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COMPOSITIONAL AND MORPHOLOGICAL EVALUATION OF EDIBLE SALTS: PRELIMINARY RESULTS

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Abstract

Nutritional habits have as a result the uptake of the elemental content of various foods in the human body. Salt (NaCl) constitutes an integral part of human diet needs. As a consequence, knowledge concerning the composition of edible salt is critical. The aim of the present study is to evaluate the components of 8 edible salt samples that are available in the Greek retail market. Samples were classified according to their color as follows: white (WS1, WS2), black (BS1, BS2), pink (PS1), red (RS1), blue (BLS1) and pale brown (BRS1). The research revealed that all samples mainly consist of Cl and Na. Himalayan Black Salt (BS2) also contains S, whereas the Hawaiian Red Salt (RS1) contains Fe. Additionally, most of the samples contain low levels of Al, Ca, K, Mg, P, S, Si and O as impurities. Concerning the morphological characteristics, salt particles appear irregular, rounded and in two cases as cubic crystals referring to the crystal structure of NaCl. Backscattered images confirm the presence of other mineral phases besides NaCl.

Keywords: Sea salt, Rock salt, Sodium chloride, Human consumption.

Περίληψη

Οι διατροφικές συνήθειες του ανθρώπου έχουν ως αποτέλεσμα την πρόσληψη των ουσιών που περιέχονται στις διάφορες τροφές, από τον ανθρώπινο οργανισμό. Το αλάτι (NaCl) αποτελεί ένα αναπόσπαστο συστατικό των αναγκών της ανθρώπινης διατροφής. Επομένως, είναι σημαντικό να είναι γνωστό το περιεχόμενο της σύστασής του. Ο στόχος της παρούσας εργασίας είναι η αζιολόγηση της σύστασης 8 διαφορετικών δειγμάτων αλατιών προς κατανάλωση, τα οποία διατίθενται στην ελληνική αγορά. Τα δείγματα αυτά ταζινομήθηκαν με βάση το χρώμα, χρησιμοποιώντας τους εξής χαρακτηρισμούς: λευκό (WS1, WS2), μαύρο (BS1, BS2), ρόδινο (PS1), ερυθρό (RS1), κυανό (BLS1) και ανοιχτό καστανό (BRS1). Όλα τα δείγματα αποτελούνται κυρίως από Cl και Na. Το μαύρο αλάτι Ιμαλάϊων (BS2) περιέχει επιπλέον και S, ενώ το κόκκινο αλάτι Χαβάης (RS1) περιέχει Fe. Ενώ, ως προσμίζεις συμμετέχουν τα Al, Ca, K, Mg, P, S, Si και O. Μορφολογικά τους χαρακτηρίζονται ως τυχαία, έως στρογγυλεμένα και σε μόνο δυο περιπτώσεις σχηματίζουν κυβικές δομές, παρόμοιες με αυτές του NaCl.

Λέξεις κλειδιά: Θαλασσινό αλάτι, Ορυκτό αλάτι, Χλωριούχο νάτριο, Ανθρώπινη διατροφή.

1. Introduction

The word salt relates to the ancient Greek word $\delta\lambda\varsigma$ (genitive: $\delta\lambda\delta\varsigma$). $\lambda\lambda\varsigma$ means either "salt", the substance which enhances the flavour in food, or "sea" (Babiniotis, 2010). However, nowadays salt refers to any salty material despite its relation to the sea.

Edible salt (NaCl) is worldwide the most commonly used food additive, providing improvement of taste and preservation of food. Its biological necessity lies on the fact that sodium and chlorine, the two main elements that it provides, are very important for the human body (Musaiger *et al.*, 2008; Soylak *et al.*, 2008; Cheraghali *et al.*, 2010). Since food chain is a common pathway for human exposure to many elements, the analysis of food samples for their elemental concentration is very important and has been continuously performed (Haddy, 2006; Steinhauser *et al.*, 2006; Tuzen and Soylak, 2007). The various properties of the chemical elements are essential for human life. However, when some elements are found in high concentrations, they can be considered as toxic. Edible salt may contain various chemical substances and due to its excessive use, information about its elemental content is critical (Zukowska and Biziuk, 2008; Zarei *et al.*, 2011).

The aim of the present study is to determine the general and morphological characteristics of 8 different types of edible, refined and unrefined, salts available in the Greek retail market and to evaluate their mineralogical and chemical composition.

2. Materials and Methods

A variety of refined and unrefined edible salts was examined in this study. Eight pre-packed salt sa mples available in the Greek market were purchased, either directly from the market or from vendo rs. Salts were examined in their bulk form, since they are used for human consumption in the way t hey are packed.

2.1. Sample Identification

The salt samples that were studied represented various origin locations, grain sizes, particle shapes, colors, sources and prices. However, as presented in Table 1, they were classified according to the ir color since it has been probably affected by their composition (which will be further investigated). Salts were classified in 6 groups: white (WS1, WS2), black (BS1, BS2), pink (PS1), red (RS1), b lue (BLS1) and pale brown (BRS1).

