

Eco-friendly and efficient monitoring of physico-chemical parameters of some mineral water from Slanic Moldova (Romania) during storage in different conditions – a case study

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Abstract. In this study, six natural mineral waters (from sources named Ibis, 5, 10, 14, 15, "Sonda 2") with therapeutic potential from Slanic Moldova area (Romania) were assessed for physico-chemical parameters during storage in different conditions (bottled in PET or glass containers and kept at 20–22 °C or 4 °C) for a period of maximum 360 days. The main parameters investigated were pH, conductivity, total dissolved solids, salinity, as well as the major ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , F^- , Cl^- , SO_4^{2-} , HCO_3^-), using fast and environmentally friendly instrumental techniques (electrochemical and spectrometric / UV-Vis and ICP-MS). The physico-chemical indicators were measured at six time intervals (within 24 hours, after 7, 30, 90, 180 and 360 days) and the results obtained indicated that the pH variation was significant for the majority of samples kept at room temperature in PET containers (between 0.4 pH units - Spring 15 and over 2 pH units - springs 10, 14, Ibis and 5), while cold storage is most favorable for all natural mineral water samples. The monitoring of the chemical parameters determined during cold storage in glass containers did not reveal statistically significant variations and therefore it can be considered that these natural mineral waters are characterized by the stability of the chemical composition. For the entire analyzed period, the smallest variations of all twelve analyzed parameters were recorded for "Sonda 2", in all storage conditions, followed by springs Ibis, 15, 14, 10 and 5 stored at 4 °C in glass containers.

Keywords: natural mineral water; storage; electrochemical and spectrometric methods; quality indicators; statistical analysis.

1. Introduction

Popular since ancient times, mineral waters have attracted the attention of both scientists and authorities, being bottled and marketed in Europe since the 16th century, and the first regulations regarding their exploitation and marketing, which were the basis of current European legislation, date from the beginning of the 19th century [1, 2].

According to international legislation, "the composition, temperature and other essential characteristics of natural mineral water shall remain stable within the limits of natural fluctuation; in particular, they shall not be affected by possible variations in the rate of flow" [3]. At the same time, these natural mineral waters are characterized by their high purity at the source, respectively free of contaminants of anthropogenic origin. Scientific literature confirms the fact that, due to their varied origin, the composition of natural mineral waters is unique for each water source and gives it a characteristic taste and specific properties, beneficial for human health, which can also be exploited for therapeutic purposes [4–21].

In this context, the mineral water industry represents an important sector in Romania, with a good international reputation, covering over 60 % of the mineral water reserves of Europe (known as the homeland of mineral waters). However, only a fifth of these resources are exploited [22], currently 78 varieties of bottled natural mineral waters are recognized [23].

Also, due to its over 2000 springs, in Romania there are numerous spa resorts, with treatment bases, which use these natural mineral waters directly from the source, Slanic Moldova being one of them [24–26]. The Slanic Moldova Resort located at the base of the Nemira Mountains in the Eastern Carpathians is famous for its springs of carbonated, bicarbonated, slightly sulfurous, chlorinated, sodium, hypertonic, hypotonic and oligomineral waters, which have various curative properties for internal use (digestive, hepatobiliary disorders, urinary, metabolic and nutritional) and for external use (treatment of degenerative rheumatic and diarthritic diseases, cardiovascular and respiratory diseases, gynecological diseases, etc.) [27–33].

Considering the importance of these mineral waters from Slanic Moldova for health, our studies aimed at obtaining new experimental data on the characteristics

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of these waters, data that would confirm the sustainability of the proposal regarding the expansion of their valorisation from the perspective of bottling and storage for a longer period of time.

Also, access to safe mineral waters must be ensured under the conditions of the bottling, transport and storage process, including both the physico-chemical and microbiological indicators, in compliance with the legislation in force. For these waters there are no limits regarding the content of major components, but only for the microbiological characteristics, the toxicity of some minor components or some compounds that may come from the packaging used for storage [1, 3, 34–42].

Thus, our previous studies allowed us to emphasize the presence of trace elements that were not mentioned in the literature, the evaluation of the content of major ions and the preservation of the character of these waters over time [43], as well as their microbiological stability during storage [44].

Knowing that the chemistry of bottled water may change during transportation or storage, particularly when containers are exposed to different temperatures or kept for an extended period of time and considering the positive result regarding the stability of the microbiological indicators during storage, the present

work represents a continuation of the investigation regarding the bottling potential of these waters.

Thus, the purpose of this study was to monitor the stability of the representative physico-chemical parameters (pH, conductivity, total dissolved solids, salinity, major ions: Na^+ , K^+ , Ca^{2+} , Mg^{2+} , F^- , Cl^- , SO_4^{2-} , HCO_3^-) of these waters with therapeutic potential, during the storage period under different conditions, using fast, accurate and environmentally friendly instrumental methods (electrochemical methods, UV-Vis spectrometry and ICP-MS).

2. Experimental

2.1. Location and selection of studied natural mineral waters

Five representative natural mineral water springs for internal use (1bis, 10, 14, 15 and “Sonda 2” (abbreviated S2)), and one for external use (Spring 5), were selected taking into account the development directions of the Slanic Moldova resort as well as our previous studies [40, 43, 44].

