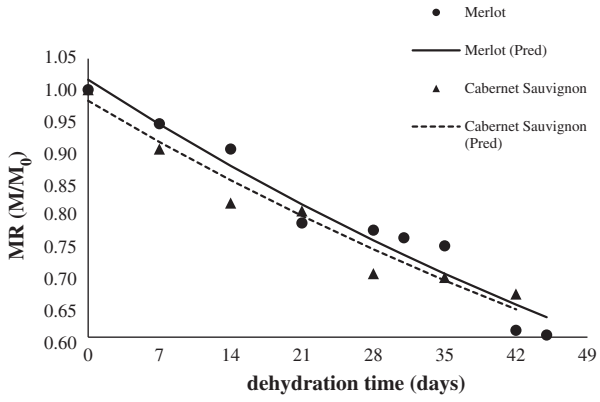

Fig. 2. Experimental data and values predicted by the Handerson and Pabis model for moisture ratio versus drying time for Cabernet Sauvignon and Merlot grapes.

and lactic, citric and succinic acids were not detected in the samples. The pH values varied during the dehydration process, increasing significantly as a result of the decrease in the free acids. In slow dehydration processes the reduction in the amount of organic acids may be due to the anaerobic metabolism of the grapes causing the degradation of malic acid (Bellincontro, De Santis, Mencarelli, Nardin, & Villa, 2002; Chkaiban et al., 2007).

3.3. Phenolic compounds and antioxidant activity

The total phenolic (TP) content oscillated during the dehydration process (Table 1). The results show an initial increase in the TP content in the initial days of the process, followed by a decrease, with the content increasing again at the end of the process. The oscillations observed in the TP content during the dehydration process may be due to the effect of the concentration of the phenolic compounds as a result of water loss caused by the dehydration, as well as the reduction of these compounds by the oxidative enzymes or their participation in condensation and polymerization reactions (Figueiredo-González, Cancho-Grande, & Simal-Gándara, 2013; Mencarelli et al., 2010).

A relationship between total monomeric anthocyanins (TMA) and the red colour intensity (CI) of the samples was observed (Table 1). Both varieties showed oscillating values for the content of TMA and CI during the dehydration process, but at the end of the process a significant increase in TMA and CI was observed for the grapes that were dehydrated by 40%. The changes in the TMA content and CI are probably due to the diffusion of pigments from the skin to the grape pulp, and may also result from the polymerization of monomeric anthocyanins to their condensed forms during the process (Marquez, Serratosa, Lopez-Toledano, & Merida, 2012; Serratosa et al., 2008). Furthermore, the copigmentation reactions between anthocyanins and other phenolic compounds result in an enhancement of the red colour intensity of the samples (Figueiredo-González, Cancho-Grande, & Simal-Gándara, 2013).

Generally, the content of individual phenolic compounds increases with the dehydration process, mainly due to the concentration effect or the hydrolysis of polymerized phenolic compounds (Marquez et al., 2012; Serratosa et al., 2008). In addition, the abiotic stress caused by the water loss can increase the content of some phenolic compounds through the induction of metabolic pathways, like stilbene synthase gene expression and phenylpropanoid metabolism (Rizzini, Bonghi, & Tonutti, 2009; Versari, Parpinello, Tornielli, Ferrarini, & Giulivo, 2001; Zamboni et al., 2008) which generates precursors for many different categories of phenolic compounds.

