Sensory Quality of Portuguese Natural Mineral Waters: Correlation with Chemical Composition

Jenny Sumara Sozo[1], Ana Pardal[1,2], Maria João Carvalho[1], Adelaide Almeida[1,2], Humberto Chaves [1,2], Maria de Fátima Carvalho[1,2*]

[1] Instituto Politécnico de Beja, Departamento de Tecnologias e Ciências Aplicadas, Rua Pedro Soares, Campus do IPBeja AQ2, 7800-295 Beja, Portugal

[2] FibEnTech-Materiais Fibrosos e Tecnologias Ambientais, R. Marques de Avila e Bolama, 6201-001 Covilhã, Portugal

* Corresponding author's email mfcarvalho@ipbeja.pt

ABSTRACT

Portugal is one of the richest countries in terms of the variety of natural mineral waters in relation to the territorial size. The aim of this work was to characterize the sensory features of eleven Portuguese natural mineral waters and correlate those with their chemical characteristics. The study of the Piper diagram concluded that the vast majority of these waters have low or very low mineralization content, with total mineralization values not more than 500 mg/L, predominantly sodium bicarbonate or mixed sodium. The sensory analysis was carried out by 10 trained panelists according to ISO 8586:2012 and showed that the tasters were able to distinguish the sensory attributes of the waters, and thus it was possible to establish some correlation between the physical-chemical and sensory parameters. With Principal Component Analysis (PCA), it was possible to explain the percentage of variance between the main chemical components of the studied waters and its sensory characteristics. A significant positive correlation of Total Dissolved Solids (TDS) with HCO_3^- (0.97), Ca^{2+} (0.93) and Mg^{2+} (0.91) was shown, as well as the pH of the natural mineral waters with the salty (0.71) and the sweet (0.69) taste. The sweetest waters were Monchique Chic (3.4) and Monchique (3.3) and the least sweet was Luso. The most acidic were Vitalis (3.4) and Luso (3.3) and the least acidic ones were Monchique Chic (1.9) and Vimeiro Original (1.8). In terms of the salty taste, the most salty samples were Monchique (4.2) with significant differences between all the other samples, and the least salty one was Salutis (1.8). The bitter waters were Monchique Chic (3.5) and Vimeiro Lisa (3.4) and Vitalis was the least bitter (2.3). The water with the highest score in mineral flavor was Vimeiro Original (4.9) and the lowest one was Salutis (2.7).

Keywords: Portuguese natural mineral waters; sensory analysis; chemical composition; Piper's diagram; PCA.

INTRODUCTION

According to FDA (Food and Drug Administration, 2017), mineral waters differ from other types of water by trace minerals and trace elements that are present in the source, which is protected from contaminants, and depend on the characteristics of the rocks there. Minerals are extracted through geochemical processes, and chemical treatments or disinfection are prohibited, except for special circumstances such as removal of undesirable elements that may be present, regulated by specific legislation (in Portugal by the Decree-Law No 156/98 of June 6, art. and Decree-Law No 72/2004 of 25 March, art. 6).

Minerals are not synthesized by living organisms, it is critical that they obtain these minerals by diet. Numerous metabolic functions depend on minerals, making them essential to the human body for maintaining pH, osmotic pressure, energy production, muscle contraction, and others (Biziuk & Kuczynska, 2007). It is important to emphasize that the amount ingested, as well as biokinetics, absorption among others, are

individual factors that can be attributed to the bioavailability of these substances in the organism (Jafari & McClements, 2017; Robson, 2003).

Currently, there around 3.000 brands of bottled water available and the trend of growing demand, leads to the creation of new companies or brands (Mascha, 2006; European Federation of Bottled Water, 2018). In Europe, bottled water sales accounted for 46% of the non-alcoholic beverages market, with 83% for natural mineral waters (European Federation of Bottled Waters, 2017). In 2017, Portugal exhibited an increase (8.3% in volume) in the consumption of mineral and spring waters both in national market and exportations (APIAM, 2019).

The water content is dependent on its salt content, cations and anions, which may contribute positively or negatively to taste sensations, depending on the chemical composition and the amounts present (Burlingame *et al.*, 2007). Total dissolved solids content has been the most commonly used parameter for sensory evaluation of water, both odor and taste (Whelton, 2007; Dietrich, 2009). Directive 98/83/EC establishes the maximum levels of total solids soluble in water for human consumption in Europe, which may not exceed 1600 mg/L (EC, 1988); however, there is no established limit for mineral waters (Azoulay, Garzon & Eisenberg, 2001), the legislation only clarifies that these waters should not contain any organoleptic defects, which could come from materials in contact with food (Directive 2009/54/EC, Regulation (EC) No 1935/2004). According to FDA, the water considered "mineral" should contain between 500 and 1500 mg/L of total soluble solids (Von Wiesenberger, 1991).

