Contribution to the study of Nanofiltration influence on ^{87}Sr/^{86}Sr isotopic ratio of wine

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The main goal of this study is to evaluate the nanofiltration influence on ^{87}Sr/^{86}Sr isotopic ratio of wine. Nanofiltration of model solutions and of three white wines and three red wines from three different DO (Designation of Origin) – *Palmela*, *Óbidos* and *Dão* was carried out using a cellulose acetate membrane with hydraulic permeability of 0,313 kg/(h.m^2.bar). Initially, ethanol, tartaric acid and strontium rejections were assessed, through nanofiltration of model solutions. Original wines and resulting nanofiltration fractions (initial feed, final feed and permeate) were evaluated in terms of mineral composition and ^{87}Sr/^{86}Sr isotopic ratio. Through nanofiltration of model solutions, it was verified a low rejection to ethanol and high rejections to tartaric acid and strontium. High rejections to Rb and Sr were also observed during wine NF essays. Regarding ^{87}Sr/^{86}Sr isotopic ratio no significant changes were verified between initial and final feeds.

KEYWORDS: wine, nanofiltration, authenticity, geographical origin, ^{87}Sr/^{86}Sr isotopic ratio

INTRODUCTION

A growing consumer concern about products origin and quality has been verified. In wine industry, origin assumes more importance because of its influence on wine commercial value. Nowadays, wine authentication is being target of many studies in order of tools development to authentication/frauds detection. Wine certification includes some aspects, such as geographical origin, harvest year/age, grape variety(ies) and technologies used during vinification.

Related to wine geographical origin evaluation, several studies have been published based on their physico-chemical composition, namely on phenolic profile[1,2], mineral profile[3–8], rare earth elements[9,10], stable isotopes[11–13] and lead organic compounds[14]. Some authors considered the use of several markers simultaneously to assure wine authenticity. Between wine constituents, mineral elements are the most promisors as geographical origin markers. Although present in trace concentrations in wine, these elements have a direct relation with soil and are not degraded during vinification process.

Namely, the ^{87}Sr/^{86}Sr isotopic ratio has been sorely studied as geographical origin marker. The use of ^{87}Sr/^{86}Sr isotope ratio is a well established tool for dating and tracing the origin of rocks and minerals. Strontium is an alkaline-earth metal with four stable isotopes in following proportions: ^{84}Sr: 0,55-0,58 %; ^{86}Sr: 9,75-9,99 %; ^{87}Sr: 6,94-7,14 % and ^{88}Sr: 82,29-82,77 %[15]. While ^{84}Sr, ^{86}Sr and ^{88}Sr isotopes occur in constant relative proportions, ^{87}Sr gradually increases in minerals due to ^{87}Rb radioactive β-decay. Usually, older rocks show higher ^{87}Sr/^{86}Sr isotopic ratio for the same initial Rb/Sr value. Therefore, ^{87}Sr/^{86}Sr isotopic ratio changes with geological age and, consequently, with geographical location, being an indicator used in geological materials[16,17,3]. ^{87}Sr/^{86}Sr isotopic ratio in natural materials ranged between 0,702 and 0,740, being this range tighter for wines[18].

The potential application of this parameter as a geographical origin marker, is based on the assumption that a relation between soil, plants and wine exists.

Therefore, this ratio should not be significantly modified during wine processing. Some studies stated that plants and rocks from the same local have similar $^{87}Sr/^{86}Sr$ isotopic ratios, since plants absorb elements in the same proportions they are presents in soil [4,19,20]. Plant absorption depends on different factors, such as grape variety, plant age, plant health, root depth, soil pH, drainage and climatic conditions. According with published results, $^{87}Sr/^{86}Sr$ isotopic ratios in several wines are consistent with respective rocks, soils and grapes values [21,22,23]. Nevertheless, the use of fertilizers, rainwater and dust deposition can influence this ratio [19,21].