Table 2 shows the values for the individual phenolic compounds in the Cabernet Sauvignon and Merlot grape samples CST0, CST30, CST40, MT0, MT30 and MT40. According to Table 2 the CST40 sample showed a significant increase in the content of gallic, protocatechuic, vanillic, syringic, caffeic and *p*-coumaric acids, (+)catechin, (−) epicatechin, quercetin, kaempferol, *trans*-resveratrol and tyrosol compared to the CST0 sample. On the other hand, the MT40 sample showed a significant increase in the content of caffeic acid, (+) catechin, (−)epicatechin, myricetin, *trans*-resveratrol and tyrosol compared to MT0 sample. In relation to the control samples, the increase in these individual phenolic compounds of CST40 and MT40 samples was not proportional to the weigh loss of the grapes. The results obtained for the CST30 and MT30 samples indicate that some phenolic compounds participate in oxidation reactions, mainly through the actions of enzymatic polyphenol oxidase and peroxidase pathways (Mencarelli et al., 2010), and lower values are observed for some individual phenolic compounds. Furthermore, the possibility of the polymerization and co-pigmentation of phenolic compounds during the dehydration period and their subsequent degradation may explain the oscillations encountered (Figueiredo-González, Cancho-Grande, & Simal-Gándara, 2013). As suggested by Serratosa

Table 1
Results for water activity (Aw), soluble solids content (SSC, Brix), tritatable acidity (meq/L), pH, organic acids (g/100 g grape berries), total polyphenols content (TP, mg gallic acid/100 g grape berries), total monomeric anthocyanin (TMA, mg malvidin-3-glucoside/100 g grape berries) and colour intensity (CI,index) of Cabernet Sauvignon and Merlot grapes during dehydration process.