The location and a short description of each selected source are presented in Figure 1 and Table 1.

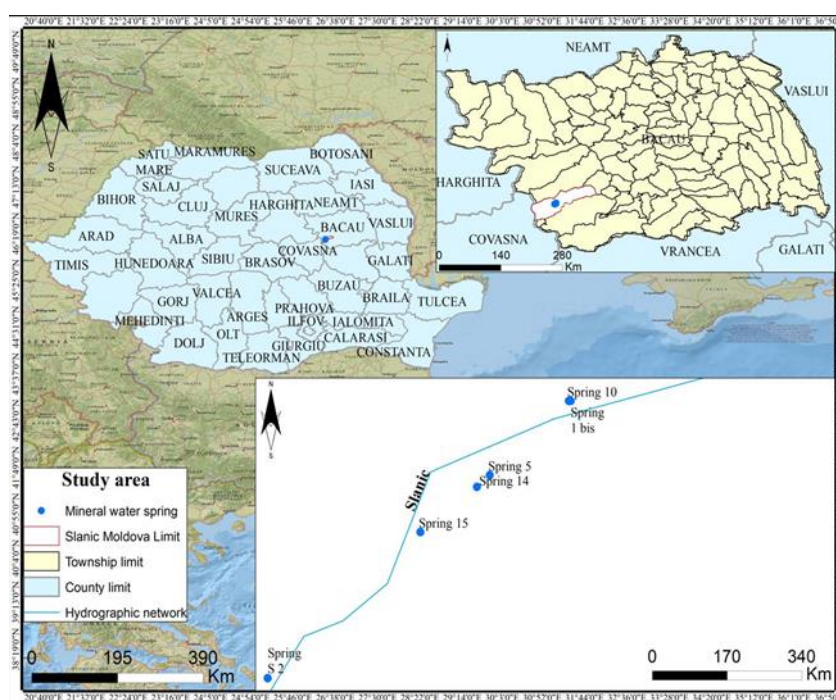


Figure 1. Geographical framing of the sampling sites of the mineral water from Slanic Moldova, Bacau County (Romania).

Table 1. Localization and properties of selected natural mineral waters from Slanic Moldova [25, 27, 32, 33].

Springs for internal use	
1bis: Elevation 492.60 m, latitude: 46°12'12.37638"N, longitude: 26°25'51.25926"E;	<ul style="list-style-type: none"> discovered in 1874, it is located on the right bank of the Slanic stream, about 1 km from the resort and it comes out of the rock at Piciorul Boroisului; hypertonic water, with high content of essential minerals and trace elements.
10: Elevation 494.60 m, latitude: 46°12'12.37843"N, longitude: 26°25'51.14747"E;	<ul style="list-style-type: none"> located on the right bank of the Slanic stream and was highlighted in the years 1805-1820; belongs to the upper underground aquifer system, being constituted by a single strong emergence; hypertonic, carbonated, bicarbonated, chlorinated water, that contains significant amounts of Li and Mn.
14: Elevation 507.719 m, latitude: 46°12'08.88949"N, longitude: 26°25'45.41132"E;	<ul style="list-style-type: none"> located on the left bank of the Slanic stream, it was put into use in 1958; belongs to the upper underground aquifer system of the fissured type cantoned by the native Paleogene flysch deposits;

Springs for internal use	
▪	hypertonic, carbonated, bicarbonated, ferruginous water, that contains the highest amounts of Li, Mn, Cu, and Ag.
15:	Elevation 508.719 m, latitude: 46°12'07.05442"N, longitude: 26°25'41.89160"E; ▪ located on the right bank of the Slanic stream it intercepted the Kliwa sandstone horizon and then the Lower Oligocene horizons, it was put into use in 1954; ▪ carbonated, bicarbonated, sodium-chlorinated, ferruginous water, with a more content in Ag.
S2:	Elevation 515.993, latitude: 46°12'01.13167"N, longitude: 26°25'32.37564"E; ▪ located on the right bank of the Slanic stream, near the trout, with a depth of 70.90 m, was homologated in 1980; ▪ hypotonic, alkaline water (pH = 8), and rich in trace elements (Li, Cr, Cu, Se, Sr, Ba, Be, V, Ga, Rb).
Spring for external use	
5:	Elevation 480.286 m, latitude: 46°12'09.36427"N, longitude: 26°25'46.21132"E; ▪ located on the right bank of the Slanic stream, it has been used since 1807 when it was discovered by nobleman Mihalache Spiridon; ▪ the source belongs to the upper underground aquifer system; ▪ siliceous and ferruginous water, very rich in trace elements (B, Li, Cr, Cu, Zn, Se, Sr, Ba, Be, V, Co, Ga, As, Cs).

These selected mineral water sampling points are accessible to the public and have a relatively constant flow.

2.2. Sampling

The sampling campaign was performed in January 2020. A total of 144 samples (Table 2) were collected according to ISO 19458, from the six springs in 500 mL containers made of sterile glass (LBG 3.3, with blue threaded lid (GL 45), graduated, transparent, autoclavable) according to ISO 4796, and polyethylene terephthalate - PET (brand LABBOX, sterile, without thiosulphate, with polyethylene lid with safety ring). The bottles were thoroughly rinsed with the sample

(three times), filled to the top, and then transported to the laboratory on the same day and stored for a maximum period of 360 days, in the absence of light, under different temperature conditions: room temperature (20-22 °C) and refrigeration conditions (4 °C).