Bearing in mind the application of this isotopic ratio as a geographical origin marker, deep knowledge on the effect of several oenological practices is mandatory. Among potential technologies, nanofiltration justify special interest as it can be applied in Enology for different purposes, namely for alcohol content reduction.

In wine industry, nanofiltration has been studied to wine dealcoholisation, wine and must concentration and must rectification. Membrane processes consist in a filtration that occurs under pressure, whose feed is done tangentially to filter mean (membrane). Membrane is a selective barrier whose interactions with feed solution are dependent on membrane material and structure. Feed are divided into two streams: permeate (stream that is preferentially permeated by membrane) and concentrate (stream that contains rejected compounds). The great advantage of membrane processes is their selectivity, allowing the removal only of specific substances.

In particular, nanofiltration membranes present good permeability to ethanol and high rejection coefficients to aromatic compounds, which allows wines partial dealcoholisation without significant changes in their physico-chemical composition [32]. In published results, the retention of some polysaccharides in wines treated by ultrafiltration was verified [40]. In white wines, polysaccharides were removed by microfiltration (10% removal) and ultrafiltration (16% removal) [26]. During nanofiltration of red wines, it was observed permeate flux reducing, caused by high molecular weight compounds like polysaccharides and polyphenols [41]. In wines dealcoholisation using membrane contactors, aroma losses below 20% were observed [42], through osmotic distillation the main changes were in volatile compounds and color intensity and tonality [43], through inverse osmosis no modifications in phenolic profile and antioxidant activity were observed [44].

Although nanofiltration effects on wine physico-chemical characteristics have been studied, to the best of our knowledge, there is no information about its influence on mineral composition and on $^{87}Sr/^{86}Sr$ isotopic ratio.

MATERIAL AND METHODS

Material and reagents. Membrane was prepared with cellulose acetate (*Sigma-Aldrich*), formamide ($\geq$ 99,5%, *Sigma-Aldrich*) and ketone (99,7%, *Labchem*) using a rectangular glass plate, a casting knife with constant thickness (0,25 mm), a plastic tray, an acetate sheet and a chronometer.

For membrane characterization NaCl (99,9%, *VWR Prolabo*), Na_2SO_4 (Anhydrous, 99%, *Scharlan*), $CaSO_4$ (Anhydrous, 99% *Sigma-Aldrich*) and glucose (D(+)-Anhydrous Glucose, *Panreac*) were used.

Model solutions were prepared with ethanol (96% (v/v), *S.D.C.*), tartaric acid (99,5%, *Merck*), Sr solution (1000 mg/L in 0,5 M HNO_3, *Reagecon*) and NaOH ($\geq$ 98,5%, *Sigma-Aldrich*).

For ICP-MS analyzes monoelement standard solutions of Be, Co and In 1000 mg/L (*Merck*) and a multielement solution with Mg, Cu, Rh, Cd, In, Ba, Ce, Pb and U 10 µg/L (*Perkin-Elmer*) were used. Wash, blank and standard solutions were prepared with ultrapure concentrated HNO_3 *Ultrex II*

70% (v/v) (*J.T. Baker*). ICP-MS equipment calibration was established with a standard solution with 30 elements (Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, In, Cs, Ba, Hg, Tl, Pb, Bi, U) 10 mg/L (*Perkin-Elmer*). For ICP-MS internal standardization, standard solutions of Rh and Re 1000 mg/L (*Merck*) were used. Analytics calibration and stability control in $^{87}Sr/^{86}Sr$ isotopic ratio analysis were made with $SrCO_3$ (50 µg/L), prepared from certified reference material *NIST SRM 987* ($SrCO_3$).

For wine samples digestion, a H_2O_2 solution was used (*Trace Select 30% (v/v), Fluka*).

For Sr and Rb chromatographic separation, the following solutions were used: HCl 32% (v/v) (*Merck*), EDTA Triplex III p/analysis (*Merck*), NH_3 25% (v/v) (*Merck*), HNO_3 bidistilled 65% (v/v) (*Sigma-Aldrich*).