As regards the sensory quality, the concern of supply networks in providing quality water comes from long standing (Suffet *et al.*, 1995). This sector has a sensory wheel, an auxiliary instrument for water profile analysis, to ensure the quality of the product, especially in terms of odor and taste (Deinger *et al.,* 2004; Vingerhoeds *et al.*, 2016). Natural mineral waters, due to their purity characteristics, do not pass through sensory quality control; however, this is an approach of significant importance for their characterization. Rey-Salguero *et al.* (2013) present in their study a proposal of sensory wheel for natural mineral waters in connection with its chemical mineral components, bringing a significant advance in terms of tools available for the sensory classification of this particular group of waters. Recently,

a group of specialists called "Tastes, Odours, and Algal Toxins in Drinking Water Resources and Aquaculture" was created by International Water Association (IWA), with the purpose of ensuring that the waters have desirable qualities of taste and appearance (IWA, 2019).

The interest in the physico-chemical composition of mineral waters is reflected in the large number of published works that explore the theme (Barroso *et al.*, 2009; Lourenço *et al.*, 2010, Astel *et al.*, 2014, Eggenkamp & Marques, 2013; Kończyk *et al.*, 2019; Bertoldi *et al.,* 2011); however, the studies that correlate the chemical composition with sensory characteristics are still scarce, especially in bottled mineral waters, due to the difficulty in describing water, with characteristics of low taste and odor.

In order to establish efficient methodologies for the sensory analysis of waters, new protocols have been successfully established (Teillet *et al.*, 2010; Rey-Salguero *et al.,* 2013; Sipos *et al.,* 2017) that have promoted the training of judges with success, enabling to draw a sensory profile for each water (Vingerhoeds *et al.*, 2016). The studies that correlate the influence of minerals on the taste of water from treatment plants were conducted in Denmark, where the chemical composition of the samples and the sensory attributes were determined through a panel of judges (Marcussen *et al.*, 2013). In relation to bottled waters, the studies of this nature were carried out in Spain (Platinakov *et al.*, 2013); however, the chemical and sensory characteristics of Portuguese natural mineral waters has not been studied. In order to achieve this study goal, tap water was used in order to familiarize the panelists to the characteristics of mineral water, which are quite different from the usual chlorine tap water.

In view of this panorama and the enormous diversity of waters that can be found in Portugal, this study aims to be a pioneer study of sensory characterization of 11 Portuguese natural mineral waters and therefore try to correlate the results with the physico-chemical composition, performing the chemometric analysis of the results.

MATERIALS AND METHODS

Samples

Portuguese natural mineral waters

The natural mineral waters of 11 different Portuguese brands were acquired commercially.

Figure 1 show the geographical origin of each mineral, where it can be seen that most were located in the center and in the north of Portugal, and only 2 were from the south.

Mineral contents such as total dissolved solids (TDS), chloride (Cl^-), sulfate (SO_4^{2-}) nitrate (NO_3^-), bicarbonate (HCO_3^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) potassium (K^+), and pH of the natural mineral waters, were presented in Table 1, according to the bottled labels.

The pH of the studied waters ranged from 5.1 to 9.5, indicating acidic to alkaline proprieties. There is a correlation between pH and mineralization, cation and anion levels. The less mineralized waters have lower pH. The waters with higher levels of bicarbonate have the most alkaline pH, and have to be extracted from greater depths, being more enriched by minerals. Decree-Law n. 152/2017, which deals with drinking water, recommends that the water should have the pH values ≥ 6.5 and ≤ 9.5, and for non-carbonated water contained in bottles or other containers, the minimum pH can be reduced to 4.5. All waters analyzed in this work are within the limits established for pH.

The total dissolved salts, quantified by total mineralization, are the immediate parameter to natural waters grouping. Decree-Law nº 156/98and DIRECTIVE 2009/54/EC classify it in the group from "very low mineralized", i.e. with total mineralization not exceeding 50 mg/L; "oligo mineral or less mineralized", which means the water having a total mineralization of 500 mg/L or less and "rich in mineral salts", the water having a total mineralization of more than 1500 mg/L. Thus, all the waters studied in this work were with a low or very low
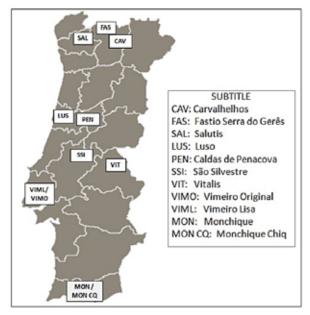

Figure 1. Geographical origin of natural mineral Portuguese waters

mineralization, with the exception of VIMO, which is considered a mineralized water.