Drying time (days)	Aw	SSC	Titratable Acidity	pH	Tartaric acid	Malic acid	TP	AMT	IC
Cabernet Sauvignon									
0	$0.987^{a} \pm 0.01$	$19.92^{a} \pm 0.28$	$105.77^{a} \pm 2.73$	$3.26^{b} \pm 0.01$	$0.37^{e} \pm 0.01$	$0.31^{a} \pm 0.00$	$67.46^{c} \pm 1.81$	$21.81^{c} \pm 0.13$	$15.94^{a} \pm 0.01$
7	$0.981^{b} \pm 0.01$	$20.67^{b} \pm 0.28$	$112.00^{a} \pm 1.88$	$3.06^{c} \pm 0.01$	$0.23^{a} \pm 0.02$	$0.27^{c} \pm 0.00$	$93.31^{a} \pm 2.96$	$39.48^{f} \pm 0.12$	$25.25^{g} \pm 0.16$
14	$0.980^{b} \pm 0.01$	$22.00^{c} \pm 0.20$	$120.00^{b} \pm 1.63$	$3.29^{ab} \pm 0.02$	$0.24^{a} \pm 0.01$	$0.22^{b} \pm 0.01$	$101.48^{b} \pm 3.13$	$27.85^{e} \pm 0.06$	$23.50^{f} \pm 0.05$
21	$0.973^{c} \pm 0.02$	$22.83^{d} \pm 0.14$	$133.30^{c} \pm 3.39$	$3.26^{b} \pm 0.04$	$0.14^{b} \pm 0.01$	$0.30^{a} \pm 0.01$	$90.88^{a} \pm 1.63$	$27.08^{a} \pm 0.24$	$20.31^{d} \pm 0.05$
28	$0.972^{c} \pm 0.01$	$23.33^{d} \pm 0.28$	$134.60^{c} \pm 3.39$	$3.30^{a} \pm 0.04$	$0.26^{a} \pm 0.01$	$0.23^{b} \pm 0.03$	$81.14^{d} \pm 1.80$	$20.70^{b} \pm 0.15$	$17.53^{c} \pm 0.01$
35	$0.970^{d} \pm 0.01$	$24.92^{e} \pm 0.14$	$145.30^{d} \pm 3.39$	$3.20^{d} \pm 0.01$	$0.18^{c} \pm 0.01$	$0.29^{ad} \pm 0.01$	$92.07^{a} \pm 2.69$	$25.70^{d} \pm 0.01$	$16.34^{b} \pm 0.05$
42	$0.967^{e} \pm 0.01$	$24.92^{e} \pm 0.14$	$143.30^{d} \pm 3.39$	$3.30^{a} \pm 0.02$	$0.33^{d} \pm 0.02$	$0.27^{cd} \pm 0.00$	$94.67^{ab} \pm 3.22$	$27.24^{a} \pm 0.09$	$22.67^{e} \pm 0.32$
Merlot									
0	$0.984^{a} \pm 0.02$	$19.92^{a} \pm 0.14$	$91.10^{a} \pm 8.60$	$3.36^{ab} \pm 0.02$	$0.24^{e} \pm 0.04$	$0.15^{c} \pm 0.00$	$59.28^{a} \pm 1.48$	$12.22^{b} \pm 0.02$	$10.94^{b} \pm 0.05$
7	$0.978^{b} \pm 0.01$	$20.83^{ab} \pm 0.28$	$102.30^{ad} \pm 3.82$	$3.13^{b} \pm 0.12$	$0.10^{d} \pm 0.00$	$0.12^{a} \pm 0.00$	$101.05^{c} \pm 5.37$	$20.85^{a} \pm 0.15$	$27.54^{f} \pm 0.17$
14	$0.977^{c} \pm 0.01$	$21.75^{b} \pm 0.25$	$103.30^{ad} \pm 2.10$	$3.39^{ab} \pm 0.13$	$0.20^{ab} \pm 0.01$	$0.15^{c} \pm 0.01$	$89.50^{b} \pm 1.71$	$23.63^{g} \pm 0.06$	$25.84^{e} \pm 0.01$
21	$0.972^{d} \pm 0.01$	$23.33^{c} \pm 0.28$	$104.60^{bd} \pm 1.63$	$3.39^{a} \pm 0.05$	$0.22^{c} \pm 0.05$	$0.13^{b} \pm 0.02$	$110.84^{d} \pm 1.49$	$27.61^{h} \pm 0.14$	$28.98^{g} \pm 0.39$
28	$0.971^{e} \pm 0.01$	$24.33^{cd} \pm 0.28$	$109.00^{bcd} \pm 3.82$	$3.46^{a} \pm 0.03$	$0.20^{a} \pm 0.01$	$0.14^{b} \pm 0.00$	$65.07^{a} \pm 2.74$	$18.64^{e} \pm 0.05$	$23.04^{c} \pm 0.09$
31	$0.969^{f} \pm 0.01$	$24.75^{de} \pm 0.25$	$107.00^{bcd} \pm 7.41$	$3.40^{a} \pm 0.04$	$0.22^{bc} \pm 0.01$	$0.15^{d} \pm 0.00$	$63.46^{a} \pm 2.57$	$14.15^{c} \pm 0.30$	$9.25^{a} \pm 0.05$
35	$0.963^{g} \pm 0.01$	$25.50^{ef} \pm 0.86$	$115.33^{bc} \pm 5.49$	$3.36^{a} \pm 0.04$	$0.21^{ab} \pm 0.01$	$0.15^{d} \pm 0.00$	$85.00^{b} \pm 1.56$	$21.85^{f} \pm 0.09$	$24.76^{d} \pm 0.05$
42	$0.955^{h} \pm 0.02$	$26.00^{f} \pm 0.22$	$117.00^{c} \pm 4.76$	$3.40^{a} \pm 0.02$	$0.20^{a} \pm 0.00$	$0.13^{e} \pm 0.01$	$91.52^{b} \pm 1.71$	$20.65^{a} \pm 0.06$	$34.43^{i} \pm 0.04$
45	$0.955^{h} \pm 0.01$	$27.83^{g} \pm 0.28$	$117.70^{c} \pm 3.84$	$3.54^{a} \pm 0.08$	$0.23^{c} \pm 0.04$	$0.12^{a} \pm 0.00$	$119.62^{e} \pm 5.06$	$17.71^{d} \pm 0.08$	$31.44^{h} \pm 0.08$

Results are expressed as means ± standard deviation ($n = 3$). Different letters for the same analytical parameter represent significant differences according to the Tukey test ($p \leq 0.05$) among samples of the same variety.

et al. (2008) the dehydration process is a balance between synthesis and oxidation processes.

