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ORIGINAL RESEARCH PAPER

QUALITY ASSESSMENT OF SLANIC-MOLDOVA MINERAL WATERS STORED IN REUSABLE BOTTLES

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Abstract: This paper reports the preliminary results concerning the evaluation of the effect of time and storage conditions on some physico-chemical characteristics (*p*H, conductivity, total dissolved solids and salinity) for 9 mineral waters samples collected from Slănic-Moldova and stored in reusable plastic drinking water bottles. The experimental data show that for the first storage period, respectively 1 month for the samples kept at ambient temperature and 3 months for the samples stored at 4 °C, there were no changes in the analyzed parameters. Significant variations in *p*H and conductivity were observed after 6 months for 7 out of 9 samples stored at 4 °C and after 3 months for 6 out of 9 samples stored at 20 °C. Also, is noted that the samples stored at 4 °C (in the dark) for 12 months preserved their characteristics better than those stored at ambient temperature for 9 months.

Keywords: *mineral water, physico-chemical characterization, reusable drinking water bottles, storage condition*

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INTRODUCTION

The people were constantly looking for good, healing water, and the Roman Colonizers were the ones who laid the foundations of the first spas in Europe (on the current territories of Italy, France, Belgium, Germany, Romania, etc.) and they were also the ones who transported the miraculous minerals waters in clay amphorae throughout the empire [1 – 5].
Both the richness and the great diversity of natural resources, as well as its geographical position, made Romania one of the countries with a long tradition in the use of mineral waters. In 1938, there were 56 bottling facilities throughout the country, to which were added a series of “filling” points of local interest, including one spring from Slănic-Moldova (1936). Nowadays, a large part of these, have been developed and refurbished or the bottling activity has been abandoned for others (also the case for Slănic-Moldova) [3 – 5].
The total quantities of natural mineral waters handled in Romania in 2016, both licenses under approval (308,629 thousand L) and under the licenses in force (1,374,883 thousand L), are 1,683,512 thousand L [6, 7].
The mineral waters from Slănic-Moldova, also named "Pearl of Moldavia", due to their complex composition, have numerous curative properties being used in the treatment of many diseases. These mineral waters are for example used for the cure of digestive, hepatobiliary, rheumatoid arthritis and cardiovascular diseases, in respiratory therapy (aerosol and inhalations), electrotherapy and hydrotherapy, physiotherapy pools, etc. [3 – 5, 8, 9].
The access to safe mineral waters is essential for a healthy and sustainable human life. One of the biggest threats to public health is the presence of pathogens in water that can lead to several diseases such as giardiasis, gastroenteritis, cholera, cryptosporidosis, etc. [10]. An increase in the number of bacterial pathogens in bottled waters has been reported in various studies [11 - 14].
The quality of bottled water may deteriorate due to subsequent handling, transportation and storage conditions. The development of microorganisms can take place through agencies, such as flakes introduced by human skin, especially in the case of non-ozonated, non-carbonated mineral waters [15]. Bottling and packaging can contribute to a variety of inappropriate chemical contaminants. The migration of volatile and semi-volatile organic substances from packaging materials in water increases in direct proportion to the storage period, temperature and sun exposure [16].
According to the European (2009/54/EC) [17] and Romanian (HG 1020/2005) [18] laws, the mineral water should not be treated and should be bottled at the source to preserve its natural composition. There are no restrictions with regard to the major chemical components, but for the toxic elements strict limits are imposed [19].
In addition to microbiological characteristics, a large number of scientific procedures and tools have been developed to assess the water contaminants [20]. Therefore, the investigation of the drinking water quality includes the analysis of different parameters such as *p*H, turbidity, conductivity, total suspended solids (TSS), total dissolved solids (TDS), total organic carbon (TOC), and heavy metals [21 – 24]. These parameters can affect the drinking water quality, if their values are higher than the safe limits set by the World Health Organization (WHO) and other regulatory bodies [10].