With regard to ions, magnesium is one of the most abundant cations in our body (WHO, 2009) fundamental for several metabolic processes, Decree-Law nº152/2017 recommends that the concentration in drinking water should not exceed 50 mg/L, because this ion, along with calcium, is one of the determining factors for hardness (Mendes and Oliveira, 2004). There is no limit to the calcium levels; however, it is desirable that the calcium level not exceed 100 mg/L. Additionally, the total hardness, as calcium carbonate, should be between 150 and 500 mg/L $CaCO_3$. The limits for sodium are 200 mg/L, for chloride and sulfate the maximum concentration are 250 mg/L and 50

Table 1. Label information of Portuguese mineral natural waters

Sample	TDS (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	HCO_3^- (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	pH
PEN	32.0	9.1	1.2	1.8	2.6	0.7	1.0	5.7	<DL	5.3
CAV	180.0	<DL	7.1	<DL	144.0	5.7	<DL	51.4	1.4	6.8
FAS	34.0	4.2	1.0	<DL	8.0	1.3	<DL	4.1	0.6	6.0
LUS	43.0	9.0	14.0	1.6	13.0	0.7	1.7	7.4	<DL	5.8
MON	298.0	<DL	<DL	0.3	114.0	0.9	<DL	110.0	<DL	9.5
MON CQ	297.0	38.0	51.0	0.3	111.0	1.1	0.1	105.0	1.9	9.4
SAL	32.0	7.6	<DL	<DL	<DL	<DL	<DL	5.6	<DL	5.1
SSI	189.0	30.0	<DL	<DL	141.0	29.0	<DL	27.0	<DL	7.6
VIML	52.0	10.0	<DL	<DL	22.0	4.0	1.4	7.9	0.3	6.4
VIMO	1035.0	198.0	<DL	<DL	448.0	119.0	30.0	139.0	4.4	7.3
VIT	26.0	7.2	<DL	1.3	0.3	0.4	0.7	4.2	<DL	5.7

mg/L for nitrates. The Decree-Law nº 152/2017 does not refer to the limits for potassium and bicarbonate. The waters evaluated in this study were in accordance with the values allowed in the actual legislation, attesting its quality with respect to the chemical composition.

Tap water

Tap waters were collected from water supply system of two different regions (Beja – BJ and Montes Velhos – MV, a village at 30 km from Beja), which have different water sources (from different dams) as well as different chlorine treatments. After collection, both waters were stored at a temperature between 10-15 °C until analysis.

Cations quantification was carried out by Ion Chromatography in a Metrohm chromatograph with conductivity detector through a METROSEP C4-250/4.0 column, with dimensions of 4.0 x 250 mm and particles of 7.0 μm. The eluent used was 1.7 mmol/nitric acid/0.7 mmol/dipicolinic acid, in the injection volume of 1.0 μL, with flow of 1.10 mLmin^{-1}, temperature of 20.0 °C and pressure of 12.2 MPa. For the calculation of concentration a standard multiparameter curve was used, structured in 5 points.

The anions quantification was carried out in Ion Chromatograph, model 930 compact IC Flex, Metrohm, equipped with a conductivity detector, on a Metrosep A Supp 5 – 250/4.0 column. The eluent used was 1.0 mM $NaHCO_3$/3.2 mM Na_2CO_3, flowing at 0.700 mL min^{-1}, at a temperature of 30.0°C and a pressure of 13.95 MPa. The concentration calculations were performed based on a standard multiparameter curve structured in 6 points.

For the TDS determination the crucibles were dried at 180°C for 1 hour, cooled in a dryer to constant weight. The triplicates of the samples were filtered through glass membrane and collected into the crucibles where they were evaporated. After evaporation, the samples were dried at 180 °C until constant weight (APHA, 2012). The pH measurement was performed in a WTW InoLab apparatus.