Gallic acid is the principal compound of the hydroxybenzoic acids and is present in great quantities in grapes and wines. According to Table 2, the Cabernet Sauvignon variety showed an increase in the content of all hydroxybenzoic acids, whereas the Merlot variety shows a decrease in these compounds. The divergence in the content of hydroxybenzoic acids for two grape varieties has previously been observed in other studies (Bonghi et al., 2012; Marquez et al., 2012). These results suggest that there is a genotype effect rather than a change in the metabolic pathways for hydroxybenzoic acids.

In this study, we observed that the hydroxycinnamic compounds in their free form (caffeic acid, *p*-coumaric acid, and ferulic acid) had values above 160 μg/100 g of grape berries, which is in contrast to the results reported by Marquez et al. (2012). This result suggests that dehydration, at 7 °C and low relative humidity, promotes the action of the enzyme cinnamyl esterase, similar to the maturation of wines in bottles, where the hydroxycinnamic acid esters are hydrolysed to the

Table 2
Total content of individual phenolic compounds (μg/100 g grape berries) and antioxidant activity (μmol TEAC/100 g grape berries) for Cabernet Sauvignon and Merlot grapes with different percentages of dehydration.

	Cabernet Sauvignon			Merlot		
	CST0	CST30	CST40	MT0	MT30	MT40
Hydroxybenzoic acids						
Gallic	$57.92^{b} \pm 0.68$	$34.20^{a} \pm 0.43$	$65.54^{c} \pm 0.78$	$103.84^{b} \pm 7.78$	$84.71^{a} \pm 6.87$	$75.18^{a} \pm 6.96$
Protocatechuic	$15.89^{b} \pm 0.54$	$12.75^{a} \pm 0.76$	$19.01^{c} \pm 0.58$	$58.16^{a} \pm 4.58$	$57.49^{a} \pm 0.15$	$33.98^{b} \pm 0.46$
Vanillic	$104.74^{a} \pm 0.67$	$105.99^{a} \pm 5.06$	$118.95^{b} \pm 2.85$	$213.89^{c} \pm 4.23$	$135.62^{b} \pm 2.19$	$112.66^{a} \pm 1.09$
Syringic	$119.11^{a} \pm 3.86$	$121.13^{a} \pm 2.72$	$133.58^{b} \pm 3.04$	$128.76^{a} \pm 0.15$	$123.91^{a} \pm 0.67$	$80.30^{b} \pm 3.42$
Ellagic	$515.98^{c} \pm 3.43$	$325.44^{a} \pm 2.45$	$437.89^{b} \pm 0.54$	$796.29^{c} \pm 2.90$	$716.66^{b} \pm 4.68$	$450.21^{a} \pm 8.67$
Hydroxycinnamic acids						
Caftaric	nd[a]	nd	nd	nd	nd	nd
Caffeic	$879.32^{a} \pm 8.27$	$981.25^{b} \pm 0.82$	$1224.91^{c} \pm 3.86$	$2495.69^{b} \pm 0.54$	$1337.13^{a} \pm 2.42$	$2534.76^{c} \pm 19.18$
p-Coumaric	$372.81^{b} \pm 1.22$	$336.37^{a} \pm 2.68$	$390.21^{c} \pm 7.40$	$371.88^{c} \pm 10.26$	$270.73^{b} \pm 0.53$	$238.93^{a} \pm 1.06$
Ferulic	$206.22^{a} \pm 0.23$	$163.23^{b} \pm 3.55$	$191.64^{a} \pm 10.17$	$261.54^{b} \pm 12.92$	$206.16^{a} \pm 1.30$	$213.81^{a} \pm 12.13$
Flavanols						
(+)Catechin	$28.18^{b} \pm 1.11$	$34.46^{a} \pm 0.32$	$34.70^{a} \pm 1.47$	$29.71^{a} \pm 0.13$	$43.21^{b} \pm 3.51$	$50.79^{c} \pm 0.71$
(−)Epicatechin	$801.64^{a} \pm 4.41$	$768.47^{a} \pm 33.12$	$867.60^{b} \pm 5.78$	$439.70^{b} \pm 9.95$	$344.97^{a} \pm 0.90$	$547.38^{c} \pm 2.88$
Flavonols						
Myricetin	$320.93^{c} \pm 4.40$	$279.01^{a} \pm 7.25$	$295.18^{b} \pm 3.61$	$178.45^{b} \pm 02.08$	$121.09^{a} \pm 7.12$	$237.53^{c} \pm 1.01$
Quercetin	$119.71^{b} \pm 0.19$	$108.60^{a} \pm 0.49$	$124.86^{c} \pm 1.01$	$154.05^{c} \pm 0.61$	$123.01^{b} \pm 0.37$	$96.09^{a} \pm 0.08$
Kaempferol	$39.59^{b} \pm 0.29$	$36.98^{a} \pm 0.11$	$40.90^{c} \pm 0.57$	$53.36^{c} \pm 1.12$	$49.87^{b} \pm 0.33$	$32.18^{a} \pm 1.10$
Others						
trans-Resveratrol	$346.97^{a} \pm 1.48$	$348.86^{a} \pm 0.09$	$351.66^{b} \pm 0.10$	$356.91^{a} \pm 0.76$	$361.37^{b} \pm 0.76$	$374.70^{c} \pm 2.45$
Tyrosol	$36.50^{a} \pm 0,80$	$123.85^{b} \pm 1.23$	$144.06^{c} \pm 1.13$	$54.46^{a} \pm 1.00$	$53.89^{a} \pm 1.15$	$66.82^{b} \pm 2.62$
Antioxidant activity						
ABTS	$195.03^{a} \pm 0.20$	$230.86^{b} \pm 0.11$	$248.89^{c} \pm 0.90$	$231.63^{a} \pm 0.78$	$228.11^{b} \pm 0.31$	$248.37^{c} \pm 0.17$
DPPH	$182.82^{a} \pm 0.29$	$194.76^{b} \pm 0.11$	$211.48^{c} \pm 0.83$	$166.64^{a} \pm 1.64$	$165.74^{a} \pm 0.36$	$214.29^{b} \pm 1.23$