The assessment of natural mineral water's stability is very important, as the fluctuations observed in the composition of the water could imply a risk of contamination, which makes regular monitoring necessary.
This study aimed to evaluate the effect of time and storage conditions as well as temperature on the stability of some physico-chemical characteristics of several Slănic-Moldova mineral waters stored in reusable plastic drinking water bottles. The assessment of the quality of mineral waters was done in terms of *p*H, conductivity, total dissolved solids - TDS and salinity for water stored in refrigerator (4 °C – in the dark) and at room temperature (20 °C – in indirect sunlight).

MATERIALS AND METHODS

Sampling

In Slănic Valley there are over 20 mineral water springs (Figure 1). They are spread over a distance of about two kilometers, from the confluence of Slănic River with Slănicel River (550 m altitude) to the confluence of Slănic River with the Scărişoara brook, grouped by 3-4 or isolated at 50-150 m from each other. Most springs are located on the right bank of the river.

Figure 1. *Map of some mineral water sample locations in Slănic-Moldova [25]*

This study was conducted for 9 mineral springs from Slănic-Moldova (1 bis, 5, 10, 14, 15, Sonda 2, Sfântul Spiridon, Cascada and 6). All water samples were collected in June, 2019 and were not conserved. The mineral water samples have been collected in reusable plastic (poly(ethylene terephthalate) – PET) bottles of 500 mL capacity, which had been washed previously with distilled water.

Physico-chemical analyses

The parameters analyzed during this study include *p*H, conductivity, TDS and salinity. Physicochemical analyses were carried out using standard methods [18, 26, 27].
The *p*H, conductivity, TDS and salinity were measured in the research laboratory of "Vasile Alecsandri" University of Bacau, using a Thermo Scientific™ Orion™ Versa Star Pro™ *p*H/Conductivity Multiparameter Benchtop Meter (Thermo Fisher Scientific, USA). The device has dedicated electrodes for measuring these parameters. Each of them can also measure the temperature of water. *p*H was measured by a ROSS Ultra

*p*H/ATC Trode electrode. The measurement of conductivity, TDS and salinity was performed with DuraProbe conductivity cell 013005MD. The measuring range for electrical conductivity is from 1 $\mu S\cdot cm^{-1}$ to 200 $mS\cdot cm^{-1}$ (in a temperature range of 5 ºC to 70 ºC). For total dissolved solids (TDS) the range was 0 $mg\cdot L^{-1}$ to 19,999 $mg\cdot L^{-1}$ in a temperature range of 5 ºC to 70 ºC. Our salinity sensor and testing equipment uses the measurements of electrical conductivity (EC) and temperature to provide a measurement of salinity in Practical Salinity Units (PSU).

Calibrations of each electrode with specific buffers were performed periodically (before the measurements performing) in order to ensure that the analytical methods were accurate and reliable. The value of each determination was taken after submerging the specific electrode in the water sample and the reading was recorded. After the measurement of each sample, the electrode was rinsed with distilled water to avoid cross contamination among different samples.

Two different storage conditions were examined: storage in refrigerating conditions (4 °C) and storage at room temperature (20 °C), in indirect sunlight.

Measurements were carried out after five storage periods during maximum one year:

a) 24 hours, 1 month, 3 months, 6 months and 9 months for bottled mineral waters stored at room temperature;

b) 24 hours, 3 months, 6 months, 9 months and 12 months for bottled mineral waters kept in refrigerator.

RESULTS AND DISCUSSION

*p*H

*p*H is classed as one of the most important water quality parameters. Measurement of pH relates to the acidity or alkalinity of the water.

According to the results presented in Figure 2, for the samples stored in refrigerator, after 12 months, the *p*H variation is practically insignificant and in the case of spring 14 the *p*H remains constant (*p*H = 6.5). For spring 5 there is a slight decrease from 4.7 (after 24 hours) to 4.2 (after 12 months) and for the other springs (1bis, 10, 15, Sonda 2, St. Spiridon, Cascada and 6) the increase recorded varies between 0.2 (spring 15 and St. Spiridon) and max. 0.6 *p*H units (Sonda 2).

In the case of samples kept at room temperature and analyzed over a maximum period of 9 months, the *p*H variation is significant for the majority of sources (between 0.7 *p*H units – springs 5 and Cascada, and 0.9 *p*H units - springs 10, 14, 15 and 6). The largest difference was registered in the case of spring 1 bis, respectively the transition from the acidic domain (6.2) to the basic domain (8.8). The most stable sample stored at room temperature proved to be those from Sonda 2, with a *p*H variation of 0.4 units (from 8.1 to 8.5).