Sensory evaluation

The focus was to achieve a group of panelists with skills for mineral waters, carrying out assessments by ISO 8586:2012 (Sensory analysis – General guidelines for the selection, training and monitoring of selected assessors and expert sensory assessors). Thus, in order to evaluate

the olfactory capacity of the tasters, the odor recognition test was carried out to identify volatile compounds of different substances. There were 16 odors from different aromatic families (Boelens, de Valois, Wobben, and van der Gen, 1971; Ahmed, Dennison, Dougherty, and Shaw, 1978; Nagata and Takeuchi, 1990; Buettner and Welle, 2004; Culleré, Escudero, Cacho, and Ferreira, 2004; Czerny *et al*., 2008; QunSun, 2011). The tasters were instructed to make short inhalations, after shaking the boxes, in order to promote uniformity of the inside content, and subsequent release of volatile compounds. After identifying the odor, it was recorded in an evaluation form. For further verification of correct answers, and to be able to participate in the panel, it is necessary to obtain a minimum percentage of 80% of correct answers.

In order to assess taste acuity by ISO 3972:2011 (Sensory analysis – Methodology – Method of investigating sensitivity of taste), the evaluation of the acuity of each taster to distinguish elemental tastes: acid, bitter, sweet and salty, in different concentrations, was carried out. The substances corresponding to the fundamental tastes were presented in known order by means of an aqueous solution of known concentration in a total of 8 cups of elemental tastes and 1 glass of natural mineral water. The data were described in a specific form, where they were later expressed as percentage of correct answers, which should be at least 77.7%. Subsequently, to the evaluation of gustative acuity, and in order to improve the discriminatory performance of the tasters, the triangular test was carried out, with the elemental tastes, and corresponding concentrations, in which the tasters verified a lower sensitivity, in order to determine their gustative differentiation skills.

The sensory analysis sessions were carried out by 10 trained male and female panelists at the Sensory Analysis Laboratory of the Centre for Food Science and Technology of the Agrarian School of the Polytechnic Institute of Beja (Portugal), under controlled temperature and humidity. Each taster analyzed the samples in independent booths, designed according to ISO 8589: 2007 to avoid influence among tasters, as well as to respect impartiality and objectivity of the test. The samples were always presented with random coding and evaluated by all panelists who were well qualified, as previously described.

Each series of 4 samples presented to the tasters in different sessions were grouped by virtue of their total dissolved solids levels. Indeed, and

since the total dissolved solids (TDS) has become the most common parameter in water taste studies (Dietrich, et al., 2006; Burlingame et al., 2007; Devesa et al., 2010; Gallagher et al., 2014; Raich-Montiu et al., 2014; Wheltonet al., 2007), International regulations and recommendations establish the maximum levels for TDS with important differences: 1000 mg/L in the WHO Guidelines (WHO, 2011), and 1600 mg/L in Europe, which corresponds to a 2500 μS cm^{-1} conductivity at 25°C (EC, 1988), and therefore, the presentation of samples was planned by this chemical parameter. During each session, the tasters were given samples of encoded natural mineral waters and a blank, which consisted of MilliQ® ultra-pure water, and were instructed to perform mouthwash at each tasting. The perceived sensory attributes were recorded in a descriptive sensory form, with an unstructured scale, defining an intensity value that varied from «few» to «a lot», corresponding respectively to values between 1 and 9, where 1 corresponds to «few» and 9 to «a lot». The attributes considered for the evaluation of the waters under study were: transparency, odor, chlorine odor, sweet, salty and bitter taste, mineral flavor and earth flavor (Rey-Salgueiro *et al*., 2013; Platikanov et al., 2017).

Statistical analysis

The parameters analyzed in the sensory and chemical profile were submitted to a one-way ANOVA variance analysis, and a Tukey post-hoc test, considering a significance level of 5% (p <0.05). Subsequently, a mathematical procedure

was applied to reduce the dimensionality of this data set, through Principal Component Analysis (PCA). In order to prevent the values with larger scales from dominating the main components, the self-escalation was pre-processed to standardize the combination of information of different natures. The software used was STATISTICA 8.0 (StatSoftInc., Tulsa, OK, USA). the GW_Chart, program made available, free of charge, by USGS, was used for the construction of Piper diagrams.

RESULTS AND DISCUSSION

Analytical results

On the basis of the concentrations of major ions and cations, it was possible to construct the Piper triangular diagram, where the hydrochemical faces of each sample were identified (Figure 2). As shown in the diagram, most of the study samples were concentrated at the vertices of the triangles corresponding to the sodium and bicarbonate ions. The upper losangle shows the hydrochemical classification of each water. In general, sodium was the dominant cation, which may be associated with bicarbonate or chloride. Therefore, the waters are predominantly sodium bicarbonate, sodium chlorate or mixed sodium. Tap water (Figure 3) are classified as mixed (Piper, 1944).