According to European and Romanian legislations [3], the sampled natural mineral waters were bottled at the source and no chemicals were added as it is supposed to be consumed by humans.

The first determination of all parameters for samples stored in different conditions was carried out within a time-interval of no more than 24 hours after sampling.

Table 2. Planning of storage and analysis conditions.

Natural mineral water springs	Storage and analysis plan				Total
	1 day/7 days/30 days/90 days/180 days/360 days				
	Glass, refrigerating condition (4 °C), in absence of light	Glass, room temperature (20 °C), in absence of light	PET, refrigerating condition (4 °C), in absence of light	PET, room temperature (20 °C), in absence of light	
1bis	6	6	6	6	24
5	6	6	6	6	24
10	6	6	6	6	24
14	6	6	6	6	24
15	6	6	6	6	24
S2	6	6	6	6	24
TOTAL samplings	36	36	36	36	144

2.3. Measurement techniques

For each water sample, the electrochemical (pH, conductivity – EC, Total Dissolved Solids – TDS and salinity - SAL) and spectrometric determinations (UV-Vis and ICP-MS) were performed, in triplicate, using the standard testing procedures [1, 45–49], according to

Romanian [34] and international [3, 35, 50, 51] regulations.

Table 3 displays information on the analytical methods and equipment used to determine the twelve monitored parameters, as well as the existing provisions in the legislation regarding the values of these quality indicators of natural mineral waters.

Table 3. Methods and equipment used form physico-chemical and chemical parameters.

Parameter	Method adopted* / Equipment
Physico-chemical parameters	
pH	Electrometric method [46, 47] / Thermo Scientific™ Orion™ Versa Star Pro™ Multiparameter Benchtop Meter (Thermo Fisher Scientific, USA) provided with ROSS Ultra pH/ATC Trode electrode and DuraProbe conductivity cell 013005MD
EC [mS/cm]	
TDS [ppm]	
Salinity [PSU]	

Parameter	Method adopted* / Equipment
<i>Major ions</i>	
Na ⁺ [mg/L]	Atomic spectroscopic method - ICP-MS [48] / Inductively coupled plasma mass spectrometer (Agilent 7500cx, Agilent Technologies, California, USA)*
K ⁺ [mg/L]	
Ca ²⁺ [mg/L]	
Mg ²⁺ [mg/L]	
F ⁻ [mg/L]	Spectrophotometric/LCK 323/Method 8029 [49] / UV-Vis spectrophotometer (HACH DR 3900, Hach, Colorado, USA)**
Cl ⁻ [mg/L]	Spectrophotometric/LCK 311/Method 8207 [49] / UV-Vis spectrophotometer (HACH DR 3900, Hach, Colorado, USA)**
SO ₄ ²⁻ [mg/L]	Spectrophotometric/LCK 353/Method 8051 [49] / UV-Vis spectrophotometer (HACH DR 3900, Hach, Colorado, USA)**
HCO ₃ ⁻ [mg/L]	Determined by calculation/ Titrimetric method/ SR EN ISO 9963/2-2002/ UV-Vis spectrophotometer [49]**

2.4. Programs used for data processing

All collected data were statistically analyzed using XLSTAT version 2021 software for Excel (Microsoft Office version 2013). The mean (M) and standard deviation (SD) of each parameter were calculated.

The analysis of Pearson's correlation was used to evaluate the strength of statistical relationship between parameters. The Pearson coefficient indicates how strong the correlation is, its range being from -1 to +1 [52, 53]. The interpretation for different values of the Pearson's correlation index is depicted in Table 4.

Table 4. Interpretation of the Pearson's correlation coefficients.

Range of correlation coefficient	Interpretation
0.00 – 0.10	No correlation
0.10 – 0.39	Weak correlation
0.40 – 0.69	Moderate correlation
0.70 – 0.89	Strong correlation
0.90 – 1.00	Very strong correlation

A modified Schoeller–Berkalo diagram was carried out allowing visualizing the changing trend of the chemical composition in water samples from the study area. This type of chart is often used in similar analyses [12, 54].

The maps were drawn using ArcMap 10.2 software by ESRI and the WaterShed application [55].

3. Results and discussion

3.1. pH

According to the results presented in Figure 2, in the case of PET containers samples kept at room temperature, and analyzed over a maximum period of 12 months, the pH variation was significant for most sources (between 0.4 pH units recorded for Spring 15 and over 2 pH units for springs 10 and 14). The biggest differences were registered in the case of springs 5 and 1bis, namely the transition from the acidic range to the basic range (from 4.6 to 7.4 for Spring 5 and 6.2 to 8.8 for Spring 1bis).

