



## **An Analysis of Bioelements in the Source Waters of Sanok District on the Border of the Eastern and Western Carpathians and their Impact on the Functioning of the Human Body**

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### **1. Introduction**

The cradle of contemporary balneotherapy and physical therapy were the peoples inhabiting the lands of the Mediterranean basin. Ancient Egyptians, Greeks and Romans discovered the healing values of the surrounding nature. Hippocrates (460-380 BC) and Asklepiades (120-56 BC) were considered the precursors of medical art in ancient times, who mainly used the benefits of sunlight and water (Rak 2011). Wojciech Oczko (1537-1599), the court physician of Stefan Batory and Zygmunt III (Tchórzewska-Cieślak and Rak 2005) is considered to be the father of Polish balneology. An important concept of balneology is crenotherapy. Crenotherapy is a drinking therapy with mineral waters. The following types of mineral waters are distinguished:

Natural spring water is water originating from documented underground resources, extracted with one or more natural or drilled holes, originally pure chemically and microbiologically, not differing in properties and mineral composition from water intended for human consumption, specified in the provisions on collective supply in water (Tchórzewska-Cieślak and Rak 2006).

Natural mineral water is water originating from documented resources of groundwater, extracted with one or more natural or drilled holes, originally pure chemically, microbiologically, characterized by stable mineral composition and properties of physiological significance, resulting in beneficial effects on human

health, according to specific requirements (Tchórzewska-Cieślak and Rak 2005, Tchórzewska-Cieślak and Rak 2006, Rozporządzenie 2011).

Bottled medicated water is water intended for sale in unit packaging, originally clean, untreated underground water from one deposit, whose chemical composition and physical properties determine a specific therapeutic effect, confirmed by the results of pharmacological research (Tchórzewska-Cieślak and Rak 2006, PN-Z- 11001-1).

Pharmacodynamic factors are the minimum content of selected chemical components (so-called specific components) or the minimum value of the physical properties of water that causes their therapeutic effect (Rozporządzenie 2016, Michalski 2006). The basic components of mineral waters whose content in water determines its degree of mineralization include: anions: chloride, bicarbonate and sulphate, and cations: sodium, potassium, calcium and magnesium (Tchórzewska-Cieślak and Rak 2006). It is worth remembering that natural mineral waters not only supplement water losses, but also shortages of some of the bio-elements that are essential for the proper functioning of the body. Essential for the body bioelements taken from mineral water are bioactive and easily digestible (Błaszczuk and Tuszyński 2007).

The basic process conditioning the existence of Earth's Shell - called the biosphere – is photosynthesis, taking place in green parts of plants with the participation of chlorophyll, using solar energy, in the presence of minerals. The role and share of individual bioelements in biochemical processes occurring in living organisms are largely determined by the atom's structure (Gertig and Przysławski 2006).

Taking a quantitative criterion of difference in the occurrence in the body and the ranges of recommended intake, these bioelements are divided into macroelements and microelements. You can also distinguish a three-level division, which also takes into account the so-called ultra-trace elements (Gertig and Przysławski 2006).

Macroelements – elements whose content in the body on a dry matter basis is greater than 0.01%, and safe or recommended intake is greater than 100 mg/day. These include calcium (Ca), phosphorus (P), magnesium (Mg), sodium (Na), potassium (K), sulfur (S), chlorine (Cl), as well as carbon (C), hydrogen (H), oxygen (O), nitrogen (N) (taking into account only the content criterion in the body).

Microelements – elements whose content in the body in terms of dry mass is less than 0.01%, and safe and recommended consumption is less than 100 mg/day. Includes iron (Fe), zinc (Zn), copper (Cu), iodine (I), selenium (Se), fluorine (F), chromium (Cr), manganese (Mn), molybdenum (Mo), boron (B), cobalt (Co), nickel (Ni), silicon (Si), tin (Sn), vanadium (V). These elements are often referred to as "trace".

Ultra trace elements – are elements whose content in the body in terms of dry mass is less than 0.00001%. These include silver (Ag), gold (Au), rad (Ra), and some elements from the group of microelements (according to different authors) (Gertig and Przysławski 2006), eg selenium, vanadium and strontium.

The aim of the article was EXPERIMENTAL IDENTIFICATION of sodium (Na), chlorine (Cl), calcium (Ca), sulfur (S) and iron (Fe), boron (B) and strontium (Sr) occurring in elevated concentrations in the source waters of Sanok District. It was necessary to experimentally demonstrate a high content of macroelements (Na, Cl, Ca, S), microelements (Fe, B) and ultra-trace element strontium (Sr) in the selected 6 sources.

The aim of the work was to characterize the above-mentioned bioelements in chemical terms, functions in the human body and the role and occurrence in groundwaters. In addition, it was recommended to present the results and interpretations of the analyzed source waters, including trace elements (bioelements) (selenium, molybdenum). The content of these elements in spring waters was determined by the most advanced analytical methods of modern chemistry.

## 2. Research area

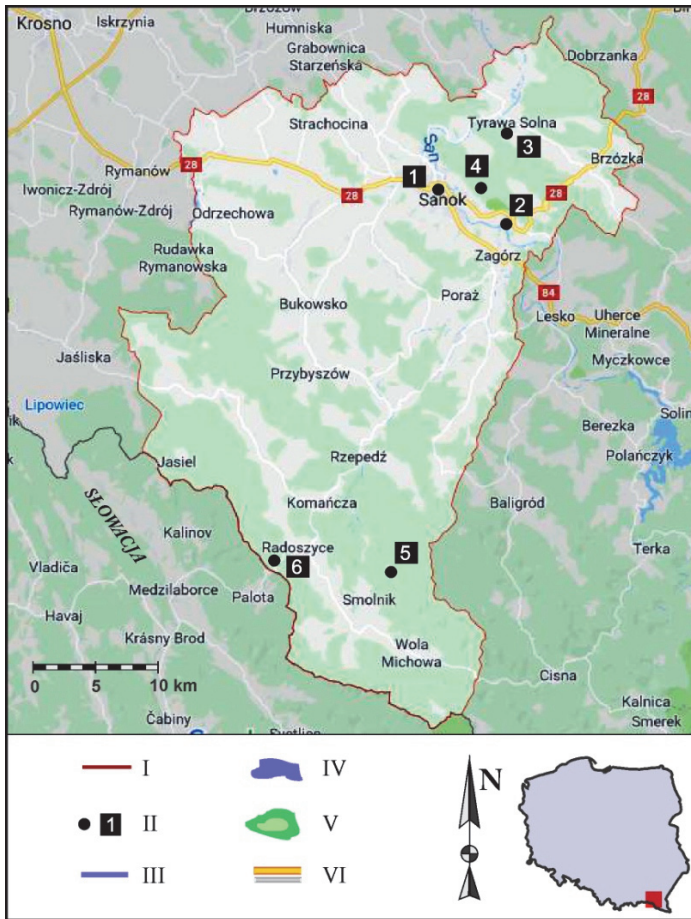
All researched sources occur in the Sanok Powiat, whose area in terms of geology and structure belongs to the outer (flysch) Carpathians. In addition, all sources are located on the border of the Eastern and Western Carpathians (Fig. 1).