Table 2 presents a characterization summary of the natural mineral waters studied, according Directive 2009/54/EC which shows that natural mineral waters predominantly have low mineral content or very low mineral content. It also shows
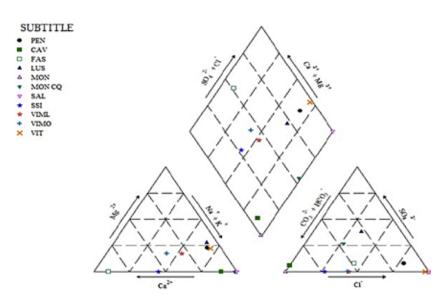

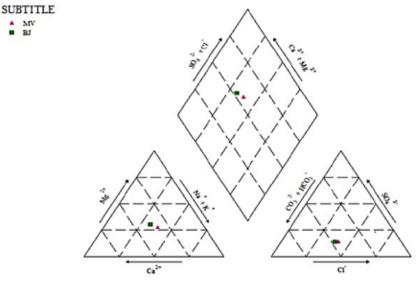**Figure 2.** Piper diagram of Portuguese natural mineral waters.

Figure 3. Piper diagram of tap water

Table 2. Characterization of each natural mineral waters

WATER	Low mineral content	Verylow mineral content	Mineralized	Rich in mineral salts	Contains bicarbonate	Containss ulphate	Contains chloride	Contains calcium	Contains magnesium	Contains sodium	Suitable for a low-sodium diet
PEN		X			X	X	X	X	X	X	X
CAV	X				X	X		X		X	
FAS		X			X	X	X	X		X	X
LUS		X			X	X	X	X	X	X	X
MON	X				X			X		X	
MON CQ	X				X	X	X	X	X	X	
SAL		X					X			X	X
SSI	X				X		X	X		X	
VIML	X				X		X	X	X	X	X
VIMO	X				X		X	X	X	X	
VIT		X			X		X	X	X	X	X

the presence of bicarbonate, sulfates, chlorine, calcium, magnesium and sodium in particular samples, classifying which waters are recommended for low sodium diets.

Directive 2009/54/EC and Decree-Law nº 156/98 of 6 June define that a suitable water for a low-sodium regime is that which has a sodium content of less than 20 mg/L. The mineral waters PEN, FAS, LUS, SAL, VIML and VIT have this characteristic, corresponding to 54.54% of the samples studied in this paper. These data corroborate with those found by Bertoldi *et al.* (2001). After analyzing 571 bottled natural mineral waters from 23 European countries, it was concluded that most of the samples, i.e. 58.1%, could be defined as "suitable for a low sodium diet". The waters with sodium

contents higher than 20 mg/L are VIMO, MON, MON CQ, CAV e SSI, starting from the lowest to the least concentrated. Several studies have been conducted to establish the relationship between the consumption of Chlorinated Sodium Water on blood pressure, and it can be concluded that these can contribute to hypertension, even with salt-restricted diets (Albertini *et al.*, 2007).

The importance of the presence of other constituents in the water was presented in a study by Sauner *et al.,* (2004), evaluating the effect of mineral water rich in magnesium (337 mg/L), calcium (232 mg/L) and bicarbonate (3388 mg/L) in the composition of urine and formation of calcium oxalate crystals, concluded that these resulted in favorable changes in urinary pH as

well as contributed to the excretion of lithogenic substances and crystallization of calcium oxalate. However, the waters evaluated in this work have lower levels of magnesium, calcium and bicarbonate than those tested by Sauner *et al.* (2004).

Sensory analysis

Tap water

The total dissolved solids content (TDS), chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), bicarbonate (HCO_3^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+) potassium (K^+), and pH of the two waters, are presented in Table 3. For each of the sensory variables analyzed the scores assigned by each taster for tap water and for each of the natural mineral waters are presented in Tables 4 and 5.

Among the tap water samples, it was the MV sample that presented the highest value for the chlorine odor and earthy flavor, and mainly on

sample BJ, these characteristics were greatly attenuated. For MV it was possible to feel the chlorine odor, probably due to the treatment done at the water distribution stations for consumption. The chlorine levels found in this sample were higher than that of the other tap water sample, as shown in the ion chromatographic analyses (Table 3). High concentrations of the chloride ion in water may cause restrictions on its use due to its flavor and the laxative effect it causes in individuals who are familiarized to low concentrations. However, the EU legislation has a maximum permissible value of 250 mg/L. In relation to the most pronounced earthy flavor, it was the MV sample that assumed it, which might be related to the presence of geosmin, a substance produced by actinomycete cultures, which could eventually be present in the pipes (AWWA, 1995). This tap samples were well characterized and perfectly distinguished from the mineral waters by the panelists, which fact supported the main goal of its

Table 3. Mineral content and pH of tap water

Sample	TDS (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	HCO_3^- (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	pH
MV	1142.0	95.5	51.6	<DL	176.0	43.5	21.3	53.9	5.7	7.5
BJ	1121.0	90.5	42.6	<DL	189.3	51.9	25.9	48.8	4.4	7.5

Note: DL – Detection limit; BJ – Beja; MV – Montes Velhos.