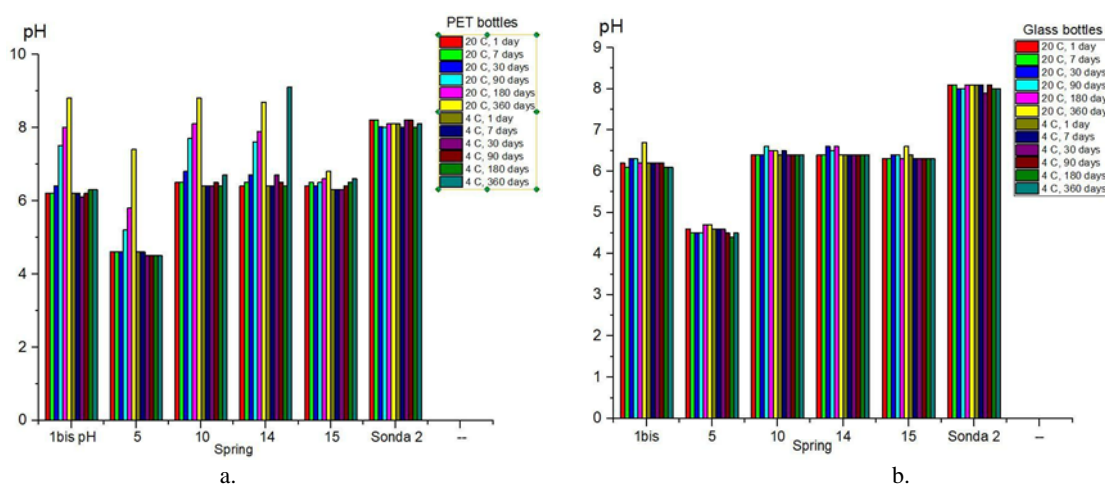


Figure 2. pH variation of natural mineral waters bottled in PET (a) and glass (b) containers stored at 4 °C and 20 °C.

For the samples stored in PET containers in the refrigerator, after 360 days, the pH variation is practically insignificant in the case of springs 5 (M = 4.533, SD = 0.051), 1bis (M = 6.216, SD = 0.075) and S2 (M = 8.100, SD = 0.089). For springs 10 and 15, an increase of a maximum of 0.3 pH units was recorded in the entire studied interval, while for Spring 14, in the last six month of storage, a significant increase of 2.7 pH units was recorded. The most stable sample stored at

room temperature was found to be Spring S2 with a pH variation of 0.1 pH units (from 8.1 to 8.2 after 7 days and it returns to the value 8.1 after 360 days).

In the case of samples kept at room temperature in glass containers, and analyzed over a period of 360 days, springs 10, 14 and S2 kept their pH constant or it showed a variation of maximum 0.1 pH units. Spring 1bis, although showed a variation of 0.5 pH units, has a much better evolution in glass containers at room temperature

compared to the PET container in the studied time interval. Spring 5 showed a slight variation in pH, from 4.6 to 5.2 pH units, an increase that does not change its slightly acidic character. All samples kept in glass containers at 4 °C registered very small variations of 0.1 (the case of springs 1bis, 15 and 14) and respectively 0.2 (springs 5, 10 and S2) pH units with standard deviations varying between 0.040 and 0.083.

3.2. Conductivity

From the six springs analyzed (Figure 3), the lowest conductivity value is presented by Spring 5 (0.47

mS/cm), followed by Spring S2 (2.64 mS/cm) – which belong to the category of low and medium mineral content [3], while the rich mineralized springs 1bis, 10, 15 and 14 have significantly higher conductivity values between 12.4 and 19.8 mS/cm.

The results graphically represented in Figure 3 indicate that, both in the case of springs with low conductivity and those with high conductivity, the storage behavior was similar: relatively constant preservation of the values in the first 90 days, followed by a slight decrease in the last 6 months of storage.

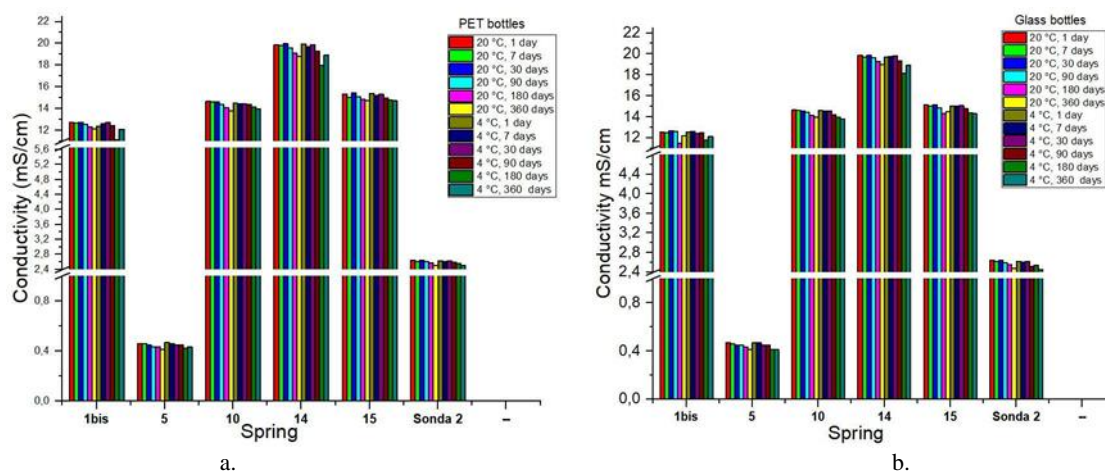


Figure 3. Conductivity variation of natural mineral waters bottled in PET (a) and glass (b) containers stored at 4 °C and 20 °C.