The outer (flysch) Carpathians, which are the outermost unit of the Carpathians, are built of sedimentary rocks formed in the geosynclinal reservoir. These are different varieties of sandstone and slate; along with minor marls, keratoses and limestones. The lithological diversity of Jurassic-Cretaceous-Paleogene-Neogene sediments and the style of disturbances allow to distinguish external tectonic-facies units in the Carpathians: Magura, Dukla, Grybów, Pre-Magura, Silesia, Podlasie and Skole (Paczyński and Sadurski 2007). There are tectonic units in the Sanok Powiat: Silesia, Podlasie and Skolska (Międzybródź-Mrzygłód-Tyrawa Solna) (Rajchel 2016a).

In the region of the external Carpathians, there is considerable potential for the intake of mineralized waters, both deeper parts of flysch formations and their subsoil. These waters, often found in areas with physiographic conditions particularly favorable for the development of spa treatment, should be used as curative (Paczyński and Sadurski 2007).

The Jasielsko-Ustrzycki subregion also including the Sanok Powiat abounds in chloride, iodide and chloride-bicarbonate waters, iodide often accompanying oil deposits (Tyrawa Solna) (Rajchel 2016a). Such waters were encountered in a large number of oil wells, the largest of which are located in the anticlinal zones of the central Carpathian synclinorium (Porowski 2006). The

possibilities of using these waters for medicinal purposes, apart from three spas (Iwonicz Zdrój, Rymanów Zdrój, Polańczyk), are practically unlimited.



**Fig. 1.** Localisation of test points, I – the borders of the Sanocki powiat; II – test point with code number: 1 – Sanok Chopin source, 2 – Bykowce San, 3 – Tyrawa Solna, 4 – Liszna, 5 – Mików, 6 – Radoszyce; III – rivers, streams; IV – lakes, water reservoirs; V – forests; VI – national, local roads

Source: Author's own studies based on cartographic materials supplied by the Google maps

**Table 1.** Identification of the water sample

Place	Position Sample	Code	GPS N	GPS E	Altitude [m]	Water source	Minerals [mg.dm <sup>-3</sup> ]	Type of water
SANOK The Source of Chopin	1	PCH	49°33.765'	22°11.929'	329	spring	Calcium Ca > 150 Sod Na < 20	„Natural mineral water, containing calcium” „Natural mineral water, low-Sodium”
BYKOWCE SAN	2	BYK	49°32.180'	22°16.434'	293	spring	Iron Fe > 10	„Specific healing iron water”
TYRAWA SOLNA	3	TRS	49°36.280'	22°16.843'	274	spring	HBO <sub>2</sub> metabolic acid > 10 Sodium Na > 1000 Chlorine Cl > 2000 Calcium Ca > 150 Strontium Sr > 10	„Specific therapeutic boron water” „Natural mineral water, containing chloride sodium and calcium”
LISZNA	4	LIS	49°34.214'	22°14.753'	365	spring	Sulphides S <sup>2-</sup> > 3 Molybdenum Mo = 0.0005	„Specific curative sulphide water”
MIKÓW	5	MIK	49°17.311'	22°08.380'	546	spring	–	„Natural spring water from Bieszczady Mountains”
RADO- SZYCE	6	RAD	49°17.790'	22°01.554'	575	spring	General hardness. = 10° dH Low-mineral water < 500	„The Miraculous Spring” „soft water” „Natural spring water from Bieszczady Mountains”

In many locations, it is possible to utilize the already closed petroleum wells often requiring reconstruction. Drilling new holes, which can be successful, is recommended in points especially climatically suited for developing spa treatment in them (Paczyński and Sadurski 2007).

Of all the sources studied, four of them are located in Sanok, Bykowce, Tyrawa Solna and Liszna in the Sanok commune, while the other two flow out in Mików and Radoszyce belonging to the Komańcza commune (Table 1). None of the sources researched by the authors are currently used for economic or spa purposes.

### **3. Methodology**

An analysis of water from six sources from the eastern and southern parts of the Sanok powiat was conducted (Fig. 1). Each sample was marked with a three-letter code and a number of the station from which water was collected (1-6) was assigned. Geographical coordinates were determined for each position. The source that is at the place of religious cult was called „The Miraculous Spring” (Chowaniec 2007). Basic physico-chemical parameters of water samples were measured, ie pH, redox potential ORP (Oxidation Reduction Potential) oxidation-reduction potential (Horne and Goldman 1994), conductivity, EC (Electrical Conductivity), electroconductivity, temperature. There were portable instruments for measuring pH, ORP, EC potential and temperature (all quantities depend on temperature) (Łach 2011).

The "Macroelements" are included the determination results of calcium, magnesium, sodium and potassium using atomic absorption spectrometry (ASA) (Atomic Absorption Spectrometry) (Szczepaniak 2002). The "macro elements" also include phosphorus and sulfur, which were determined using ICP-OES (Inductively Coupled Plasma - Optical Emission Spectroscopy) optical inductively coupled plasma emission spectroscopy. In contrast, chlorine was analyzed argentometrically (PWSZ 2018).

Microelements (1 + 2), including iron, zinc, heavy metals, copper, chromium, nickel, manganese (Barycka and Skudlarski 2001) were determined using the ASA method. In addition, the amount of non-metals such as iodine, fluorine in the analyzed samples was determined using Ion Chromatography (Ion Chromatography) ion chromatography (fluorine WSSE 2019). Other non-metals, ie. silicon, boron and important element of molybdenum were analyzed using ICP-OES. It should be remembered that the information about "traces" at Microelements (1 + 2) refers to the criterion of the division of bioelements presented in the INTRODUCTION of this work. One should not confuse "trace" quantities of bioelements found in living organisms, with "trace" amounts of elements found in groundwater (spring). Boron and silicon, for example, are micronutrients present in trace amounts (< 0.01%) in organisms, whereas, in the studied groundwaters (source), their amount is considerable (even a dozen or so milligrams in cubic

decimeter). The same phenomenon applies to strontium (ultra-small elements). The ICP-OES method was designated for vanadium (ultra element).

As for the methodology, this can be seen two interesting cases. The first one concerns the analysis of strontium, which was carried out using the ICP-MS method (PETROGEO 2019). The second case is selenium analysis performed by three different methods (ASA, ICP-OES, ICP-MS), ICP-MS (Inductively Coupled Plasma) mass spectrometry with ionisation in inductively coupled plasma. Most often (this is not the rule) metals are determined using the ICP-OES method, and nonmetals using the ICP-MS method. This applies in particular to methods using plasma light sources (ICP) and fluorescent lamps that allow high-energy transitions, and thus excitation of non-metals. Therefore, the first of these methods is designated bar (metal). Strontium (ultra element) and bar occur in relatively large quantities after calcium and magnesium in groundwater. Therefore, the content of these elements was included in the calculation of the amount (sum) of cations [ $\text{mg} \cdot \text{dm}^{-3}$ ], in the investigated waters. The last cation from this table is the lithium already traditionally marked by the "plasma" method.

To prepare data for analysis of alkaline earth metals (calcium, magnesium) for water sample (6), the formula for calculating water hardness (Chorostyński and others 2018) was used:

$$\text{Two} = \sum_{i=1}^k c_i m_i$$

where:

Two – general hardness of water [ $\text{mmol} \cdot \text{dm}^{-3}$ ],

c – concentration of metal cation [ $\text{mg} \cdot \text{dm}^{-3}$ ],

m – multiplier of metal cation [ $\text{mmol} \cdot \text{mg}^{-1}$ ].