Results are expressed as means ± standard deviation ($n = 3$). Different letters in the same line represent significant differences according to the Tukey test ($p \leq 0.05$) among samples of the same variety.

[a] nd = not detected.

free forms of the corresponding acids (Monagas, Gómez-Cordovés, & Bartolome, 2006).

This study shows that the concentration of flavanols, principally (+) catechin and (−)epicatechin, increases during the dehydration process. Both grape varieties had higher levels of flavanols in the CST40 and MT40 samples and (−)epicatechin had higher values than (+)catechin, a result also reported by Marquez et al. (2012) and Mencarelli et al. (2010) who studied grape dehydration. Based on these results and considering that dehydration does not affect the synthesis of flavanols (Bellincontro et al., 2009; Moreno et al., 2008), the increase in catechin and epicatechin content can be attributed to the concentration effect caused by water loss.

During dehydration the flavonol compounds can be concentrated or synthesised by specific gene expression (Bonghi et al., 2012). Our results showed a significant increase in the content of quercetin and kaempferol for the Cabernet Sauvignon grapes and myricetin for the Merlot grapes during the dehydration process. An increase in the content of flavonol compounds, principally quercetin, has previously been observed in other studies (Bonghi et al., 2012; Mencarelli et al., 2010). These results confirm that an increase in the flavonol contents is one of the main metabolic events characterizing grape berries undergoing postharvest dehydration (Bonghi et al., 2012).

Table 2 shows that during the dehydration process an increase in the content of *trans*-resveratrol in the samples was observed. The highest levels of *trans*-resveratrol were observed in the CST40 and MT40 samples, confirming that the *trans*-resveratrol concentration increases proportionally with the intensity of dehydration (Bonghi et al., 2012). As observed by other authors, biotic and abiotic stress stimuli, caused by water loss during dehydration, induce stilbene synthase production (Mencarelli et al., 2010; Versari et al., 2001). Along with the *trans*-resveratrol contents, high values were observed for tyrosol in the CST40 and MT40 samples.