After 180 days of storage in PET containers (Figure 3a), it can be seen that the decrease in conductivity for the water samples from springs 5 and S2 has the same slope both at 4 °C and at 20 °C.

The decreases recorded during the 360 days of storage in PET containers at room temperature, for the analyzed samples, were the following: Spring 15 - 3.8 % ($M = 15.08$, $SD = 0.265$), Spring 1bis - 4.6 % ($M = 12.51$, $SD = 0.253$), Spring 14 - 5.3 % ($M = 19.52$, $SD = 0.472$), Spring 10 - 5.7 % ($M = 14.34$, $SD = 0.343$), Spring S2 - 4.9 % ($M = 2.59$, $SD = 0.050$) and Spring 5 - 10.9 % ($M = 0.44$, $SD = 0.020$).

In the case of natural mineral water samples stored in glass containers (Figure 3b), both at 20 °C and at 4 °C, after 360 days of storage, a similar behavior was observed, i.e. a decrease in this parameter: 3.1-3.3 % (Spring 1bis), 4.4-4.1 % (Spring 14), 4.4-5.0 % (Spring 15), 4.6-5.3 % (Spring 10), 6.0-6.5 % (Spring S2) and 12.8 % (Spring 5).

3.3. Total Dissolved Solids (TDS) and salinity (SAL)

Small variations in the conductivity of mineral waters in the studied range are a reflection of the stability of the chemical composition in close correlation with the variations of TDS (Figure 4) and salinity (Figure 5).

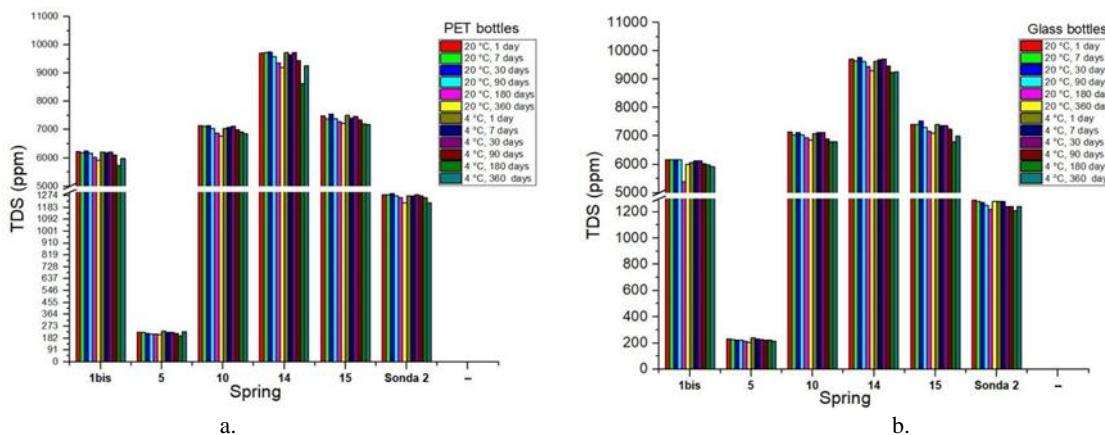


Figure 4. TDS variation of natural mineral waters bottled in PET (a) and glass (b) containers stored at 4 °C and 20 °C.

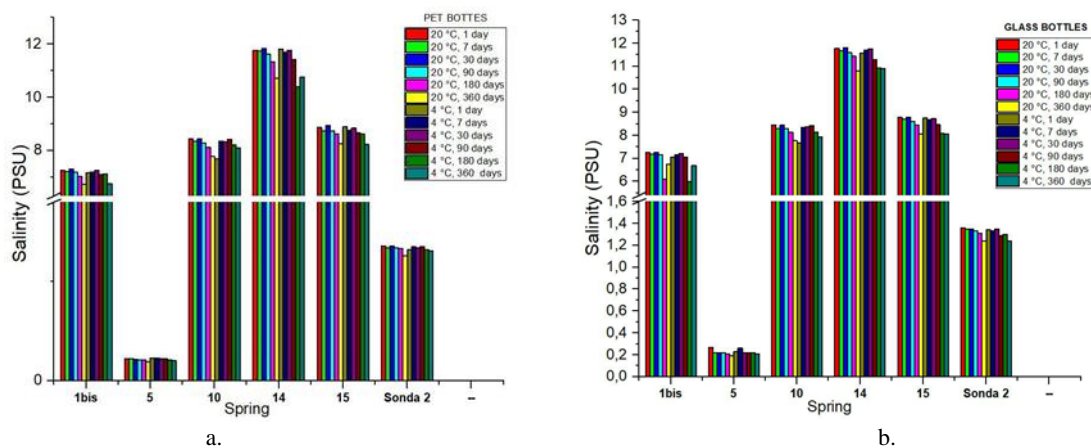


Figure 5. Salinity variation of natural mineral waters bottled in PET (a) and glass (b) containers stored at 4 °C and 20 °C.

In accordance with the conductivity, the behavior during storage was similar in the case of five out of the six springs (1bis, 10, 14, 15, S2): keeping the values relatively constant during the first 90 days, followed by a slight decrease during the last 6 months of storage.