Purified water (conductivity < 0,1 µS/cm) used to solution preparation and material washing was produced using a *Seralpur Pro 90 CN* apparatus. For solution preparation only plastic material was used. With the aim of decontamination, all the material was immersed in a HNO3 20% (v/v) bath for at least 24h and rinsed three times with purified water.

Wines. In this work, three white wines and three red wines from three different DO (Designation of Origin) – *Óbidos*, *Palmela* and *Dão* were used.

Membrane preparation and characterization. A cellulose acetate nanofiltration membrane was used and prepared through inverted phases method, using a polymeric solution of cellulose acetate (17%), formamide (30%) and ketone (53%) [46]. With the aim to reduce pore size and obtain a nanofiltration membrane, the membrane prepared was annealed by immersing in a deionized water bath at 95ºC during 11 minutes.

Membrane was characterized by hydraulic permeability and rejection coefficients to NaCl, Na_2SO_4, $CaSO_4$ and glucose. These essays were performed at 6 bar with a recirculation flow of 1,4 L/min, being solutes concentration of 300 ppm. Salts concentrations in nanofiltration fractions were determined using a *Crison GLP 32* conductometer and glucose concentrations were obtained using a TOC *Dohrmann 3300*.

Mineral analysis. Multielemental composition and isotopic ratio were determined with a *Perkin-Elmer SCIEX Elan 9000 ICP-MS* apparatus, equipped with a crossflow nebulizer, a Scott-type spray chamber made of Ryton and nickel cones. A peristaltic sample delivery pump with four channels, model *Gilson* and an autosampler *Perkin-Elmer AS-93 Plus*, protected by a laminar-flow-chamber clean room class 100 were used. The system was controlled by software *Elan – 6100Windows NT* (Version 2.4).

Operating conditions used were as follows: r.f. power of 1200 W; cooling argon flow of 15 L/min; nebulizer argon flow between 0,94 and 0,98 L/min; auxiliary argon flow of 1,5 L/min; sample uptake rate of 1,0 mL/min.

ICP-MS instrumental parameters used in mineral composition analysis were as follows: r.f power of 1200W; sample uptake rate of 0,85 mL/min; nebulizer argon flow between 0,85 and 0,95 L/min; dwell time of 50 ms; 6 sweeps/reading; 1 reading/replicate; 1 replicate; time per run of 67 s.

This technique was applied in according with the protocol described by Catarino et al. (2006)[47], after 1:10 dilution with deionized water.

$^{87}Sr/^{86}Sr$ isotopic ratio – Samples preparation. *Wines Digestion by HPMW*. In this stage, samples were digested in order to eliminate negative influence of organic matter on Sr and Rb chromatographic separation.

For digestion of the wine samples, a *Milestone ETHOS Plus Microwave Labstation* was used, equipped with a Milestone *HPR-1000/6m* monoblock high

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pressure rotor with six positions (closed system, maximum operating pressure of 100 bar) and TFM Teflon vessels, one of them used to control temperature during operation.

Samples digestion was based on protocol described by Catarino et al. (2010)[48] with some adaptations. Each vessel contained 2 mL of wine, 2 mL of H_2O_2 and 4 mL of deionized water. At each run, a blank solution was prepared (2 mL of H_2O_2 and 6 mL of deionized water) for contamination control.

$^{87}Sr/^{86}Sr$ isotopic ratio – Samples preparation. *Sr and Rb chromatographic separation.* Sr and Rb chromatographic separation was carried out, according with protocol described by Castro (2015)[49], in a *HIPEX Duran* (12 mm intern diameter and 200 mm bed size) filled with cationic resin *Dowex 50W-X8/400 (Sigma-Aldrich)* until around 13 cm. Chromatographic separation is compound by four stages: resin activation/pre-treatment; resin conditioning; sample preparation/dilution and elution stages.