Ca multiplier =  $0.02495 \text{ mmol} \cdot \text{mg}^{-1}$

Mg multiplier =  $0.04114 \text{ mmol} \cdot \text{mg}^{-1}$

With the water hardness (6) expressed in millimols in cubic decimeter, it is easy to calculate the hardness of this water in German degrees ( $^{\circ} \text{dH}$ ) and determine the type of hardness based on tabular data eg soft water (Krause 1993).

When we have the silicon concentration in the tested samples, the concentration of orthosilicic acid can be calculated. Based on the boron content, the concentration of metaboric acid can be calculated.

Classical analysis of anions: chlorides – argentometry (PWSZ 2018), sulphates (VI) – turbidimetry (WSSE 2019), bicarbonates – alkacimetry (PWSZ 2018), allowed to calculate mineralization (cations + anions + undissociated substances) [ $\text{mg} \cdot \text{dm}^{-3}$ ] and specify its type.

#### 4. Results

The physicochemical parameter, measured using a pH meter, was the hydrogen ion exponent (pH). The reaction was determined for 6 spring waters (1-6), two waters showed an alkaline pH > 8 (3,4). At the source, the ORP parameter was measured for all tested waters, for two waters (2,4) it assumed a negative value, which indicates the reducing properties of these waters. Water (2) showed the potential of ORP (-110 mV) and water (4) (-123 mV). The electroconductive (EC) indicator (conductivity) in  $\mu\text{S} \cdot \text{cm}^{-1}$  was the highest for water (3) and it was  $\text{EC} > 5000$ , in other samples it did not exceed 950. In contrast, for water (6) it was the lowest ( $340 \mu\text{S} \cdot \text{cm}^{-1}$ ), which indicates low salinity (mineralization) (Table 2). Table 3 presents the determination results of alkali metals (sodium, potassium) and alkaline earth metals (calcium, magnesium). A significant amount of sodium had water (3), more than  $1000 \text{ mg} \cdot \text{dm}^{-3}$ , the same water contained calcium  $> 150 \text{ mg} \cdot \text{dm}^{-3}$ . Water (1) also shares this inequality for calcium. Table 3 contains the results of analyzes for phosphorus, chlorine and sulfur. Of these three non-metals, the most interesting result is the chlorine content in water (3), which exceeded  $2,000 \text{ mg} \cdot \text{dm}^{-3}$ . It should be remembered that Table 3 includes macroelements, i.e. those that occur in living organisms in large quantities, while one of the non-metals (phosphorus) in spring waters, as it results from the analysis, is less than  $0.10 \text{ mg} \cdot \text{dm}^{-3}$ . Similarly, very low sodium content was demonstrated in water (1) with high calcium content (Table 3).

Microelements 1 (bioelements found in trace amounts in living organisms) (Table 4) are metals (iron), heavy metals (zinc, copper) and non-metals (iodine, fluorine, silicon). An interesting fact is the content of iron in water (2) above  $10 \text{ mg} \cdot \text{dm}^{-3}$ . The quantities of other bioelements are standard for groundwater (zinc) and copper  $< 0.01 \text{ mg} \cdot \text{dm}^{-3}$ , iodine  $< 0.3 \text{ mg} \cdot \text{dm}^{-3}$ , fluorine  $< 0.1 \text{ mg} \cdot \text{dm}^{-3}$ . The silicon content is also average for spring waters and amounts to several or several mg.

Microelements 2 (bioelements found in trace amounts in living organisms) (Table 5), are metals (important biometal) molybdenum, heavy metals, chromium, nickel, manganese (noble metal) and nonmetal boron. The heavy metals chromium and nickel are found in the tested (source) waters in quantities lower than  $5 \mu\text{g} \cdot \text{dm}^{-3}$ . For water (2), the concentration of manganese exceeded  $1000 \mu\text{g} \cdot \text{dm}^{-3}$ , and the boron concentration for water (3) reached about  $3000 \mu\text{g} \cdot \text{dm}^{-3}$ . Molybdenum is a bio-element determined in the smallest quantities, below  $1 \mu\text{g} \cdot \text{dm}^{-3}$ , two waters (5, 6) showed the molybdenum concentration so low that the result ( $< \text{LOQ}$ ) was below the limit of quantification.



**Table 2.** Physicochemical parameters

Parameter	pH	±%	ORP	±%	conductivity EC	±%	Temperature
Unit	unitless	-	[mV]	-	[ $\mu\text{S}\cdot\text{cm}^{-1}$ ]	-	[°C]
Method	potentiometry	RSD	potentiometry	RSD	conductometry	RSD	Thermometer
Sample							
1	7.70	6.70	+131	4.10	920	3.50	9
2	7.55	4.20	-110	5.30	818	3.40	9
3	8.07	7.80	+170	6.80	5750	6.70	10
4	8.03	5.30	-123	4.70	820	4.20	15
5	7.72	6.10	+70	4.30	500	5.50	12
6	7.56	6.40	+60	4.80	340	3.10	10

% RSD – relative standard deviation expressed in percentage, significance level  $p = 0.95$   $n = 3$

**Table 3.** Macroelements

Element [ $\text{mg}\cdot\text{dm}^{-3}$ ]	Calcium	±%	Phosphorus	±%	Magnesium	±%	Sodium	±%	Chlorine	±%	Potassium	±%	Sulfur	±%
Method	ASA	RSD	ICP-OES	RSD	ASA	RSD	ASA	RSD	Argento- metry	RSD	ASA	RSD	ICP-OES	RSD
Sample														
1	154	2.7	0.07	4.2	7	1.1	2.3	2.6	9	6.4	0.6	1.2	51	4.8
2	106	3.2	0.02	4.6	24	2.4	11.8	1.3	16	5.2	0.5	2.8	0.3	5.7
3	195	2.4	0.08	5.3	31	3.6	1012.1	3.8	2025	8.4	17.0	3.4	5	4.2
4	89	1.3	0.03	2.7	10	2.5	65.0	2.4	34	5.7	2.2	1.4	20	1.3
5	73	4.7	0.01	5.4	21	3.4	8.7	1.7	6	4.2	0.7	1.3	6	3.8
6	63	1.2	0.04	5.6	4	2.5	8.4	1.8	5	6.8	1.3	1.8	4	2.8

**Table 4.** Microelements 1 (traces)

Element [mg·dm <sup>-3</sup> ]	Iron Fe	±%	Zinc Zn	Copper Cu	Iodine I	Fluorine F	Silicon Si	±%
Method	ASA	RSD	ASA	ASA	CHROMAT. ION.	CHROMAT. ION.	ICP- OES	RSD
Sample								
1	0.02	7.4	<0.01	<0.01	<0.3	<0.10	11.35	4.1
2	11.60	2.3	<0.01	<0.01	<0.3	<0.10	12.76	3.9
3	0.20	6.2	<0.01	<0.01	<0.3	<0.10	10.66	4.8
4	0.07	7.8	<0.01	<0.01	<0.3	<0.10	8.83	2.7
5	0.03	5.9	<0.01	<0.01	<0.3	<0.10	6.82	3.3
6	0.02	6.4	<0.01	<0.01	<0.3	<0.10	7.07	3.4