The antioxidant activity results determined by ABTS and DPPH methods (Table 2) showed that the 40% dehydrated samples presented higher antioxidant activity than the control and 30% dehydrated samples, a result also observed by Moreno, Peinado, and Peinado (2007). The increase in the antioxidant activity of the dehydrated grapes is related to an increase in the concentration of some individual phenolic compounds and the final content of TP. Analysis of the correlation between phenolic compounds of both sample varieties and antioxidant activity showed positive correlations with total polyphenols, flavanols, flavonols and stilbene compounds. The phenolic compounds that presented the strongest correlation with antioxidant activity, determined by ABTS and DPPH methods, respectively, were total polyphenols (R = 0.74 and 0.92), (+) catechin (R = 0.65 and 0.32), (−)epicatechin (R = 0.46 and 0.61) and *trans*-resveratrol (R = 0.53 and 0.22).

3.4. Mineral composition

Fifteen mineral elements were identified and quantified in the control and dried grape samples as seen in Table 3. The mineral content of the samples varied according to the grape variety and was also influenced by the dehydration percentage. Potassium is the element present in highest concentrations for both varieties (119.49–135.59 mg/100 g grape berries) and the dehydrated grape samples had higher levels of this element in relation to the control samples. Potassium is the predominant inorganic cation in the grape musts and wines, and the highest concentration has been observed in wines made from botrytized grapes (Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2006).

Calcium, magnesium and sodium are macroelements commonly extracted from soil and they are involved in technological processes, influencing the turbidity and precipitation of salts (Dos Santos et al., 2010; Ribéreau-Gayon et al., 2006). The contents of Mg, Ca and Na increased during the dehydration process and for 30 and 40% dehydration the highest increase in relation to the grape control samples was observed.

The microelements are important constituents of wines due to the involvement of these elements in oxidation processes, as well as colour changes and the stability of the wine. They are also essential elements for living beings (Catarino, Curvelo-Garcia, & Bruno de Sousa, 2008). The results for the Rb, Mn, Fe and Zn contents demonstrated that the dehydration generates an increase in the final content of these microelements. For both grape varieties the Rb content was highest in the samples with 30% dehydration, whereas for Fe and Mn the highest levels were observed after 40% dehydration. The increase in Zn and Rb in the dehydrated samples is associated with the diffusion of these elements from the grape skin to the pulp (Arcari et al., 2013; Galgano et al., 2008).

The presence of the elements Pb, Cu, Al, Ni, Cr, Sr and Ba in grape musts is mainly due to agricultural practises applied in the vineyards,

Table 3
Elemental composition (μg/100 g grape berries) of Cabernet Sauvignon and Merlot grapes with different percentages of dehydration.