Table 4. Tap water scores assigned by tasters on sensory assessments

Water	Transparency	Odor	Chlorine odor	Sweet	Acid	Salty	Bitter	Flavour Mineral	Flaour Earthy
MV	7.7± 1.3[a]	3.4± 2.7[a]	3.9± 2.5[a]	3.5± 2.2[a]	2.5± 1.5[a]	2.1± 1.5[a]	2.7± 1.3[a]	3.8± 1,8[a]	3.9± 1.6[a]
BJ	8.0± 0.9[a]	1.6± 1.3[a]	1.9± 1.4[b]	3.4± 2.6[a]	3.1± 1.4[a]	3.8± 2.7[a]	2.7± 1.9[a]	4.6± 2,4[a]	2.1± 1.1[b]

* a, b,… different letter in column means significantly differences between the samples ($p < 0.05$).

Table 5. Scores of natural mineral waters assigned by tasters in sensory assessments

Water	Transparency	Odor	Chlorine odor	Sweet	Acid	Salty	Bitter	Flavour Mineral	Flavour Earthy
FAS	8.4± 1.0	1.4± 0.7	1.5± 0.7	3.0± 1.7	3.1± 1.8	2.2± 1.0[b]	2.7± 1.3	3.5± 1.7	1.7± 1.3
MON	8.4± 0.5	1.6± 0.7	1.4± 0.7	3.3±1.9	2.7± 1.8	4.2± 1.9[a]	3.2± 1.5	3.8± 2.3	1.8± 1.1
CAV	7.8± 1.2	1.6± 1.0	1.7± 0.8	3.1± 2.1	2.4± 1.9	2.7± 1.9[b]	2.7± 1.6	3.7± 1.9	1.3± 0.5
SAL	7.6± 1.6	1.7± 1.3	1.4± 0.7	2.8± 1.8	2.3± 1.2	1.8± 0.4[b]	2.9± 1.8	2.7± 1.7	1.5± 0.7
VIT	8.0± 1.1	1.8± 1.0	1.4± 0.5	2.7± 2.1	3.4± 2.2	2.2± 1.1[b]	2.3± 0.8	3.2± 1.6	1.6± 0.8
LUS	8.3± 0.7	1.7± 1.1	1.5± 1.0	2.1± 0.6	3.3± 1.6	3.2± 1.7[b]	2.6± 1.6	3.6± 1.6	2.2± 2.1
VIML	8.1± 0.9	1.4± 0.5	1.2± 0.4	3.1± 2.0	3.0± 1.2	2.8± 1.4[b]	3.4± 1.3	3.4± 1.2	2.6± 1.8
PEN	8.2± 1.0	1.6± 1.0	1.3± 0.5	2.8± 1.2	3.1± 1.8	2.3± 1.6[b]	2.5± 1.1	3.4± 1.4	1.7± 0.8
VIMO	8.0± 1.1	1.2± 0.4	1.5± 0.7	3.2± 2.7	1.8± 0.6	3.3± 2.2[b]	2.4± 1.3	4.9± 1.8	1.8± 1.0
SSI	8.3± 0.7	1.6± 0.7	1.8± 1.5	2.9± 1.8	2.4± 1.6	2.9±1.6[b]	3.0± 1.7	4.4± 1.6	1.8± 1.0
MON CQ	8.4± 0.7	1.7± 1.1	1.5± 1.0	3.4± 2.2	1.9± 1.0	2.7± 1.7[b]	3.5± 2.2	4.1± 2.1	2.1± 1.6

* a, b,,…different letter in column means significantly differences between the samples ($p < 0.05$).

use – qualify the panelists by their skills to taste waters, and moreover to distinguish minerals and also the tap ones. Nonetheless, in other studies with tap and bottled water, the consumers could not distinguish between water samples in a blind taste test (Debbeler et al., 2018).

Among the analyzed natural mineral waters, there was no significant difference in the variables transparency, smell and chlorine smell. These results were already expected, since the natural mineral waters have a high degree of purity and absence of any type of additive that can influence the turbidity / coloring and odor characteristics. The mineral waters MON, MON CQ and VIMO obtained the highest scores for the 'sweet' attribute, being also the most mineralized and with higher pH and HCO_3^- contents, these features can provides sweet sensation in the mouth.