$^{87}Sr/^{86}Sr$ isotopic ratio – Samples preparation. *Filtration.* In order to avoid/minimize EDTA deposition in ICP-MS equipment, elution fractions with Sr were acidified to 1% with bidistilled nitric acid and placed in a fridge during 24h. Posteriorly, samples filtration was carried out using a syringe filter *Acrodisc PVDF* 0,45 µm with diameter of 25 mm.

$^{87}Sr/^{86}Sr$ isotopic ratio determination. $^{87}Sr/^{86}Sr$ isotopic ratio was determined by ICP-MS according with protocol described by Martins et al. (2014) [50].

ICP-MS instrumental parameters used in $^{87}Sr/^{86}Sr$ isotopic ratio analysis were as follows: sweep mode – peak hopping; 1 MCA channel; dwell time of 30 ms (^{86}Sr), 35 ms (^{87}Sr) and 20 ms (^{88}Sr); 500 sweeps/reading; 1 reading/replicate ; 3 replicate; time per run of 247 s.

Stability control was made periodically. Calibration was established between samples in order to detect changes. All samples were analyzed in duplicate.

Nanofiltration. Nanofiltration was carried out using a commercial equipment *Celfa P-28,* containing a feed tank, a heat exchanger, a circulating pump, a plane membranes module, a potentiometer to circulation flow regulation, a valve to concentrate flow, a manometer and a valve to pressure regulation.

Before starting, membrane was compacted through deionized water permeation, at a transmembrane pressure 20% higher than operating pressure for 3 hours, to avoid pressure effects on membrane structure throughout subsequent experiments. Between each essay, deionized water was permeated up to 90% of initial flux recovery.

Nanofiltration. *Model solutions essays.* To better understanding of wine nanofiltration results, model solution with ethanol, tartaric acid and strontium were permeated.

At a first step, ethanol rejection was evaluated through hydroalcoholic solutions permeation with ethanol concentrations of 8, 10, 12, 14 e 16 % (v/v). These essays occurred at a transmembrane pressure of 6 bar with recirculation flow of 1,4 L/min and at 15 bar with recirculation flow of 2,1 L/min. Tank was filled with 500 mL of solution. Ethanol concentration was determined with TOC *Dohrmann 3300.* For each nanofiltration fraction (initial feed, final feed and permeate) analysis, a volume of 10 mL was collected.

At a second stage, three solutions with different ethanol concentrations (9, 12 e 16% (v/v)), 0,5 mg/L of strontium, 3 g/L of tartaric acid and pH of 3,5 were permeated. The pH adjustment was made with NaOH 10 M solution. These essays were carried out at 15 bar with a recirculation flow of 2,1 L/min. Tank was filled with 500 mL of solution. Ethanol and tartaric acid concentrations were determined by FTIR and Sr concentration by ICP-MS. For each

nanofiltration fraction analysis, a volume of 40 mL was collected.

Nanofiltration. *Wine essays.* Three red wines and three white wines from three Portuguese DO (*Óbidos*, *Palmela* e *Dão*) were treated by nanofiltration at 17 bar with a recirculation flow of 2,1 L/min. In each essay, tank was filled with 500 mL of wine, being collected 60 mL of each nanofiltration fraction. Nanofiltration fractions were evaluated in terms of mineral composition and $^{87}Sr/^{86}Sr$ isotopic ratio.

RESULTS AND DISCUSSION

Membrane characterization. The hydraulic permeability of the prepared membrane was of 0,313 kg/(h.m^2.bar).

The rejection coefficients observed were 90,3% to NaCl, 95,3% to Na$_2$SO$_4$, 92,8% to CaSO$_4$ and 90,3% to glucose. It was observed a higher rejection to divalent salts than NaCl (monovalent) and a high rejection to glucose, characteristic behavior of nanofiltration membranes. Considering permeate volume in relation to feed volume, these essays occurred in total recirculation without feed concentration.