2.2. Sample Analyses

Elemental analyses of the salt samples, as well as their particle size and morphology, were evaluated with a JEOL JSM-840A scanning electron microscope (SEM) at the Electron Microscopy Laboratory in the Faculty of Sciences, Aristotle University of Thessaloniki. The microscope was equipped with an energy dispersive spectrometer (EDS) INCA 300, providing spot analyses. The samples were coated with carbon with an average thickness of 200A°, using a vacuum evaporator JEOL-4X. The operating conditions were 20 kV accelerating voltage and 0.4 mA beam current. Beam diameter was 1 µm while the time of each measurement was 60sec.

3. Results and Discussion

Organoleptic characteristics and some physical properties of all the salt samples are presented in Table 1. Samples represented 8 commercial types of edible salts, originating from 5 different locations. Half of them (samples WS1, WS2, BS1, RS1) are, essentially, products obtained by the evaporation of seawater when heated by the sun. The rest of the samples (BS2, PS1, BLS1, BRS1) are simply crystallized salts, mainly mineral deposits known as rock salts. Classification of the rock samples was based on their color, leading to 1 sample from each locality, with the exception of white and black, out of which 2 samples were recognized (WS1 and WS2 for white, BS1 and BS2 for

black). Concerning their odor, only the Himalayan Black salt smelled like sulfur, while the Hawaiian Red Salt gave away a slightly earthy smell.

Sample	Commerci al Type	Location	Source	Color	Odor	Grain Size
WS1	Table Salt	Mediterranean Sea	Sea Salt	White	None	Very fine crystals ≤1 mm
WS2	Fleur de Sel	Mediterranean Sea	Sea Salt	White	None	Small crystals ≤2 mm
BS1	Hawaiian Black Salt	Hawaii	Sea Salt	Black	None	Very large crystals 3-10 mm
BS2	Himalayan Black Salt	Himalayas (India)	Mineral Salt	Black	Sulfur	Very fine crystals ≤1 mm
PS1	Himalayan Pink Salt	Himalayas	Mineral Salt	Pink	None	Small crystals ≤2 mm
RS1	Hawaiian Red Salt	Hawaii	Sea Salt	Red	Slightly earthy	Large crystals 2-3 mm
BLS1	Persian Blue Salt	Iran	Mineral Salt	Blue	None	Large crystals 2-5 mm
BRS1	Alpine salt	Austrian Alps	Mineral Salt	Pale Brown	None	Large crystals 1-3 mm

Table 1 – Organoleptic characteristics of the studied salt samples.

Many variations were observed in the grain size of the salt samples, as presented in Table 1. Figure 1 illustrates grains of each one of the 8 salt samples that were studied. Images were taken under a ZEISS stereoscope. The common table salt (WS1) and the Himalayan Black salt (BS2) are recognized as the most fine grained, since their crystal size is ≤ 1 mm. Small crystals are observed in the Fleur de Sel (WS2) and the Himalayan Pink salt (PS1), with their size not exceeding 2 mm. The grain sizes of all of the other samples vary between 1 and 5 mm. The only exception is the Hawaiian Black salt (BS2), since its impressively large and pyramid shaped crystals vary from 3 to 10 mm (Fig.1).



Figure 1 – Grains of the studied salt samples.

Table 2 presents qualitative characteristics, as obtained by numerous spot analyses on the edible salt samples. It is concluded that all samples mainly consist of Cl and Na. A differentiation was defined for the Himalayan Black Salt (sample BS2) since it also contains a sufficient amount of S, which can explain the odor of this sample, as indicated in Table 1 and Figure 2. The same occurs for Fe, since it was defined as an abundant element in the Hawaiian Red Salt (sample RS1, Fig. 3). However, apart from their main elemental concentration, impurities were determined in most of the edible salts and they are mentioned in Table 2. The common Mediterranean Sea table salt and the Alpine salt were identified as the purest ones, since they contained no impurities. On the other hand, Himalayan Black salt (BS2) and Persian Blue salt (BLS1) comprise more impurities than the rest of the samples (Table 2). It should also be mentioned that oxygen was determined in the composition of all the edible salts. Thus, further investigation is required in order to define the mineral phases in which oxygen participates.

Sample	Cl	Fe	Na	S	Impurities
WS1	+		+		-
WS2	+		+		Ca, Mg, S
BS1	+		+		K
BS2	+		+	+	Al, Ca, Fe, K, Mg, P
PS1	+		+		K, Mg, S
RS1	+	+	+		Al, Ca, Mg, S, Si
BLS1	+		+		Ca, K
BRS1	+		+		-

Table 2 – Qualitative characteristics of the studied salt samples.