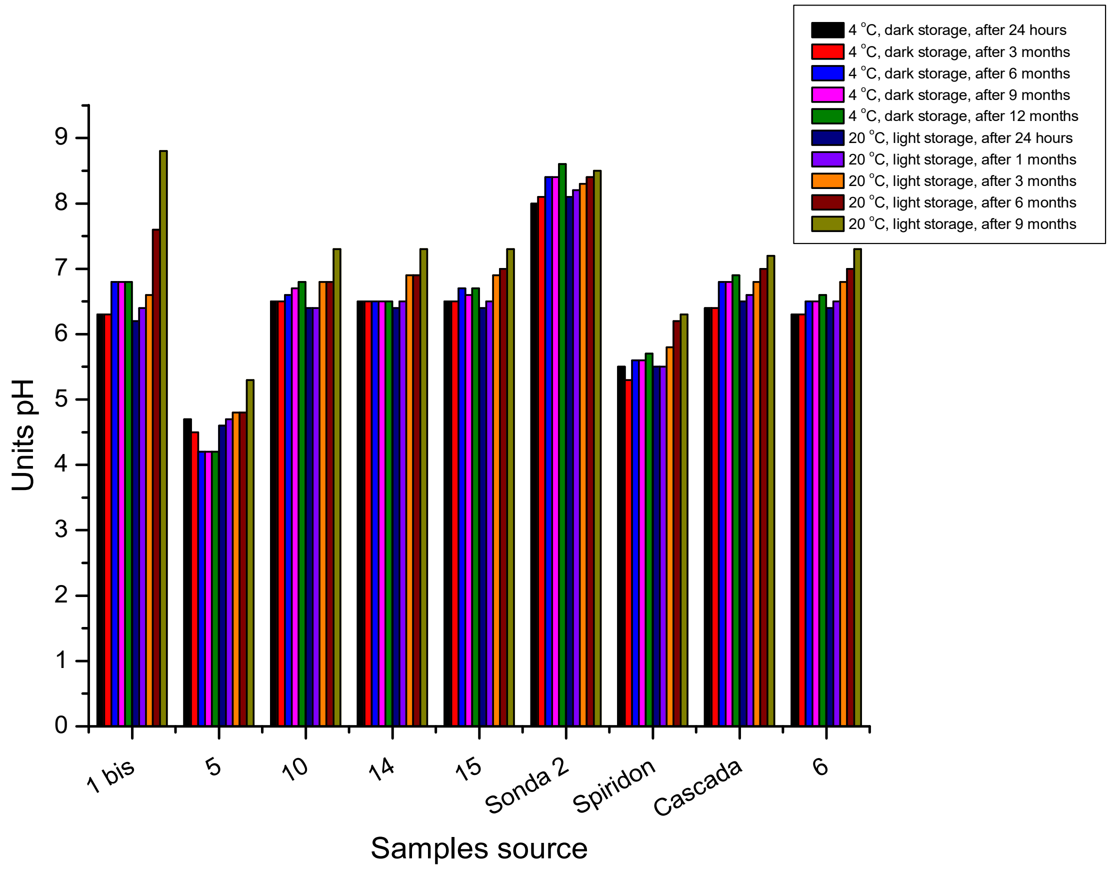

Figure 2. *pH variations during research period*

Conductivity

Electrical conductivity is the ability of any liquid medium, water in this case, to carry an electric current due to the dissolved ionic components. The measured conductivity values of all the mineral water samples analyzed during research period (12 respectively 9 month) are plotted in Figure 3.

The results show that, after 24 hours, the measured conductivity of all water samples ranges from 0.13 $mS \cdot cm^{-1}$ (St. Spiridon) to 39.10 $mS \cdot cm^{-1}$ (Cascada).

In the case of mineral waters samples kept refrigerated, after 12 months of storage, a similar behavior is found, namely a decrease of this parameter, decrease that varies between 3 % (Sonda 2) and 44 % (spring 5).