Model solutions. *Hydroalcoholic solutions.* Permeate fluxes as function of ethanol concentration in feed, obtained from permeation of hydroalcoholic solutions at 6 and 15 bar were measured and represented by **equations 3** and **4,** respectively.

$$y = 0,0045x + 1,7405 \quad \textbf{(3)}$$

$$y = -0,1431x + 5,4197 \quad \textbf{(4)}$$

At 6 bar, differences in the permeation flux with the increase of ethanol concentration in feed were not observed. On the other hand, it was observed a smooth decrease of permeate flux with the increase of ethanol concentration in feed, when permeation occurred at 15 bar.

Through permeate and feed concentrations, rejection coefficients to

ethanol in hydroalcoholic solutions with ethanol concentrations between 8 and 16% were calculated. Rejection coefficients as function of ethanol concentration are represented by **equations 1** and **2**, corresponding to permeation at 6 and 15 bar, respectively.

$$y = -3,5029x + 58,611 \quad \textbf{(1)}$$

$$y = -0,4683x + 12,328 \quad \textbf{(2)}$$

Rejection coefficients decreased with ethanol concentration in feed increasing, which means that permeability of the membrane to ethanol increases with the ethanol concentration in feed.

Model solutions. *Quaternary Solutions.* Permeate fluxes as function of ethanol concentration in quaternary solutions, obtained from permeation at 15 bar were registered and represented by **equation 5**.
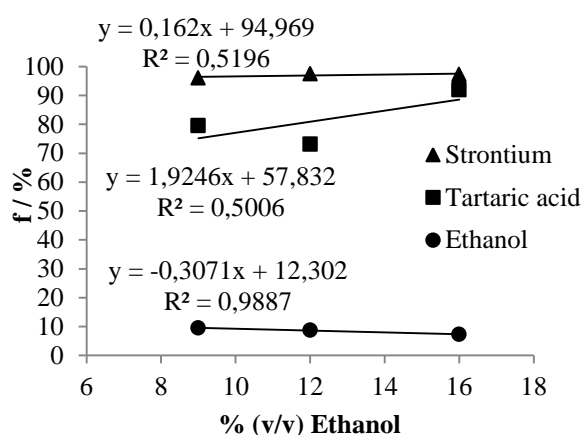
$$y = -0,1969x + 6,0997 \quad \textbf{(5)}$$

In comparison with permeate fluxes of hydroalcoholic solutions at 15 bar, it was verified that permeate fluxes of these solutions are very similar, suggesting that neither strontium or tartaric acid have some effect on them.

Through permeate and feed concentrations, rejection coefficients of ethanol, tartaric acid and Sr were calculated and results are shown in **figure 1**.

Tartaric acid and strontium rejections were higher than 70% while ethanol rejection is lower than 10%. Strontium and ethanol rejections were constants with ethanol concentration in feed, corresponding to average value of the three essays 97,0% e 8,5%, respectively.

Wines. *Fluxes.* During nanofiltration of each wine, permeate fluxes were measured, being very similar for the same type of wine. As expected, white wine fluxes are higher than red wine fluxes, since red wines have a more complex matrix.

$y = 0,162x + 94,969$
$R^2 = 0,5196$

$y = 1,9246x + 57,832$
$R^2 = 0,5006$

$y = -0,3071x + 12,302$
$R^2 = 0,9887$

▲ Strontium
■ Tartaric acid
● Ethanol

Figure 1. Rejection coefficients (f) to ethanol, tartaric acid and strontium as function of ethanol concentration in feed, obtained from quaternary model solutions permeation at 15 bar (quaternary model solutions: aqueous solutions with 9, 12 and 16 %(v/v) of ethanol; 0,5 mg/L of strontium; 3 g/L of tartaric acid and pH of 3,5).