These results are in agreement with the main conclusions obtained in a study using trained panelists to evaluate the role of major anions and cations in the water taste (Platikanov et al., 2013). The waters considered with salty feature were VIT and LUS, which curiously are not those with higher sodium contents; however, they are among those with lower pH values. One of the hypotheses for these sensory results is that due to the subtle taste of these waters, due to their low mineralization, the salty sensation may have been caused to the detriment of the acid element, because in the gustatory apparatus the salty and acid senses are perceived in nearby regions in the tongue, evidencing that this aspect should be more worked in the training of the tasters.

According to the tasters, the waters considered bitter were MON CQ, VIML and MON. Due to the high mineralization of the MON CQ and MON waters, the tasters may have been influenced by bitterness as both tastes are detected in the back of the water. In the case of VIML, the acidic pH may have influenced the evaluation, described as bitter. The tasters listed the VIMO water with the highest mineral taste, followed by the, MON, MON CQ and SSI, corroborating with the TDS values obtained, which denounces a correct evaluation of the tasters in relation to this parameter, and concomitantly the qualification of the tasters for the salty attribute. Besides, it was also notorious that the panelists had presented significant differences (p=0.037) in the salty attribute between the SAL and MON samples, which corroborated the mineral composition of this two samples in terms of Na^+ levels

(SAL- 5.6 mg/L; MON – 110 mg/L), bicarbonates (SAL – 114 mg/L; MON< DL), but mostly with the pH values (SAL – 5.1; MON – 9.5), since the MON sample was the one with the highest pH, which was detected by the panelists. However, even without significant differences, the panelists showed a trend for it with the MON CQ with pH 9.4. In general terms, all the waters had presented high scores in the positive attributes. Nevertheless, several studies have shown that high levels of minerals are not well liked (Teillet et al., 2010; Platikanov et al., 2013).

Indeed, a study concerning consumer's preference for mineral composition of bottled and tap water, with untrained volunteers assessed that the water samples with high levels of mineralization (TDS above 480 mg/L) were low scored (Platikanov et al., 2017). A graphical projection of these evaluated attributes can be observed in the following figures (Figure 4 and Figure 5).

Indeed, in this study the importance of sensory analysis is proven, since this science analyzes and interprets the reactions of the senses towards a given food in an objective and reproducible way (Stone, 2004), and thus the sensations produced by a product can be there when one wants to evaluate the sensation that a product causes, and the best way is to try it (Beriain *et al*., 1997). Some characteristics must be taken into account for certain samples; one of these characteristics is the time of perception, the time to be perceived by the taste, or the residual taste that remains in the mouth sometime after the food is swallowed (Teixeira *et al.*, 1987; Hui, 1992). In addition to the characteristics of the samples, it should be emphasized that there are probes with adequate perception for some basic tastes that may present poor or zero perception for another (Anzaldúa-Morales, 1994). The distribution of the taste buds and the local perception of the tastes can affect the taste threshold, since not all the stimuli have the same response in the different regions of the tongue (Landívar, 2001).

Indeed, the sensory analysis of mineral waters with mineralization characteristics so close may not be an easy task; however, the results of the evaluations showed that in general, the panel was consistent with the sensory perceptions. In general terms, in the absence of off-flavors, mineral content and consistent visual qualities are the major determinants of both taste and consumer acceptability of their drinking water (Devesa et al., 2018). Mineral content, usually measured as
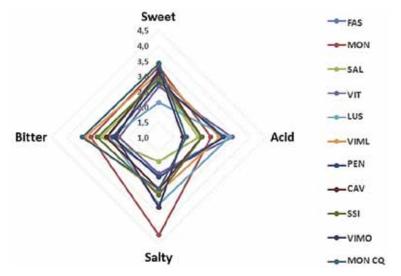
Figure 4. Sweet, bitter, acid and salty attributes of sensory profiles of the mineral waters
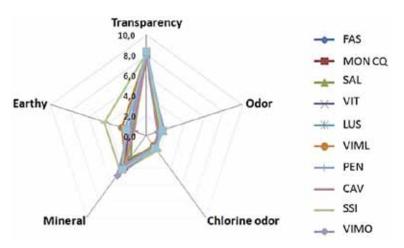

Figure 5. Transparency, odor, chlorine odor, mineral and earthy flavour attributes of sensory profiles of the mineral waters

total dissolved solids (TDS), is also the primary determinant of consumer liking in the absence of unwanted odors (Devesa et al., 2010; Marcussen et al., 2012; Teillet et al, 2010)

Correlation between variables

In order to evaluate the degree of relationship between the variables, the correlation coefficients for the natural mineral waters were measured (Figure 6), where the positive correlation is represented by the blue color and the negative by the red color, the color intensity increases along with the color correlation between variables.