After 9 months of storage at room temperature, for most samples there is an increase in conductivity ranging between 3.7 % (spring 14) and 38.8 % (St. Spiridon). In the case of Sonda 2, the conductivity remains unchanged (decrease of only 0.3 %) and for the other 3 sources there was a decrease in conductivity by 7 % (spring 6) to 10.4 % (spring 5).

Also, we can observe that the decrease of conductivity for water samples of Cascada has the same slope both at 4 °C and 20 °C. For 1bis water samples, at 4 °C a significant decrease in time was registered and at 4 °C, on the contrary, the conductivity increases, but with a lower growth rate compared to the rate of decrease observed at 4 °C.

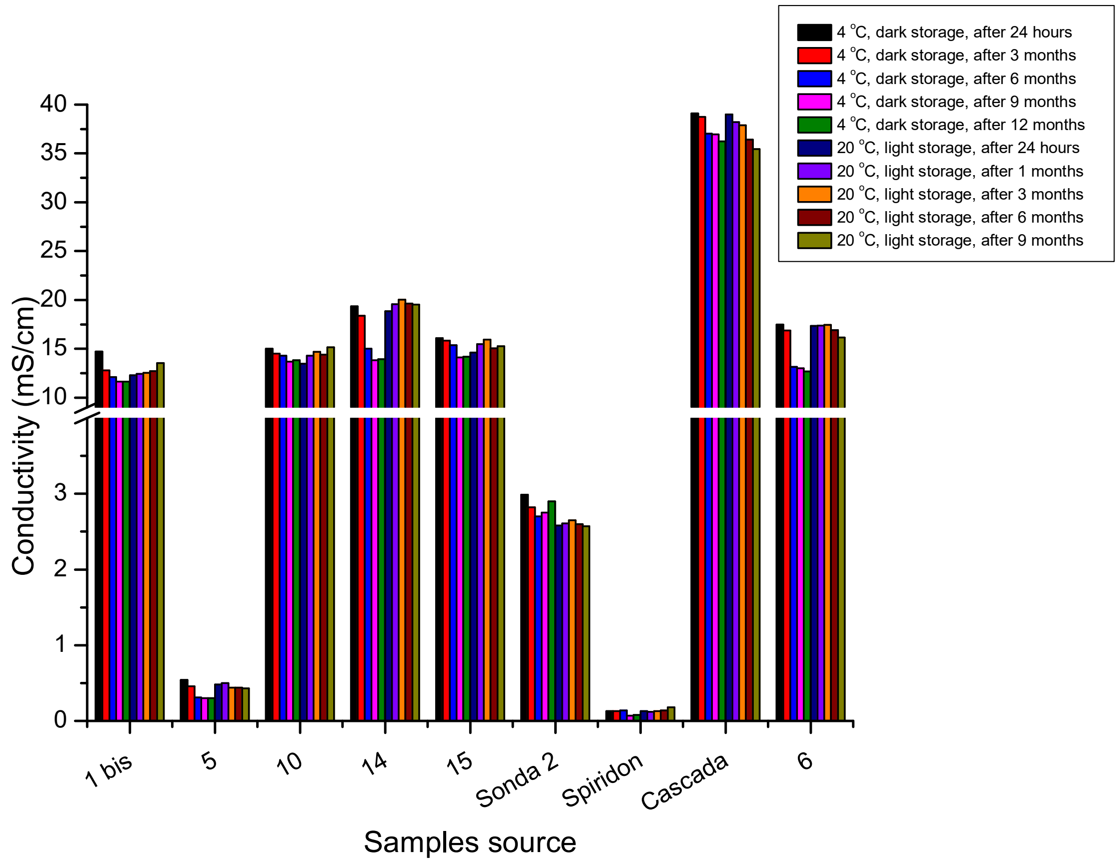

Figure 3. *Conductivity (mS·cm^{-1}) variations during research period*

Total Dissolved Solids (TDS)

Total dissolved solids (TDS) are a measure of the combined inorganic and organic substances dissolved in water.
For the samples kept cold, the variation of the TDS was in accordance with that of the conductivity throughout the storage period (12 months), finding a decrease in the interval of 1-6 months followed by stabilization in the period 9-12 months.
In the case of samples kept at ambient temperature, in months 1 and 3 there were increases for springs 5, 10, 14 and 15, followed by stabilization or slight decreases.
For the source of St. Spiridon in the first 6 months there was a slight increase from 62.75 ppm to 66.73 ppm, followed by a sudden jump of TDS in the interval of 6-9 months at 90.2 ppm.