	Cabernet Sauvignon			Merlot		
	CST0	CST30	CST40	MT0	MT30	MT40
Macroelements						
K	$125265.27^{a} \pm 1112.00$	$137482.04^{c} \pm 1232.05$	$133966.10^{b} \pm 351.80$	$119492.74^{a} \pm 806.74$	$135590.21^{b} \pm 744.99$	$132979.81^{b} \pm 1546.34$
Mg	$3896.98^{b} \pm 22.53$	$4711.93^{a} \pm 38.50$	$4712.79^{a} \pm 31.68$	$5079.02^{b} \pm 48.05$	$5600.70^{c} \pm 8.93$	$4952.36^{a} \pm 61.18$
Ca	$3287.1\ 4^{a} \pm 56.65$	$3440.79^{b} \pm 40.92$	$4168.11^{c} \pm 11.79$	$4936.90^{a} \pm 33.87$	$3974.09^{b} \pm 12.44$	$4990.87^{a} \pm 82.86$
Na	$128.52^{a} \pm 0.01$	$1939.03^{c} \pm 21.94$	$1873.10^{b} \pm 9.10$	$205.12^{a} \pm 1.77$	$2311.33^{b} \pm 12.05$	$3413.21^{c} \pm 37.66$
Microelements						
Rb	$173.53^{a} \pm 1.01$	$210.24^{c} \pm 0.61$	$206.51^{b} \pm 0.31$	$124.20^{b} \pm 0.86$	$278.53^{c} \pm 1.21$	$84.59^{a} \pm 1.28$
Mn	$76.41^{a} \pm 0.26$	$81.65^{b} \pm 0.44$	$83.49^{c} \pm 0.12$	$112.52^{a} \pm 0.87$	$189.45^{c} \pm 0.46$	$119.15^{b} \pm 1.53$
Fe	$83.35^{a} \pm 4.30$	$113.51^{b} \pm 3.68$	$131.76^{c} \pm 1.58$	$196.32^{a} \pm 1.83$	$205.91^{b} \pm 2.33$	$362.56^{c} \pm 2.68$
Zn	$42.47^{b} \pm 0.17$	$29.15^{a} \pm 0.13$	$45.07^{c} \pm 0.36$	$52.24^{b} \pm 0.74$	$36.65^{a} \pm 0.09$	$96.71^{c} \pm 0.98$
Metals						
Cu	$79.87^{a} \pm 0.05$	$110.15^{c} \pm 0.20$	$108.54^{b} \pm 0.01$	$31.56^{a} \pm 0.04$	$38.34^{b} \pm 0.14$	$51.05^{c} \pm 0.46$
Al	$30.16^{a} \pm 2.29$	$43.33^{b} \pm 0.41$	$57.84^{c} \pm 0.98$	$97.61^{a} \pm 0.75$	$130.89^{b} \pm 1.23$	$285.01^{c} \pm 2.41$
Sr	$8.73^{a} \pm 0.09$	$9.24^{b} \pm 0.10$	$10.78^{c} \pm 0.07$	$7.03^{b} \pm 0.05$	$9.79^{c} \pm 0.02$	$6.45^{a} \pm 0.02$
Ba	$8.25^{c} \pm 0.01$	$6.32^{a} \pm 0.05$	$7.69^{b} \pm 0.02$	$4.77^{a} \pm 0.02$	$5.58^{b} \pm 0.01$	$6.02^{c} \pm 0.09$
Cr	$4.98^{c} \pm 0.00$	$2.11^{a} \pm 0.17$	$2.53^{b} \pm 0.10$	$3.26^{b} \pm 0.08$	$2.51^{a} \pm 0.03$	$2.39^{a} \pm 0.04$
Ni	$0.40^{a} \pm 0.01$	$0.53^{b} \pm 0.00$	$0.55^{b} \pm 0.01$	$0.69^{a} \pm 0.00$	$0.66^{a} \pm 0.02$	$0.92^{b} \pm 0.07$
Pb	$0.07^{a} \pm 0.00$	$0.58^{b} \pm 0.00$	$0.61^{c} \pm 0.01$	$0.11^{a} \pm 0.00$	$0.10^{a} \pm 0.00$	$1.15^{b} \pm 0.01$

Results are expressed as means ± standard deviation ($n = 3$). Different letters in the same line represent significant differences according to the Tukey test ($p \leq 0.05$) among samples of the same variety.

such as the use of copper fungicides and phytosanitary products, and these elements are considered contaminants of musts, juices and wines (Catarino et al., 2008; Toaldo et al., 2013). As observed in Table 3, the contents of most of these contaminant metals was higher in the dehydrated samples, the highest concentrations being observed for copper (110.15 μg/100 g grape berries) in the CST30 sample and aluminium (285.01 μg/100 g grape berries) in the MT40 sample.

The concentrations of Sr, Ni and Pb significantly increased during the dehydration process, and the 40% dehydrated grape samples presented the highest contents. This result indicates that the increase in the Pb and Ni contents is due to the concentration effect caused by the water loss, since the must does not come into contact with steel or equipment containing these elements. Strontium is an element widely used for determining the place of origin of certain wines and studies have shown that its concentration is higher in fortified wines than in table wines from the Douro region (Almeida & Vasconcelos, 2003). The chromium content decreased with the grape dehydration for both varieties.