**Table 5.** Microelements 2 (traces)

Element [µg·dm <sup>-3</sup> ]	Chrome Cr	±%	Manganese Mn	Molybdenum Mo	±%	Boron B	±%	Nickel Ni
Method	ASA	RSD	ASA	ICP- OES	RSD	ICP- OES	RSD	ASA
Sample								
1	<5	-	<10	0.32	4.3	51	2.2	<5
2	<5	7.2	1120	0.24	5.4	18	1.7	<5
3	<5	3.8	50	0.35	3.2	2921	2.8	<5
4	<5	4.1	30	0.50	3.7	766	1.2	<5
5	<5	-	<10	<LOQ	-	18	2.4	<5
6	<5	-	<10	<LOQ	-	24	5.8	<5

< LOQ – result below the limit of quantification

Table 6 includes selected ultra-elements, which include selenium, vanadium and strontium. Strontium is present in relatively large quantities in spring waters just after calcium and magnesium (Table 7). The concentration of strontium in water (3) exceeded  $10 \text{ mg} \cdot \text{dm}^{-3}$ . For comparison purposes, three selenium analyzes in all samples were carried out using three different analytical methods to increase the accuracy and precision of the assay. The highest concentration of selenium did not exceed  $20 \text{ } \mu\text{g} \cdot \text{dm}^{-3}$ . Vanadium is an ultra-element found in organisms in the amount of 10-5% (on a dry weight basis). The same element was marked in source waters (2-5) in the amount of  $1.5 \cdot 10^{-5} \text{ g} \cdot \text{dm}^{-3}$ . The two tested waters (1, 6) had a vanadium concentration below the limit of quantification ( $< \text{LOQ}$ ).

Table 7 contains minerals already discussed earlier, with the exception of barium, which together with magnesium and strontium (the same group of the periodic table) is worth determining in underground (spring) water. Barium concentration in certain groundwaters may exceed  $1 \text{ mg} \cdot \text{dm}^{-3}$ . This happened in the case of tested water (3), for which  $[\text{Ba}^{2+}] > 3 \text{ mg} \cdot \text{dm}^{-3}$ . Lithium concentration, similarly to the barium concentration, for the same water tested (3) exceeded  $1 \text{ mg} \cdot \text{dm}^{-3}$ . Table 7 includes the sum of cations expressed in  $\text{mg} \cdot \text{dm}^{-3}$ .

Table 8 contains minerals, which include anions found in spring waters.

The following anions were determined: chlorides, sulphates (VI) and bicarbonates (Table 8). The concentration of these ions is average as for groundwater, with two exceptions: water (3) contains chlorides in the amount of more than  $2,000 \text{ mg} \cdot \text{dm}^{-3}$  (already mentioned in the discussion of table 3), the second exception is related to the concentration of bicarbonates in water (6), which is smaller than  $220 \text{ mg} \cdot \text{dm}^{-3}$ . The concentration of bicarbonates has a significant influence on the size of mineralization. In Table 8 based on the amount of silicon and boron, the calculated concentrations of undissociated substances, including orthosilicic acid  $\text{H}_2\text{SiO}_3$  and  $\text{HBO}_2$  metaboric acid, are also included. Summing up the number of cations (Table 7), anions and undissociated substances (Table 8) for the analyzed spring waters (1-6), the mineralization (Table 8) was calculated in  $\text{mg} \cdot \text{dm}^{-3}$ . Mineralization for water (3) looks very impressive, almost  $3.7 \text{ g} \cdot \text{dm}^{-3}$ , while water (6) has a very low mineralization equal to  $330 \text{ mg} \cdot \text{dm}^{-3}$ . Also noteworthy is a high level of the mentioned metaboric acid, which exceeded  $10 \text{ mg} \cdot \text{dm}^{-3}$  in water (3).

It is worth adding that for all results excluding inequality ( $<$ ), also excluding measurements below the limit of quantification ( $< \text{LOQ}$ ) (Limit of Quantification), for  $n = 3$  and the level of significance  $p = 0.95$  was given relative standard deviation expressed as a percentage (% RSD) (Relative Standard Deviations).

**Table 6.** Ultra-elements (selected)

Element [ $\mu\text{g}\cdot\text{dm}^{-3}$ ]	Selenium Se	Selenium Se	Selenium Se	Selenium Se	Vanadium V	$\pm\%$	Strontium Sr	$\pm\%$
Method	ASA	ICP-OES	ICP-MS	ICP-OES	ICP-OES	RSD	ICP-MS	RSD
Sample								
1	<3	<20	<5	<LOQ		-	600	2.3
2	<3	<20	<5	12		6.4	330	1.6
3	<3	<20	<5	16		5.7	10200	4.2
4	<3	<20	<5	3		7.1	596	1.4
5	<3	<20	<5	14		8.4	179	2.7
6	<3	<20	<5	<LOQ		-	432	1.4

< LOQ – result below the limit of quantification.

**Table 7.** Minerals (cations)

Minerals [ $\text{mg}\cdot\text{dm}^{-3}$ ]	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Sr <sup>2+</sup>	Fe <sup>2+</sup>	Mn <sup>2+</sup>	Ba <sup>2+</sup>	$\pm\%$	Li <sup>+</sup>	$\pm\%$	Cations
Method	ASA	ASA	ASA	ASA	ICP-MS	ASA	ASA	ICP-OES	RSD	ICP-OES	RSD	Total amount
Sample												
1	2.3	0.6	154	7	0.60	0.02	0.01	0.058	4.2	0.009	5.8	164.6
2	11.8	0.5	106	24	0.33	11.60	1.12	0.446	2.1	0.004	6.3	155.8
3	1012.1	17.0	195	31	10.20	0.20	0.05	3.238	1.5	1.150	5.1	1270.0
4	65.0	2.2	89	10	0.59	0.07	0.03	0.041	3.8	0.023	5.7	167.0
5	8.7	0.7	73	21	0.18	0.03	0.01	0.096	4.2	0.004	4.2	103.7
6	8.4	1.3	63	4	0.43	0.02	0.01	0.086	3.7	0.005	6.4	77.2

**Table 8.** Minerals - anions, undissociated substances, mineralization

Minerals [mg·dm <sup>-3</sup> ]	Cl <sup>-</sup>		SO <sub>4</sub> <sup>2-</sup>		HCO <sub>3</sub> <sup>-</sup>		±%		Anions		H <sub>2</sub> SiO <sub>3</sub> calculated		HBO <sub>2</sub> calculated		Undissociated		Mineralization Kt+An		Type of mineralization	
	Method	Argentometry	Turbidimetry	RSD	Acid-base titration	RSD	Total	ICP- OES	ICP- OES	Total amount	Total	ICP- OES	ICP- OES	Total	Total amount	-				
1		9	147	7.9	451	5.2	607	31.52	0.20	803	31.72	803	moderately mineralized							
2		16	1	10.2	573	4.9	590	35.43	0.07	781	35.50	781	moderately mineralized							
3		2025	13	8.1	342	2.1	2380	29.60	11.83	3691	41.43	3691	highly mineralized							
4		34	48	8.4	434	4.3	516	24.52	3.10	711	27.62	711	moderately mineralized							
5		6	19	6.5	329	5.3	354	18.94	0.08	477	19.02	477	low mineralized							
6		5	10	9.3	219	6.8	234	19.63	0.10	330	19.73	330	low mineralized							