In all the storage conditions, it was observed that in the interval of 360 days, the highest rate of decrease of both TDS (7.4-11.7 %) and salinity (13.6-29.6 %) was recorded in the case of Spring 5. In the same interval of 360 days, taking into account the two determinations (TDS and salinity), the water samples from Spring 1bis

stored in glass at 4 °C were the most stable, showing the smallest variations (a decrease of only 1.6 % in the case of TDS and only 4.9 % in the case of salinity).

The Pearson’s correlation coefficients (Table 5 and Table 6) were calculated for physico-chemical parameters of natural mineral waters samples bottled in glass containers and stored at 4 °C, measured at six time intervals as follows: in 24 hours, after 7 days, 30 days, 90 days, 180 days and 360 days.

Table 5. The correlation matrix of physico-chemical parameters for natural mineral waters from springs 1bis, 5 and 10.

	pH			EC			TDS			SAL		
	1bis	5	10	1bis	5	10	1bis	5	10	1bis	5	10
pH	1	1	1									
EC	0.50	0.45	-0.43	1	1	1						
TDS	0.34	0.64	-0.37	0.75	0.85	0.98	1	1	1			
SAL	0.57	0.46	-0.52	0.95	0.77	0.98	0.71	0.94	0.97	1	1	1

Table 6. The correlation matrix of physico-chemical parameters for natural mineral waters from springs 14, 15 and S2.

	pH			EC			TDS			SAL		
	14	15	S2	14	15	S2	14	15	S2	14	15	S2
pH	1	1	1									
EC	-0.28	-0.67	-0.09	1	1	1						
TDS	-0.56	-0.41	-0.16	0.92	0.93	0.98	1	1	1			
SAL	-0.58	-0.61	-0.10	0.90	0.99	0.99	0.99	0.95	0.97	1	1	1

The highest positive value of coefficient correlation between EC and TDS can be observed for springs 10 and S2 (0.98).

For Spring 1bis were registered the lowest values of coefficient correlation between EC and TDS (0.75) and TDS and SAL (0.71), respectively.

Concerning the coefficient correlation between EC and SAL, the lowest value can be perceived for Spring 5 (0.77).

A moderate positively correlation between pH and EC was found for samples from springs 1bis and 5. Samples from Spring 5 presented a moderate correlation between pH and TDS and pH and SAL, respectively.

3.4. Major ions

Since the results obtained in the case of the four parameters (pH, EC, TDS and SAL) have indicated that

cold storage in glass containers is the most favorable for all the natural mineral water samples, we proceeded to determine the content of major ions which are in close correlation with the physico-chemical parameters analyzed.

The determination of the concentrations of the selected major ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , F^- , Cl^- , SO_4^{2-} , HCO_3^-) was done within 24 hours of sampling, 180 days and 360 days after storage, considering that the national legislation provides a semi-annual evaluation of these parameters at the source [34].

On the Schoeller-Berkaloff diagram (Figure 6), for each spring and analyzed period, the concentrations of selected ions and the TDS values were plotted vertically according to a logarithmic scale, allowing a visual

comparison and highlighting similar variability trends between the main ions.