The results obtained by the elemental analyses of the studied samples are presented in Table 3. The most abundant elements are Cl and Na, as revealed by their mean values (in weight %) which are the highest ones (67.1 and 28.8, respectively). They take part in the composition of all the salt samples and the range of their percentage is 14.1-95.8% for Cl and 4.2-44.3% for Na. As mentioned above, S and Fe are abundant in samples BS2 and RS1, respectively. Moreover, they are present in lower amounts in some other samples (Table 2). Overall, S ranges from 0.7% to 65.7% with its mean value reaching up to 9.7%, while Fe ranges from 1.2% to 43.9% with a mean of 8.0%.

SEM observations of representative salt samples with their corresponding spectrums are illustrated in Figures 2 and 3. All samples consist of irregular, rounded particles with sizes ranging from 2 mm to less than 500 µm. In the black samples of Himalayan (BS1) and Hawaiian (BS2) salts, cubic crystals are present with cubic blemishes referring to the crystal shape of NaCl (face-centered cubic structure). Backscattered images show the presence of different mineral phases (dark grey areas) both on the surface of the salt particles (samples BS1 and PS1) as well as individual grains (sample RS1, lower left side), pointing to the existence of other mineral phases besides NaCl, as determined by EDS analyses. These mineral phases will be determined through further investigation.

The concentrations of all other elements are relatively low, since they are present as impurities. The next predominant elements are K and Ca and that were determined in 4 samples. The range of their percentage is 1.3-50.7% for K and 1.0-26.5% for Ca, while their corresponding mean values are 14.5% and 8.6%. Magnesium was determined in 4 samples with a range of 1.5-11.8% and a mean value of 4.5%. The percentage of Al ranges from 1.0% to 2.7% in 2 samples, with a mean of 1.7%. In only 1 sample (RS1) Si was determined, with a range of 1.3-2.7% and a mean value of 2.0%. Finally, it should be noted that in 1 sample (BS2) and in only 1 spot analysis, 0.9% of P was determined.

Element	Min	Max	Mean	Sample with	Sample with
	(Weight %)	(Weight %)	(Weight %)	Lower Percentage	Higher Percentage
Al	1.0	2.7	1.7	RS1	BS2
Ca	1.0	26.5	8.6	BLS1	WS2
Cl	14.1	95.8	67.1	BS1	BS1
Fe	1.2	43.9	8.0	RS1	RS1
K	1.3	50.7	14.5	BS1	BLS1
Mg	1.5	11.8	4.5	WS2	BS2
Na	4.2	44.3	28.8	BS1	WS1
Р	0.9	0.9	0.9	BS2	BS2
S	0.7	65.7	9.7	BS1	BS1
Si	1.3	2.7	2.0	RS1	RS1

Table 3 – Results of the elemental analysis of the studied edible salts and notable samples.

The lowest and highest percentage of some elements was observed in the same sample (Table 3). T his is reasonable in the case of P and Si, since they were detected in only 1 sample. Although Cl is one of the main components of the salt samples, its minimum and maximum values are observed in the same sample (BS1). Despite the fact that they were determined in almost half of the samples, l owest and highest contents of Fe and S were determined in samples RS1 and BS1, respectively (Fi g. 2, 3). Sample BS1 contains the lowest K and Na values, while the highest values were observed in sample BLS1 and WS1, respectively. The lowest amount of Al was observed in sample RS1 and the highest in sample BS2. The Mg content ranges from 1.5 wt% in the sample WS2 to 11.8 wt% i n the sample BS2. As for Ca, its lowest and highest values were determined in samples BLS1 (1.0 wt%) and WS2 (26.5 wt%), respectively.



Figure 2 – SEM microphotographs of the studied samples, with representative X-ray spectrums. Sample BS1: backscattered image; BS2: secondary image.



Figure 3 – SEM microphotographs of the studied samples, with representive X-ray spectrums. Samples RS1 and PS1: backscattered images.

4. Conclusions

The studied samples represent 8 commercial types of edible salts, of 6 different colors and originating from 5 different locations (Mediterranean Sea, Hawaii, Himalayas, Iran and Austrian Alps). Four samples include sea salts and four samples are rock salts. The size of their grains varies from very fine (≤ 1 mm) to very large (10 mm).

Bulk chemical analyses of the samples revealed that all of them consist mainly of Cl and Na. Additionally, samples BS2 and RS1 contain sufficient amounts of S and Fe, respectively. Apart from their main chemical composition, most of the edible salt samples contain low levels of Al, Ca, K, Mg, P, S, Si and O as impurities.

Concerning morphological characteristics, salt grains in all samples appear irregular and rounded with sizes ranging from $<2 \mu m$ to 2 mm. Backscattered images certify the existence of different mineral phases other than NaCl.

However, the research is in progress since a more detailed evaluation of the composition of the salt samples is required, especially concerning the trace elements that they may comprise.

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