Wines. *Mineral composition.* Sr and Rb composition of wine nanofiltration fractions, as well as rejection coefficients are shown in **table 1**.

Table 1. Sr and Rb concentration in wines and their nanofiltration fractions (WW – White wine; RW – Red Wine; I.F. – Initial feed; F.F. – final feed; P. – Permeate).

Sr concentration (µg/L)				
	I.F.	**F.F.**	**P.**	**f (%)**
Óbidos WW	24,3 (0,3)	33,7 (0,3)	0,49 (0,02)	98,0
Palmela WW	43,5 (0,1)	55,6 (0,7)	0,55 (0,03)	98,7
Dão WW	49 (1)	63,2 (0,6)	0,29 (0,01)	99,4
Óbidos RW	115 (2)	137 (3)	1,34 (0,08)	98,8
Palmela RW	58 (2)	89,9 (0,6)	6,61 (0,09)	88,7
Dão RW	176 (5)	217 (6)	0,95 (0,09)	99,5
Rb concentration (µg/L)				
	I.F.	**F.F**	**P.**	**f (%)**
Óbidos WW	498 (3)	574 (5)	8,8 (0,3)	98,2
Palmela WW	245,3 (0,5)	304 (18)	8,0 (0,2)	96,7
Dão WW	891 (32)	1042 (30)	16,89 (0,02)	98,1
Óbidos RW	599 (2)	683 (17)	13,0 (0,3)	97,8
Palmela RW	473 (17)	506 (4)	11,6 (0,3)	97,5
Dão RW	1505 (2)	1812 (35)	28 (2)	98,1

In general, nanofiltration membrane shows rejections to Sr and Rb higher than 95%. Concentrations in final feed were slightly higher than concentrations in initial feed, due to water and ethanol removal. In permeate, Sr concentrations were very low, being the highest value of 6,61(0,09) µg/L, corresponding to red wine from DO *Palmela*.

Wines. $^{87}Sr/^{86}Sr$ *isotopic ratio*. $^{87}Sr/^{86}Sr$ isotopic ratios of wine and correspondent nanofiltration fractions are present in **table 2**. $^{87}Sr/^{86}Sr$ isotopic ratios of nanofiltration fractions are also present in **figure 2**. The isotopic ratio scale represents the range of $^{87}Sr/^{86}Sr$ values observed in natural materials, referred by Rosner (2010)[18].

Table 2. $^{87}Sr/^{86}Sr$ isotopic ratio in wines and respective nanofiltration fractions (I.F. – Initial feed; F.F. – final feed; P. – Permeate).

Sample	$^{87}Sr/^{86}Sr$
Óbidos White Wine	0,7075±0,0007 a
Óbidos White Wine I.F.	0,7080±0,0008 a,b,c,d
Óbidos White Wine F.F.	0,709±0,001 b,c,d
Óbidos White Wine P.	0,707±0,001 a,b
Palmela White Wine	0,7085±0,0007 a,b
Palmela White Wine I.F.	0,7075±0,0007 a,b,c
Palmela White Wine F.F.	0,7075±0,0007 a,b,c
Palmela White Wine P.	0,7065±0,0007 a
Dão White Wine	0,7128±0,0008 c
Dão White Wine I.F.	0,713±0,000 e
Dão White Wine F.F.	0,714±0,000 e,f
Dão White Wine P.	0,708±0,000 a,b,c,d
Óbidos Red Wine	0,7093±0,0006 b
Óbidos Red Wine I.F.	0,709±0,000 c,d
Óbidos Red Wine F.F.	0,7095±0,0007 d
Óbidos Red Wine P.	0,7085±0,0007 b,c,d
Palmela Red Wine	0,7075±0,0007 a
Palmela Red Wine I.F.	0,709±0,000 c,d
Palmela Red Wine F.F.	0,7075±0,0007 a,b,c
Palmela Red Wine P.	0,708±0,001 a,b,c,d
Dão Red Wine	0,7150±0,0008 d
Dão Red Wine I.F.	0,715±0,001 f
Dão Red Wine F.F.	0,714±0,001 e,f
Dão Red Wine P.	0,709±0,001 c,d

Values presented correspond to average of two independent replicates and respective standard deviation.
Values followed by the same letter are not significantly different at the 0,05 level of significance.