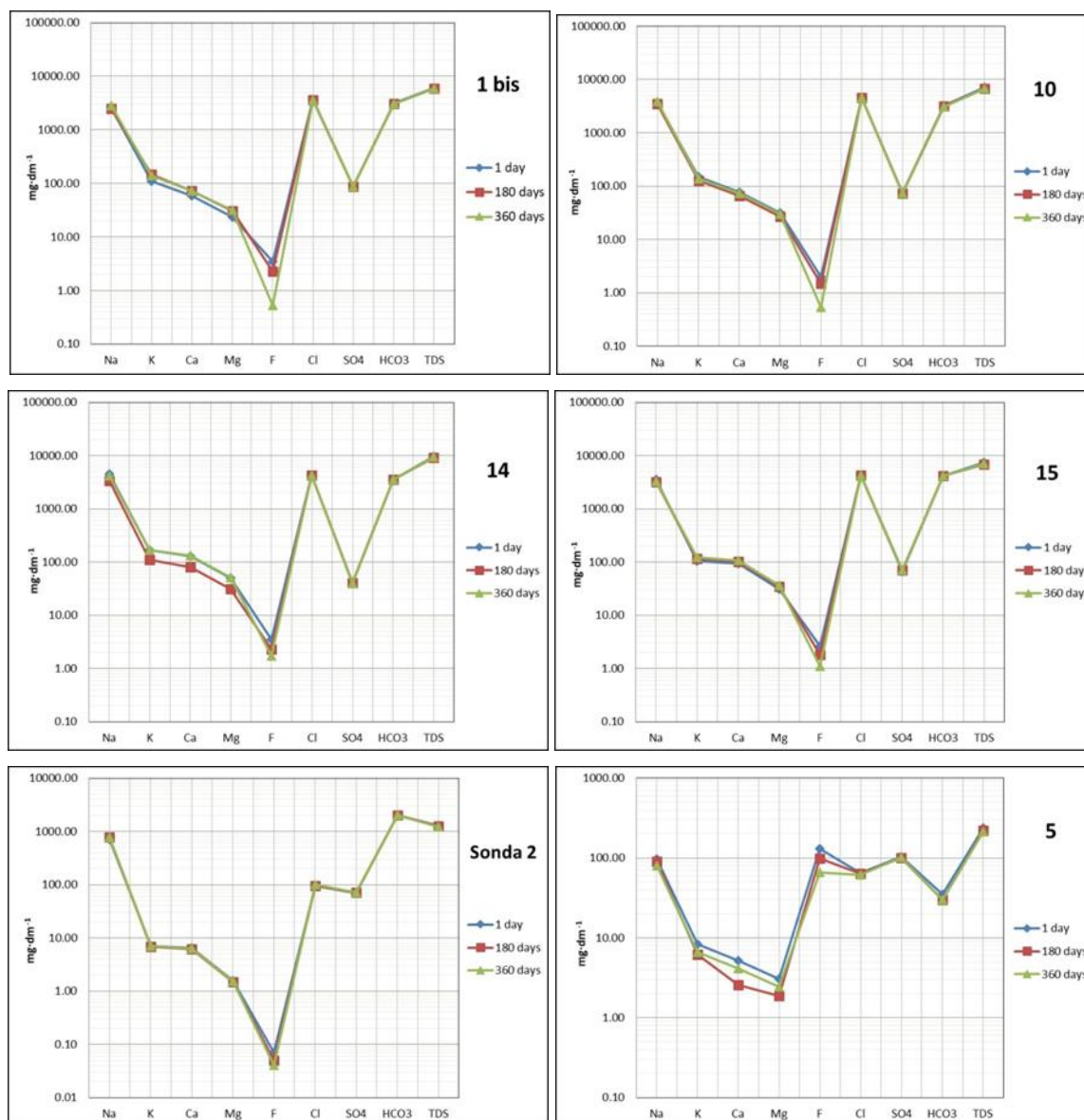


Figure 6. Schoeller-Berkaloff plots of analyzed natural mineral waters stored in glass containers at 4 °C.

It can be observed that from the four springs (1bis, 10, 14 and 15) classified in the category of mixed type ($\text{Na}^+ - \text{K}^+ - \text{HCO}_3^- - \text{Cl}^-$) water, without predominant anion [43], the lowest variability of the concentrations of major ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^-) was presented by Spring 10, followed by springs 15 and 1bis, while Spring 14 has a relatively higher variability of cation concentrations during storage.

The Spring S2 with medium mineralization [3], in which the HCO_3^- anion holds the dominant position, during the 360 days of storage in glass at 4 °C recorded the smallest variation for both cations Na^+ - 5.16 %, Ca^{2+} - 2.34 %, Mg^{2+} - 2.32 %) as well as for anions (Cl^- - 2.34 %, SO_4^{2-} - 1.01 % and HCO_3^- - 0.01 %).

In the case of the poorly mineralized Spring 5, for external use, with F^- as the predominant anion, data analysis indicates a significant variation in the concentrations of Ca^{2+} , Mg^{2+} , K^+ , F^- and HCO_3^- .

It was also observed that the fluoride ion presents in very low concentrations in all other five analyzed springs (0.053 mg/L for Spring S2 – 2.500 mg/L for Spring 14) is characterized by the greatest variability during storage (between 20.30 % and 70.80 %).

Despite the variations observed for the selected cations and anions, during storage, the prevailing chemical character of the six analyzed natural mineral waters was not affected.

Additionally, the Pearson's correlations were performed between physico-chemical characteristics and the major ions concentration measured at three time intervals (within 24 hours, after 180 days and 360 days) for all natural mineral water samples stored in glass bottles at 4 °C.

Samples from Spring 1bis (Table A from Supplementary Materials) show strong positive correlation between EC and HCO_3^- ($r = 0.837$), between HCO_3^- and F^- , Cl^- and SO_4^{2-} ($r = 0.872 - 0.920$), while strong negative correlations exists

between EC and K^+ , Ca^{2+} and Mg^{2+} ($r = -0.894 \div -0.958$), and also between divalent cations (Ca^{2+} and Mg^{2+}) with Cl^- , F^- , SO_4^{2-} and HCO_3^- ($r = -0.830 \div -0.998$). EC has moderate positive correlation with F^- , Cl^- , SO_4^{2-} and weak correlation with Na^+ .

In case of Spring 10 (Table B from Supplementary Materials), both EC and TDS show strong positive correlations with all the anions ($r = 0.780-0.999$) and K^+ , while with Ca^{2+} and Mg^{2+} the correlations were moderate. The strong positive correlation of Na^+ with pH is noted ($r = 0.992$), while with the others parameters was observed an almost total linear independence. There is an excellent correlation between K^+ , Ca^{2+} and Mg^{2+} cations ($r = 0.995-0.997$), which in turn are strongly correlated with both Cl^- and SO_4^{2-} .

For Spring 14 (Table C from Supplementary Materials), with the exception of the SO_4^{2-} anion, a strong correlation was observed between EC and the other major ions analyzed (F^- , Cl^- , HCO_3^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+}). Also, there is a very strong dependence between the four cations ($r = 0.943-0.999$), as well as that between the HCO_3^- , F^- and Cl^- anions ($r = 0.944-0.999$).