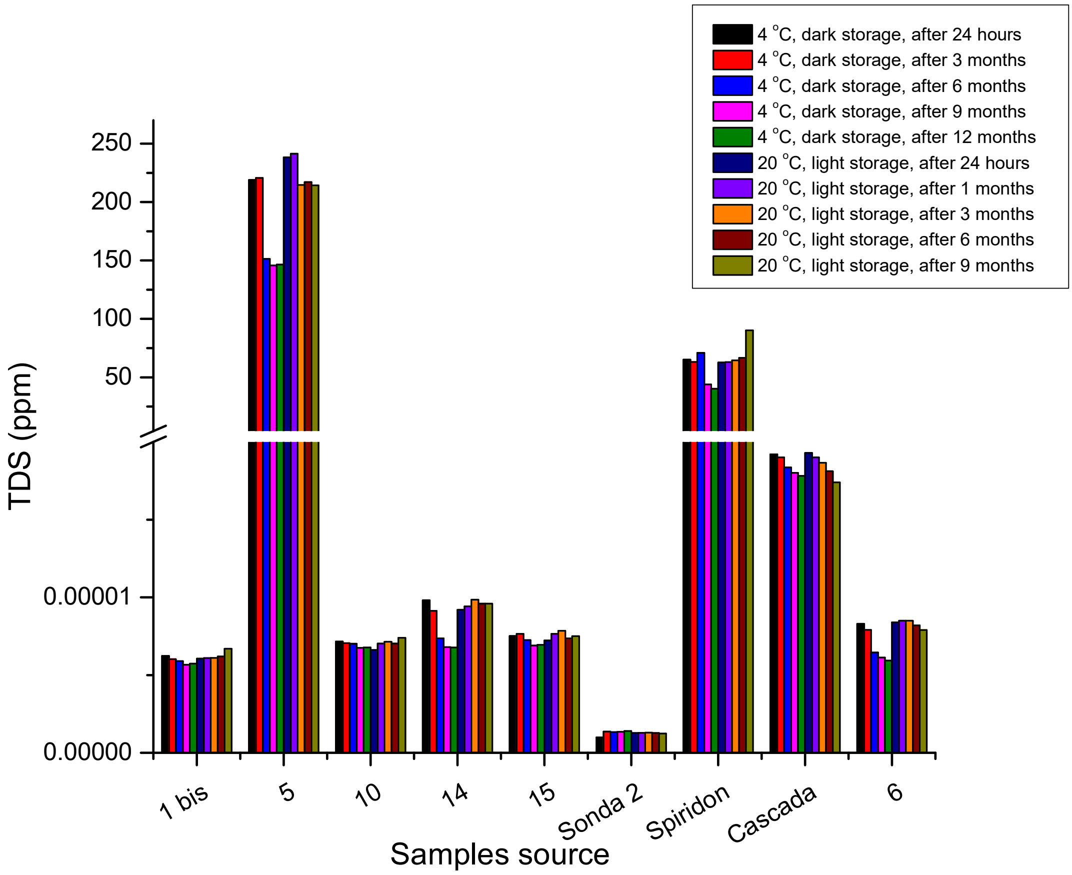

Figure 4. *Total dissolved solids (ppm) variations during research period*

Salinity

Salinity is the total concentration of all dissolved salts in water. These electrolytes form ionic particles as they dissolve, each with a positive and negative charge. As such, salinity is a strong contributor to conductivity. In accordance with the conductivity for the samples stored in refrigerator, during the research period, there was a decrease in salinity between 6 % (spring Cascada) and 36 % (spring 5). The exception is Sonda 2 for which there was an increase in salinity by 20 %.

In the case of samples kept at room temperature, there was a decrease of salinity between 6.1 % and 8.7 % for springs 5, Cascada and 6. For Sonda 2, the salinity remained the same, and for the other sources there were increases between 3.8 % (spring 15) and 50 % (St. Spiridon).