## 5. Discussion

This chapter is a thorough data analysis contained in the Results. Two waters (3, 4) showed slightly alkaline  $\text{pH} > 8$  (Table 2). The reason for this is the presence of a large amount of sodium in water (3) (Table 3) (alkali metal), whereas water (4) is sulphide water. Sulfides (hydrosulfides) of alkali metals, e.g. sodium in water (4) ( $65 \text{ mg} \cdot \text{dm}^{-3} \text{ Na}$ , Table 3) dissociate to form  $\text{HS}^-$  and  $\text{S}^{2-}$  ions. In turn, the replaced ions are hydrolyzed, resulting in the formation of hydrogen sulphide (the smell of rotten eggs) and hydroxyl ions  $\text{HS}^- + \text{H}_2\text{O} = \text{H}_2\text{S} + \text{OH}^-$ , which give the water a basic reaction. All sulphide waters are slightly alkaline (Chorostyński et al. 2018). Hydrogen sulfide, on the other hand, is a highly toxic gas and its vapors, which are released in high concentrations, can be a deadly threat to humans (Cykowska et al. 2013, Patniak 2007, Standard Methods 1998). The form in which sulfide compounds occur depends on the pH of the environment. At  $\text{pH} < 6$  the form of undissociated  $\text{H}_2\text{S}$  prevails, in the range of  $6 < \text{pH} < 8$  there are mainly  $\text{HS}^-$  bis hydrosulfite ions, and at  $\text{pH} > 8$  (water 4) the dominant form is  $\text{S}^{2-}$  sulphide ions (Hermanowicz et al. 1999, Cykowska et al. 2013). Natural sulphide spring waters with the right content of divalent sulfur are healing (spa) waters. The same applies to slightly alkaline waters (waters 3, 4) having the properties of alkaline water. Thanks to this, they have pro-health features (Chorostyński and others 2018).

The source (4) "On a Waterfall" is located next to the road from Olchowce to Liszna in the area of the Słonne Mountains Nature Park. The outflowing water is a type  $\text{HCO}_3^- - \text{Cl}^- - \text{Ca} - \text{Na} + \text{H}_2\text{S}$  with the mineralisation of  $0.7 \text{ g} \cdot \text{dm}^{-3}$  and  $\text{H}_2\text{S}$  content of  $3.8 \text{ mg} \cdot \text{dm}^{-3}$  (Rajchel 2016b). In the case of sulphidic waters, the water has the characteristics of „specific sulphurous medicinal water” if the content of sulphides (divalent sulfur) exceeds  $1 \text{ mg} \cdot \text{dm}^{-3}$  (pharmacodynamic factors - introduction) (Rozporządzenie 2016, Michalski 2006). Based on the literature (Rajchel 2016b), water (4) with a divalent sulfur content of  $3.8 \text{ mg} \cdot \text{dm}^{-3}$  is „specific sulphide medicinal” water.

Water (2) had ORP potential ( $-110 \text{ mV}$ ) and water (4) ( $-123 \text{ mV}$ ). The negative redox potential indicates the reducing properties of these waters. Water (2) is rich in iron (II)  $\text{Fe}^{2+}$  ions (which quickly oxidize to  $\text{Fe}^{3+}$  ions after water flows to the surface).  $\text{Fe}^{2+}$  ions have (Łach 2010) reducing properties (because they can be oxidized). Water (4) is sulphide water with the content of  $\text{S}^{2-}$  ions, which can oxidize, among others, to sulfur  $\text{S}^0$ , thanks to which  $\text{S}^{2-}$  ions have reducing properties. The reducing properties cause the negative ORP potential of the tested water. Water with a negative potential is an antioxidant that destroys free radicals and prevents the aging process. Water with a low redox oxidation potential (Horne and Goldman 1994, Suslow 2004) has health benefits.

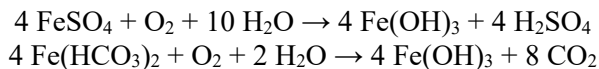
The high electroconductive index (conductivity), which for water (3) was  $EC > 5000 \mu\text{S} \cdot \text{cm}^{-1}$ , indicates high salinity of this water (high mineralization). Conversely, in the case of water (6), low conductivity ( $340 \mu\text{S} \cdot \text{cm}^{-1}$ ), this water has low mineralization. Two indicators point out mineralization of spring waters. Firstly, conductivity, secondly, mineralization calculated as the sum of cations, anions and undissociated substances. In experimental data (with correct results), there should be a high correlation between these two indicators. The EC index is often used to quickly assess the salinity of water (table 2).

In Table 3, a high concentration of two macroelements, sodium ( $> 1000 \text{mg} \cdot \text{dm}^{-3}$ ) and chlorine ( $> 2,000 \text{mg} \cdot \text{dm}^{-3}$ ) is interesting, which informs about „natural mineral water with sodium chloride content” ( $\text{NaCl} > 1000 \text{mg} \cdot \text{dm}^{-3}$ ). The same water (3) contains a large amount of calcium ( $> 150 \text{mg} \cdot \text{dm}^{-3}$ ), so it is „natural mineral water with calcium content” (Rozporządzenie 2011, Michalski 2006).

It is worth paying attention to water (1). In this water, the amount of calcium exceeded  $150 \text{mg} \cdot \text{dm}^{-3}$ , which makes this water „natural mineral water with calcium content”. At the same time, this water has extremely low sodium content (Table 3), with relatively high mineralization. It is medium-mineralized water with a total mineralization exceeding  $500 \text{mg} \cdot \text{dm}^{-3}$  (Table 8). As far as mineralization is concerned, the current valid classification of natural mineral waters is according to dissolved minerals. Low-mineralized water - below  $500 \text{mg} \cdot \text{dm}^{-3}$ , medium- mineralized water - from  $500$  to  $1500 \text{mg} \cdot \text{dm}^{-3}$ , high-mineralized water - above  $1500 \text{mg} \cdot \text{dm}^{-3}$ .

The aforementioned water (1) meets the conditions (low sodium content, average mineralization) of "natural low-sodium mineral water" (Rozporządzenie 2011, Michalski 2006, Tchorzewska-Cieślak and Rak 2005, Tchorzewska-Cieślak and Rak 2006). Water (1) contains sodium in the amount of  $< 20 \text{mg} \cdot \text{dm}^{-3}$ .

Iron was classified to microelements 1 (Table 4). Its quantity is high and exceeds  $10 \text{mg} \cdot \text{dm}^{-3}$ , water (2). Iron in groundwater usually occurs in the form of bicarbonate and iron (II) sulfate (IV) –  $\text{Fe}(\text{HCO}_3)_2$ ,  $\text{FeSO}_4$  (Kowal and Świdarska-Bróż 2000). Consequently, in underground waters, it occurs exclusively as an  $\text{Fe}^{2+}$  ion. Only the outflow of water to the surface and contact with atmospheric oxygen causes the oxidation of iron (II) compounds to iron (III) compounds and the precipitation of colloidal iron (III) hydroxide (Kowal and Świdarska-Bróż 2000).