In the case of Spring 15, very strong correlations between the physico-chemical and chemical parameters are noticeable (Table D from Supplementary Materials). It can be seen that pH shows a positive correlation with the SO_4^{2-} anion ($r = 0.999$) and K^+ , Ca^{2+} and Mg^{2+}

cations, while with F^- , Cl^- , HCO_3^- and Na^+ the correlation is strongly negative ($r = -0.884 \div -1$). With the exception of Na^+ , the anions F^- , Cl^- and HCO_3^- show a strong negative correlation with K^+ , Ca^{2+} and Mg^{2+} cations ($r = -0.933 \div -0.990$), while the SO_4^{2-} anion presents a strong positive correlation with the three cations ($r = 0.932 - 0.963$). Also, in the case of the HCO_3^- anion, a perfectly positive relationship with Cl^- ($r = 1$) and a perfectly negative one with SO_4^{2-} ($r = -1$) can be noted.

For Spring S2, the Person correlation results (Table E from Supplementary Materials) reveals that EC, TDS and SAL parameters show strong positive correlations with F^- and HCO_3^- and strong negative correlations with Cl^- , SO_4^{2-} and Na^+ , while pH is strongly positive correlated with the cations K^+ , Ca^{2+} and Mg^{2+} ($r = 0.835-0.988$). There is a strong negative correlation of F^- and HCO_3^- with Na^+ and SO_4^{2-} and on the other hand they are significantly positively correlated with Ca^{2+} and Mg^{2+} . The correlation between Cl^- and Na^+ and K^+ is also significant, and only slightly with Ca^{2+} and Mg^{2+} .

As an example of the overall agreement, for the Spring 5 (for external use), as can be seen in Table 7, all twelve parameters were interdependent, the large majority of them (the coefficients in bold) presenting strong positive correlations ($r = 0.70 - 1.00$).

Table 7. Correlation matrix between the parameters for natural mineral water from Spring 5.

5	pH	EC	TDS	SAL	F^-	Cl^-	SO_4^{2-}	HCO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}
pH	1											
EC	1	1										
TDS	0.945	0.945	1									
SAL	0.960	0.960	0.998	1								
F^-	0.856	0.856	0.977	0.966	1							
Cl^-	0.896	0.896	0.991	0.984	0.996	1						
SO_4^{2-}	0.755	0.755	0.502	0.544	0.310	0.387	1					
HCO_3^-	1	1	0.945	0.960	0.856	0.896	0.755	1				
Na^+	0.807	0.807	0.955	0.939	0.995	0.985	0.223	0.807	1			
K^+	0.983	0.983	0.871	0.894	0.749	0.801	0.862	0.983	0.686	1		
Ca^{2+}	0.805	0.805	0.569	0.609	0.385	0.460	0.996	0.805	0.300	0.899	1	
Mg^{2+}	0.874	0.874	0.669	0.705	0.498	0.568	0.978	0.874	0.419	0.947	0.991	1

The perfect positive linear relationships ($r = 1$) of HCO_3^- with EC and TDS is remarkable, as well as the very good correlations with all cations ($r = 0.805 - 0.983$) and the anions ($r = 0.755 - 0.896$). The only weak correlations were recorded in the case of SO_4^{2-} with F^- , Cl^- and Na^+ and Ca^{2+} with F^- and Na^+ .

In accordance with Adamou et al. [56], the strong correlation observed in our study, for each spring, between EC and some cations and anions indicate that the mineralization of the samples is strongly verified by these ions.

Considering the results previously presented and the maximum allowed fluctuation limit according to Art. 19/Order No. 87 (2008) [57], it is noted that the

possibilities of bottling and storage are different for each source and the smallest variations for the entire period were recorded for Spring S2, in all storage conditions, followed by springs 1bis, 15, 14, 10 and 5 stored at 4 °C in glass containers.

4. Conclusions

The study carried out represents a first investigation regarding the influence of temperature, time and type of storage container (glass or plastic) on the stability of some major physico-chemical and chemical parameters of mineral waters from Slanic Moldova, in terms of maintaining the state of waters characteristics in accordance with the legislative provisions.

The pH variation recorded for the cold stored samples is much lower over the entire analyzed period (360 days) compared to the samples stored at ambient temperature for 180 days in PET or glass containers. After 12 months, for PET containers samples kept at room temperature, the biggest differences were registered in the case of springs 5 and 1bis, namely the transition from the acidic range to the basic range.

In the case of EC, TDS and salinity, the storage behavior is similar for all storage conditions (PET or glass containers at room temperature or in the refrigerator): relatively constant preservation of the values in the first 90 days, followed by a decrease in the last 6 months of storage. Summing up the physico-chemical analysis, after 360 days, it can be stated that the cold storage in glass containers is the most favorable for all natural mineral water samples analyzed.

It should be noted the efficiency of using a simple and fast method, the electrochemical method, for monitoring such closely related parameters as EC, the amount of TDS and salinity, for which the Pearson correlation coefficient value was close to unit for all waters studied.

Also, the determination of the content of major ions in close correlation with the physico-chemical parameters analyzed for the samples stored at 4 °C in glass containers, by ICP-MS and UV-Vis spectrometry, indicates that the small variations observed, both for cations and for anions, do not affect the chemical character of the six analyzed natural mineral waters.

In addition, the Pearson correlation helped us to create an image regarding the relationship between the four physico-chemical indicators and the selected major ions, important parameters in monitoring the quality of natural mineral waters, in evaluating the storage and bottling possibilities, as well as the therapeutic potential.

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Conflict of interest

The authors declare that there is no conflict of interest regarding this research article.

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