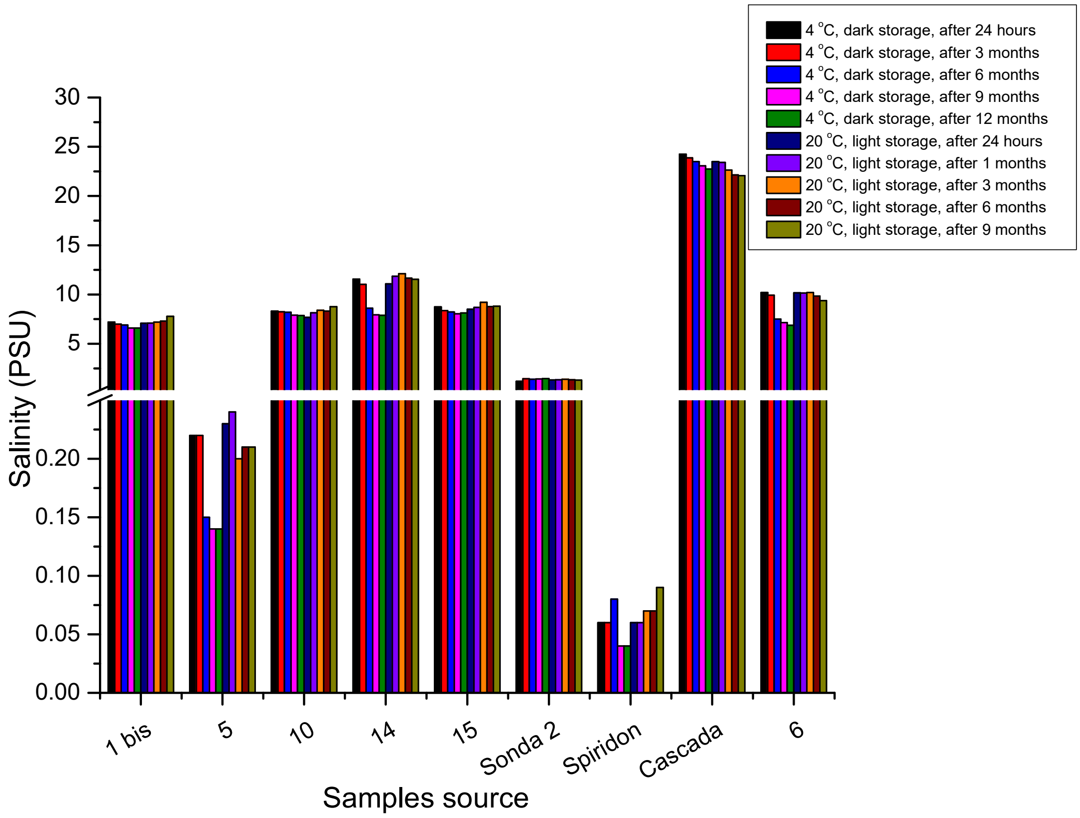

Figure 5. *Salinity (PSU) variations during research period*

CONCLUSIONS

This study presents the first investigation concerning the impact of the storage temperature and time on the stability of some physico-chemical characteristics of Slănic-Moldova mineral waters stored in commonly used bottled water recipients.

Physico-chemical analyses indicated that, after one month, the cold storage is more favorable for all the samples.

The *p*H variation recorded for the cold stored samples is much lower for the entire analyzed period (12 months) compared to the samples stored at ambient temperature for 9 months.

In the case of conductivity after 12 months, for all samples kept cold there was a decrease, the most stable being, from this point of view, Sonda 2, Cascada, 10 and 15. For the samples kept at room temperature, during the 9 months of storage, the behavior was not uniform. Only 2 samples registered a constant variation, an increase of 10 % for 1 bis and a decrease of 9 % for Cascada. The other 7 sources registered fluctuations of conductivity throughout the period, at the end being found: a decrease compared to the initial value for sources 5 and 6, stabilization in case of Sonda 2 and an increase for sources 10, 14, 15 and St. Spiridon.

The results of this preliminary study will be correlated with other determinations (dissolved oxygen content, cations and anions as well as microbiological analysis) in order to highlight the stability at bottling of these waters.

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