As shown in Table 4 (iron content) and Table 8 (content of bicarbonates and other anions), spring water (2) contains almost exclusively iron (II) bicarbonate. The analysis was carried out in a short time after taking a sample of water

from the source, it can be assumed that  $\text{Fe}^{2+}$  ion was determined (speciation analysis), not general iron. Generally, in acidic waters with low Eh (ORP) value (in our case -110 mV, water (2), table 2 iron content is higher than in waters with higher pH and Eh (ORP).) Chemistry of iron compounds is exceptionally sensitive to changes in pH and Eh (Kowal and Świdorska-Bróz 2000, Łach 2010). The reason for this is that iron has the ability to change the degree of oxidation (electron binding) (Kuras et al., 2015, Ponka 1999). In spring water (2) over  $10 \text{ mg} \cdot \text{dm}^{-3}$ , we can talk about "specific ferruginous water" (pharmacodynamic factors - introduction) (Rozporządzenie 2016, Michalski 2006).

The symptom of insufficient iron supply is anemia, which is manifested by a decrease in hemoglobin (Sułek 2003). The effect of its excess in the body may be: reduced absorption of other minerals (mainly zinc and copper), susceptibility to infection, deposition of iron in tissues, increased production of free radicals leading to an increased risk of cancer and coronary disease (Shander and Sazama 2010, Kuras and others 2015). The excess of iron in the body is demonstrated by, among others significantly elevated serum ferritin and a dramatic increase in free iron in the blood (Cook et al 1992).

Manganese has been included in Microelements 2, concentration of which in the tested water (2) exceeded  $1 \text{ mg} \cdot \text{dm}^{-3}$  (Table 5). Manganese, unlike heavy metals such as lead or cadmium, is an element necessary for the proper functioning of the body. Due to the fact that manganese ions are involved in many processes in the body, over the years it was thought that even excess of them does not result in adverse changes in the body (Gać et al., 2009). For this reason, manganese and its compounds have found a wide application in many industries. Consequently, in recent years, the concentration of manganese ions (II) has risen multiple times in the atmosphere, drinking water and food (Burgoa 2001). Chronic poisoning is the most characteristic for manganese. Symptoms similar to Parkinson's disease increase gradually and appear after a dozen of years (less often after a few years) of contact with manganese (Gać et al. 2009).

The concentration of boron in water (3) reached the value of about  $3 \text{ mg} \cdot \text{dm}^{-3}$  (table 5). This value is easily converted into the amount of  $\text{HBO}_2$  metaboric acid (Table 8) (undissociated substance). The calculated  $\text{HBO}_2$  acid in water (3) exceeded the concentration of  $10 \text{ mg} \cdot \text{dm}^{-3}$ . Based on pharmacodynamic indices, it can be assumed that water (3) is „specific therapeutic boric” water, because  $\text{HBO}_2$  concentration is higher by  $5 \text{ mg} \cdot \text{dm}^{-3}$  (Rozporządzenie 2016, Michalski 2006). At this point, it is worth paying attention to water (3). As previously shown, this water is „natural mineral water with a high content of sodium chloride” (saline), which (NaCl) can be recovered from this water in an economic manner, as discussed in historical papers (Chapter 2. Research area). Other chemical compounds have much greater economic significance for this type of water. And so in this water



there is an increased amount of boron ( $\text{HBO}_2 > 10 \text{ mg} \cdot \text{dm}^{-3}$ ) (Table 8), strontium ( $> 10 \text{ mg} \cdot \text{dm}^{-3}$ ), barium ( $> 3 \text{ mg} \cdot \text{dm}^{-3}$ ), lithium ( $> 1 \text{ mg} \cdot \text{dm}^{-3}$ ) (Table 7). This view is also supported by the literature, according to which the brines also often contain significant amounts of elements valuable from an economic point of view, such as iodine, bromine, magnesium, boron, potassium and lithium (Paczyński and Płochniewski 1996).

Boron – a chemical element with an atomic number of 5, halfmetal from p- block of the periodic table. Boron chemically resembles silicon and carbon, because it forms boranes – analogs of hydrocarbons and silicas. The reaction of boron with hot concentrated nitric acid (V) leads to the formation of boric acid  $\text{H}_3\text{BO}_3$ . Boron forms complexes with polyhydric alcohols. The reaction of boric acid with mannitol is one of the methods for determining the boron content in the sample. Boron inorganic chemistry is sometimes described as the most complex of all elements (Greenwood and Earnshaw 1984). It most often takes oxidation state (III) (Pradyot Patnaik 2003). In the vast majority of compounds, it is three-bonded, and has the ability to form compounds with multi-center bonds (Greenwood and Earnshaw 1984) (one example is diborane,  $\text{B}_2\text{H}_6$  containing three-membered electron binding B-H-B). A large number of its compounds are known, especially metal borides (Greenwood and Earnshaw 1984). Boron accumulates in the bones and nervous system, interacts with calcium (Enghag 2004). In plants, it is a component of cell walls. It takes part in the metabolism of nucleic acids.

Molybdenum is a very important bioelement (Table 5), but its quantity in spring waters is very small, below  $1 \mu\text{g} \cdot \text{dm}^{-3}$ . Although it is worth writing something more about it.

Molybdenum is a silvery-white metal, hard, conducts heat well as well as electricity. It has a very high melting point of  $2620^\circ \text{C}$ . This metal is often an addition to high-grade special steel. It increases its hardness and durability. The degree of oxidation  $+6$  in the case of molybdenum compounds is the most durable oxidation. Molybdenum forms a durable  $\text{MoO}_3$  trioxide, white in cold and yellow in hot conditions. It does not dissolve in water and diluted acids, but dissolves in alkali. Phosphoromolybdate ammonium  $(\text{NH}_4)_3\text{H}_4[\text{P}(\text{Mo}_2\text{O}_7)_6]$  precipitates as a characteristic yellow precipitate under the influence of ammonium molybdate from solutions of phosphoric acid (V) with acidified nitric acid (V) (Bielański 2012).

There are between 9 and 16 mg of molybdenum in the human body. The necessity of this element is determined by the fact that it is a component of xanthine oxidase. Molybdenum in higher concentration occurs in the liver, kidneys, adrenal cortex and bone tissue. The role of molybdenum in the body is associated with its participation in enzymes that catalyze the oxidative hydroxylation reaction. Symptoms of molybdenum deficiency include: tachycardia, headache,

vomiting, twilight blindness. The recommended daily intake is set at 75-250 µg (Gertig and Przysławski 2006).

Table 6 contains ultraelements. They include silver, gold, radium, mercury, but also some of the microelements such as selenium, vanadium and strontium. Strontium belongs to ultraelements because it is found in very small amounts in living organisms. Therefore, its impact on living organisms has not yet been tested. In this study, we will focus exclusively on strontium chemistry. Strontium, in contrast to organisms in groundwater (spring), including also tested waters (1-6), occurs in relatively large quantities, just after calcium and magnesium. In spas, the amount of strontium in the water is always given. Strontium is an element that has been determined in water (3) in an amount of more than  $10 \text{ mg} \cdot \text{dm}^{-3}$ .