$^{87}Sr/^{86}Sr$ isotopic ratio in final feed was not significantly different from $^{87}Sr/^{86}Sr$ isotopic ratio in initial feed, suggesting that no preferential permeation of any strontium isotopes have occurred. $^{87}Sr/^{86}Sr$ isotopic ratio in permeate was lower than in initial feed. These values are close of $^{87}Sr/^{86}Sr$ isotopic ratios reported for water, which is expected, since permeate is mainly compound by water. Some published values for rainwater in Paris ranged between 0,70796 and 0,71093[51]. Since $^{87}Sr/^{86}Sr$ isotopic ratio in permeate is close of values reported for water, thus both strontium isotopes were mostly rejected by membrane.

Previously, the potential influence of some technological processes on $^{87}Sr/^{86}Sr$ isotopic ratio of wine was studied and no significant effects were verified [22,45]. To the best of our knowledge, no references regarding nanofiltration effect are published.

In the experimental conditions used in this study, no significant differences in $^{87}Sr/^{86}Sr$ isotopic ratio during nanofiltration were observed, indicating that nanofiltration application in wine industry is not a limitative factor for the use of $^{87}Sr/^{86}Sr$ as geographical origin marker. The results obtained confirm the robustness of this marker in the evaluation of wine authenticity.

However, it is mandatory to collect more information about nanofiltration effects in $^{87}Sr/^{86}Sr$ isotopic ratio at different experimental conditions, namely with other nanofiltration membranes and on an industrial scale.

In order to wine authentication in terms of geographical origin, this study should be expanded to other oenological practices. The evaluation of $^{87}Sr/^{86}Sr$ isotopic ratio in soils and wines from the main DO should also be continued, with the aim of their integration in a future international database.

In particular, this study constitutes a significant contribution to the evaluation of oenological practices influence on the $^{87}Sr/^{86}Sr$ isotopic ratio and its use as geographical origin marker.
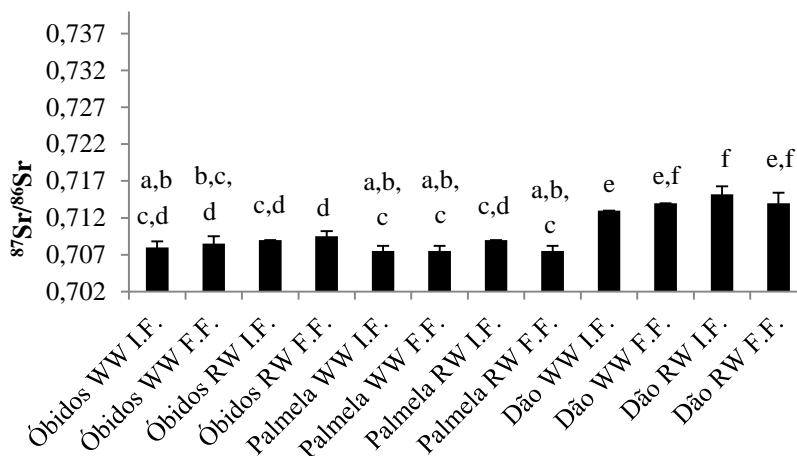
Figure 2. $^{87}Sr/^{86}Sr$ isotopic ratio in wines nanofiltration fractions (WW – White wines; RW – Red wines; I.F. – Initial feed; F.F. – final feed; P. – Permeate).

Values presented correspond to average of two independent replicates and respective standard deviation.
Values followed by the same letter are not significantly different at the 0,05 level of significance.

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