In the analysis of the physical-chemical parameters of the natural mineral waters (Figure 6a), it was possible to observe strong positive correlations between TDS and HCO_3^- (0.97), Cl^- and Mg^{2+} (0.97), HCO_3^- and Ca^{2+} (0.93) and pH with

Na^+ (0.79). Platikanov *et al*. (2013), while studying the bottled mineral water from Spain, found a positive correlation between TDS, bicarbonate and pH, corroborating with the results found in the present study. The highest negative correlations were found in NO_3^- (-0.41) and SO_4^{2-} (-0.18).

A significant positive correlation of TDS with HCO_3^- (0.97) Ca^{2+} (0.93) and Mg^{2+} (0.91) was observed, together with the physical and chemical parameters of the natural mineral waters (Figure 6b) pH with salty taste (0.71), sweet (0.69) and bitter (0.60), chlorine smell with mineral flavor (0,50) and smell with SO_4^{2-} (0,33). A strong negative correlation occurred between the attributes of transparency and smell (-0.73), as well as between the acid taste with Na^+ (-0.74) and HCO_3^- (-0.72). The previous studies of correlation between chemical content and preference have shown that globally, trained tasters preferred the calcium
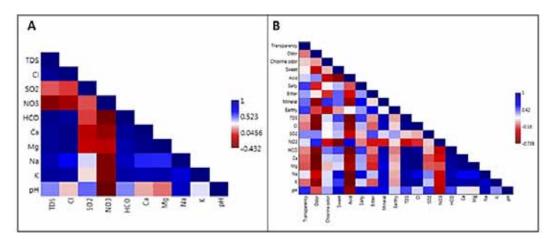
Figure 6. Correlation analysis of natural mineral water parameters
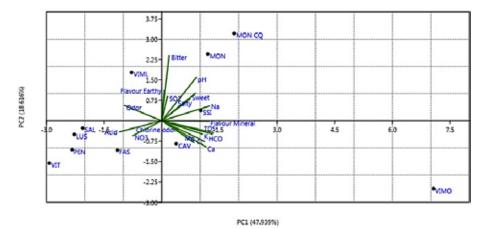A physical-chemical; B physico-chemical and sensory

Figure 7. Distribution of physico-chemical and sensory parameters according to PC1 and PC2

bicarbonate and sulfate rich waters rather than the sodium chloride waters (Platinakov *et al.*, 2017).

Principal Component Analysis

In this study the Principal Component Analysis (PCA) of a concentration matrix of 20 parameters observed in 11 bottled natural mineral waters was applied. A data matrix [X1, Y1] was used, based on the two main components model, which explained more than 60% of the variance, being 47.939% and 18.616% respectively. The graph of PC1 and PC2 (Figure 7), using the physicochemical parameters and the scores of the evaluators.

It can be verified in the graph that in PC1, the waters were distributed from left to right, increasing the TDS values, with the waters of greater mineralization being distributed more to the right, and the ones of medium mineralization in the center of these extremes, the evaluation of the mineral flavor also followed this pattern, by the evaluators. In PC2, it is related to the pH values and to bitterness

(evaluators). The pH of water strongly influences the taste of water, a range between 6.5 and -8.5 is desirable to avoid a bitter taste. This correlation can be observed with the MON and MON CQ waters, which are the ones with the highest pH among the samples evaluated, and which the tasters evaluated as the most bitter waters.

The interpretation of the first two main components allows the classification of the waters studied in two large hydrochemical groups: Very low mineralized waters and more mineralized waters, with VIMO being the most mineralized sample.

CONCLUSIONS

The study of the natural mineral waters concluded that the great majority of these waters had shown a low or very low mineralization, with values of total mineralization of not more than 500 mg/L, predominantly sodium bicarbonate or mixed sodium. Despite the contiguous

characteristics of water mineralization, the panel was generally homogeneous regarding the sensory perceptions. It was possible to correlate the physical-chemical parameters with the sensory attributes evaluated by the tasters. In the natural mineral waters, strong positive correlations were found between TDS with HCO_3^-, Ca^{2+} and Mg^{2+}, and negative correlations between transparency and smell, acidic taste with Na^+ and HCO_3^-. The multivariate analysis of data through PCA proved to be an important tool to explain the percentage of variance between the main components, contributing to the characterization of the bottled natural mineral waters of Portugal.

Acknowledgements

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