Stront – a chemical element from the group of beryllium in the periodic table. Strontium is a silvery-gray metal, similar to calcium, but more soft. On its surface, as in the case of aluminum, a protective oxide layer (passivation) is formed. Strontium forms oxides, hydroxides, fluorides and other salts of inorganic and organic acids.  $\text{Sr}^{2+}$  cations belong to the 4th analytical group and stain the flame with crimson red. Strontium is generally more chemically active than magnesium and calcium, less active than bar (MacMillan et al., 2000).

Selenium is one of the most well-known and popularized bioelements. Selenium is a microelement, but is often classified in the group of ultraelements. Such classification is very accurate, because this element (bioelement) occurs in minimal amounts both in living organisms (ultratrace element) and in minimal amounts in groundwater (source) (trace element). In all tested waters (1-6), selenium was determined by three different methods. No method gave a result higher than  $20 \text{ µg} \cdot \text{dm}^{-3}$ . The range (spread) of the results obtained was relatively small and took values of  $3 \text{ µg} \cdot \text{dm}^{-3}$ ,  $5 \text{ µg} \cdot \text{dm}^{-3}$ ,  $20 \text{ µg} \cdot \text{dm}^{-3}$ . In this case, it is not possible to calculate statistically whether the differences between the results of the different methods are significant or not, because for these results relative standard deviations were not assigned due to the fact that the obtained results are inequalities (the analysis was carried out on the limit of quantification of this element with given analytical method). Selenium, as already mentioned, occurs in minimal amounts both in living organisms and in spring (underground) waters. However, as with molybdenum, its role and importance on the functioning of the human body are so significant that it is worth paying some attention to this element.

The content of selenium in the Earth's crust is very small,  $5 \cdot 10^{-6}\%$ . Selenium is a pollutant of sulfur ores, it is an important product for the production of photocells and rectifiers. It is also used for coloring glass in ruby-red color. Selenium forms several crystalline varieties, similarly to sulfur, it can form eight atomic ring molecules. After heating, it is burned to give  $\text{SeO}_2$  (selenium dioxide) (Bielański 2012). The content of selenium in the human body ranges from 13 to

20 mg. Selenium is a component of four isoenzymes of glutathione peroxidase, indirectly also participates in fatty acid metabolism, affects the synthesis of thyroid hormones. It is a component of P, G, W selenoproteins, which play an important role in the antioxidative protection of the body. Yeast contains the most selenium. A good source of this element are also cereal products. The maximum, safe daily dose of selenium is 450  $\mu\text{g}$  a day, while the toxic dose is 700  $\mu\text{g}$  a day (Gertig and Przysławski 2006).

Selenium in geochemical terms is close to sulfur. However, it is found in the earth's crust in smaller quantities, it has extremely high dispersion. In groundwater, the migration of selenium, just like sulfur, depends on the redox conditions, the pH of the water and the activity of microorganisms. At low redox potential, the water is sulphide brine. The basic form in which selenium migrates in groundwater with the Ph similar to neutral, is  $\text{SeO}_4^{2-}$  anion. In waters with low oxidation potential characteristic for the zone of impeded water exchange, selenium usually migrates in the form of  $\text{HSe}^-$  ion. Under natural conditions in groundwater of moderate climate selenium occurs in small amounts not usually exceeding 2  $\mu\text{g} \cdot \text{dm}^{-3}$  (Macioszczyk and Dobrzyński 2002).

In Table 8, minerals were classified, including the following anions: chlorides, sulphates (VI) and bicarbonates. Table 8 also contains the content of the calculated orthosilicic acid, the amount of which was in the range of 18-35  $\text{mg} \cdot \text{dm}^{-3}$ . The amount is within the limits of the average  $\text{H}_2\text{SiO}_3$  content in groundwater (spring). However, anion analysis was performed to calculate (determine) mineralization in  $\text{mg} \cdot \text{dm}^{-3}$  and determine its type. The results are rather interesting - water (3) is highly mineralized with a mineralization of almost 3.7  $\text{g} \cdot \text{dm}^{-3}$ , whereas water (6) is low mineralized water with a 330  $\text{mg} \cdot \text{dm}^{-3}$  mineralization. Water (6) is water from the "deep" Bieszczady, one could expect a certain amount of interesting minerals. Interestingly, „Wonderful Spring” water (6) practically does not contain „minerals”, but it is, according to the definition (Introduction) (Tchórzewska-Cieślak and Rak 2005, Tchórzewska-Cieślak and Rak 2006), „natural spring water” which „does not differ in properties and mineral composition from water intended for human consumption”.

Water (6) may be interesting from another point of view. Using the formula for general hardness (Methods), on the basis of calcium and magnesium content, you can calculate the hardness of this water in German degrees ( $^\circ$  dH) and compare with tabular values (Krause 1993). Water (6) is soft water and its general hardness oscillates around 10  $^\circ$  dH. Such water does not form sedimentation during cooking, it is „crystalline” water. This property may explain the fact that tourists and the locals, taking water from the „Miracle Spring”, praise the water for the fact that you can make a very good, tasty tea.

In addition, to maintain objectivity, it should be added that too low general hardness of water may also be undesirable. It was observed that too soft waters (below 5.6 degrees German ° dH) are harmful to humans; they increase the incidence of heart disease.

The reliability of this study is evidenced by the fact that for water (4) (Natural Monument) mineralization was determined (calculated), which according to the authors is  $711 \text{ mg} \cdot \text{dm}^{-3}$  ( $> 0.7 \text{ g} \cdot \text{dm}^{-3}$ ), whereas the already quoted literary position (Rajchel 2016b) informs that the above-mentioned water contains sulphides in the amount of  $3.8 \text{ mg} \cdot \text{dm}^{-3}$  and has a mineralization above  $0.7 \text{ g} \cdot \text{dm}^{-3}$ .

Critically approaching the publication, it should be added that the study does not include such issues as: bacteriological analysis of the discussed source waters, the efficiency of individual sources and, what may sound absurd, measurement of natural radioactivity, because sources in the Podkarpacie region near Dukla (the Hermitage of St. John) show natural radioactivity. Water from several sources was examined in terms of the concentration for selected radioactive elements: radium – 226, radon and cesium – 137. Radium concentration – 226 in water from the Hermit Stream is almost six times higher than the norm for drinking water (Pociask-Karteczka and Rzeszutek 2007).

## **6. Conclusions**

- 1) Two waters (3, 4) showed slightly alkaline reaction ( $\text{pH} > 8$ ), which suggests their health-promoting properties.
- 2) Water (4) is „specific sulphuretic water” with a divalent sulfur content of  $3.8 \text{ mg} \cdot \text{dm}^{-3}$ .
- 3) Water (2, 4) is characterized by low ORP potential ( $< -100 \text{ mV}$ ), which makes them antioxidants „destroying free radicals,, (they prevent the aging process).
- 4) Water (3) is „natural mineral water with a content of sodium chloride” ( $\text{NaCl} > 1000 \text{ mg} \cdot \text{dm}^{-3}$ ) containing admixtures of economic importance: boron, strontium, bar, lit. In addition, the same water is „natural mineral water with calcium content” ( $> 150 \text{ mg} \cdot \text{dm}^{-3}$ ).
- 5) „Natural mineral water with calcium content” is also water (1). In addition, the water has a low sodium content ( $< 20 \text{ mg} \cdot \text{dm}^{-3}$ ), at the same time it is medium-mineralized water (a necessary condition), which makes it „natural low-sodium mineral water”.
- 6) „Healing specific iron water” (2) contains iron (II) in an amount above  $10 \text{ mg} \cdot \text{dm}^{-3}$  (pharmacodynamic factors), suitable for people with anemia.