3.5. Principal components analysis

In order to obtain more information on the influence of the dehydration percentage on the chemical composition of the Cabernet Sauvignon and Merlot grapes a statistical multivariate analysis of the data was carried out. The separation of the samples was obtained using principal component analysis (PCA) (Fig. 3), which was performed with the data on all mineral elements, all individual phenolic compounds, antioxidant activity (ABTS and DPPH methods), TP, TMA, CI, Aw and SSC. Factor analysis showed that the variables with the highest contribution to the separation of the samples in relation to the second component, with marked factorial loading >0.70 (data not shown), were the hydroxybenzoic acids (gallic, protocatechuic, vanillic and ellagic), the ferulic acid, quercetin and kaempferol. For the first principal component, the variables with the greatest contribution were caffeic acid, catechin, *trans*-resveratrol, TP, CI, SSC, sodium, calcium, iron, zinc, aluminium and nickel.

Scatter plots of the scores were obtained only in the case of the first two principal components, and the samples were separated by two functions (Factor 1 × Factor 2), which explain 74.97% of the total data variability. Note that the samples were separated according to the percentage of dehydration, considering Factor 2 which explains 34.20% of the data variability, verifying that the dehydration percentage influences the mineral composition, phenolic profile and antioxidant activity of the grapes. The grape varieties were separated by Factor 1, which explains 40.77% of the data variability.

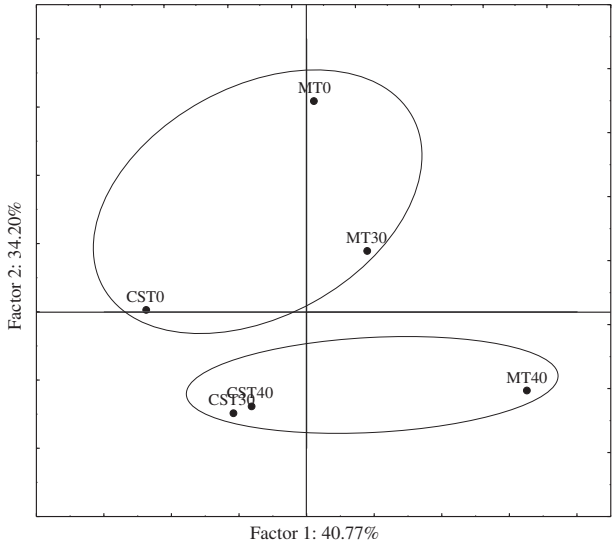

Fig. 3. Principal component analysis of the results for Aw, SSC, IC, TP, TMA, antioxidant activity (ABTS and DPPP methods), all individual phenolic compounds and all minerals for the CST0, CST30, CST40, MT0, MT30 and MT40 samples.

4. Conclusions

The dehydration process causes significant changes in the composition of grapes of the Cabernet Sauvignon and Merlot varieties, principally in the soluble solids content, mineral compounds, phenolic profile and antioxidant activity. The mathematical model that best described the dehydration process of the grapes was the Henderson and Pabis model. The reduction in the water activity is related to the concentration of soluble solids and the total acidity of the samples studied. The oscillations in the total phenolic contents during the dehydration process are explained by the biochemical reactions that occur during water loss from the berry. The 30% and 40% dehydrated Cabernet Sauvignon and Merlot samples showed an increase in some individual phenolic compounds, principally flavanols, flavonols and stilbenes. The dehydration also increases the antioxidant activity of samples of both grape varieties. The elemental composition showed that different dehydration percentages increase the main macro, microelements and contaminant elements.

Acknowledgements

The authors gratefully acknowledge the financial support from the Brazilian governmental agencies the CNPq and CAPES and are grateful to Panceri Winery for supplying the grapes and the chamber to dehydrate the samples.

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