- 7) Water (3) is „specific therapeutic boron water”, because the concentration of HBO<sub>2</sub> metaboric acid here is higher than 5 mg · dm<sup>-3</sup>. The appropriate level of boron is important for the bones and nervous system.
- 8) Two very important bioelements (selenium and molybdenum) for the body occur in spring waters in small quantities, smaller than 20 µg dm<sup>-3</sup> in the case of selenium and smaller than 1 µg · dm<sup>-3</sup> for molybdenum. These elements should be supplied with food or as a dietary supplement.
- 9) Strontium, which in water (3) has been determined in an amount exceeding 10 mg · dm<sup>-3</sup>, shows little demand in living organisms, and its supply from mineral waters is probably sufficient.
- 10) The analyzed spring waters (1-6) are low, medium and high-mineralized waters. Highly mineralized water (3) exceeded the amount of solids above 3.7 g · dm<sup>-3</sup>, while low mineralized water (6) (< 330 mg · dm<sup>-3</sup>) is recommended for tea.

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## Abstract

The analysis of underground (spring) waters concerned 6 springs located in the eastern part of the Sanok District on the border of the Eastern and Western Carpathians (analysis of bioelements). There have been detected „natural mineral waters with sodium chloride content” with chemical admixtures such as: boron ( $\text{HBO}_2 > 10 \text{ mg} \cdot \text{dm}^{-3}$ ) strontium ( $\text{Sr} > 10 \text{ mg} \cdot \text{dm}^{-3}$ ), barium ( $\text{Ba} > 3 \text{ mg} \cdot \text{dm}^{-3}$ ), Lithium ( $\text{Li} > 1 \text{ mg} \cdot \text{dm}^{-3}$ ), in a potential perspective of economic importance. The above-mentioned water from Tyrawa Solna, has a historical aspect, connected with salt-works, as signified by the name

of the village. The publicly available spring of Chopin from the Sanok park is characterized by „natural mineral water with calcium content” at the same time it is „low-sodium water” with a sodium content ( $< 3 \text{ mg} \cdot \text{dm}^{-3}$ ). The spring from Bykowiec near Sanok, has "specific healing iron water" with iron (II) content above  $10 \text{ mg} \cdot \text{dm}^{-3}$ , while the spring on the Olchowce-Liszna route called „Nad Wodospadem” („At the Waterfall”) (Nature Monument) is rich in "specific healing sulphide water" with a divalent sulphur content of  $3.8 \text{ mg} \cdot \text{dm}^{-3}$  (characteristic odour). The criterion of „specific boric therapeutic water” with  $\text{HBO}_2$  metaboric acid concentration higher than  $5 \text{ mg} \cdot \text{dm}^{-3}$  (pharmacodynamic factors) (Regulation of the Minister of Health) meets the already mentioned water from Tyrawa Solna. This water also contains large amounts of sodium potassium, calcium and magnesium, and its mineralization exceeded  $3500 \text{ mg} \cdot \text{dm}^{-3}$  (highly mineralized brine). On the border of the Eastern and Western Carpathians, moving south towards Slovakia, two sources were found in the Bieszczady Mountains (Mików, Radoszyce). Water from „Cudowne Źródło” („The Miraculous Spring”) in Radoszyce (surroundings) belongs to soft waters (hardness = 10 German degrees) and to low mineralized ones (mineralization  $< 500 \text{ mg} \cdot \text{dm}^{-3}$ ). Bioelements that are found in trace amounts in spring waters i.e. iodine  $< 0.3$  and fluorine  $< 0.1$  [ $\text{mg} \cdot \text{dm}^{-3}$ ] and selenium and vanadium  $< 20$ , zinc and copper  $< 10$ , chromium and nickel  $< 5$ , molybdenum  $< 1$  [ $\mu\text{g} \cdot \text{dm}^{-3}$ ] were also determined. Chemical analyses were performed using the following methods: AAS, ICP-OES, ICP-MS, IC, potentiometry (pH), conductometry (EC), ORP potential, turbidimetry, argentometry and acid-base titration. The influence on the functioning of the human body and some bioelements is described.

**Keywords:**

springs, bioelements, mineral waters, medical waters, trace analysis, AAS, ICP-OES, ICP-MS, IC

**Analiza biopierwiastków w wodach źródłanych Powiatu Sanok na granicy Karpat Wschodnich i Zachodnich oraz ich wpływ na funkcjonowanie organizmu człowieka**

**Streszczenie**

Analiza wód podziemnych (źródłanych) dotyczyła 6 źródeł zlokalizowanych we wschodniej części Powiatu Sanok na granicy Karpat Wschodnich i Zachodnich (analiza biopierwiastków). Wykryto „naturalne wody mineralne z zawartością chlorku sodu” z chemicznymi domieszkami: boru ( $\text{HBO}_2 > 10 \text{ mg} \cdot \text{dm}^{-3}$ ) strontu ( $\text{Sr} > 10 \text{ mg} \cdot \text{dm}^{-3}$ ), baru ( $\text{Ba} > 3 \text{ mg} \cdot \text{dm}^{-3}$ ), litu ( $\text{Li} > 1 \text{ mg} \cdot \text{dm}^{-3}$ ), w ewentualnej perspektywie o znaczeniu gospodarczym. Wymieniona woda z Tyrawy Solnej, posiada aspekt historyczny, związany z warzelnictwem soli, o czym świadczy również nazwa miejscowości. Ogólnodostępne źródło Chopina z parku sanockiego cechuje „naturalna woda mineralna z zawartością wapnia” jednocześnie jest to „woda niskosodowa” o zawartości sodu ( $< 3 \text{ mg} \cdot \text{dm}^{-3}$ ). Źródło z Bykowiec niedaleko Sanoka, posiada „wodę swoistą leczniczą żelazistą” o zawartości żelaza (II) powyżej  $10 \text{ mg} \cdot \text{dm}^{-3}$ , natomiast źródło na drodze Olchowce-Liszna „Nad Wodospadem” (Pomnik Przyrody) jest bogate w „wodę swoistą leczniczą siar-



czkową” o zawartości siarki dwuwartościowej  $3,8 \text{ mg} \cdot \text{dm}^{-3}$  (charakterystyczny zapach). Kryterium „wody swoistej leczniczej borowej” o stężeniu kwasu metaborowego  $\text{HBO}_2$  wyższym od  $5 \text{ mg} \cdot \text{dm}^{-3}$  (współczynniki farmakodynamiczne) (Rozporządzenie Ministra Zdrowia) spełnia już wspomniana woda z Tyrawy Solnej. Woda ta zawiera również duże ilości sodu potasu, wapnia i magnezu, a jej mineralizacja przekroczyła  $3500 \text{ mg} \cdot \text{dm}^{-3}$  (wysokozmineralizowana solanka). Na granicy Karpat Wschodnich i Zachodnich przemieszczając się na południe w kierunku Słowacji znaleziono w Bieszczadach dwa źródła (Mików, Radoszyce). Woda z „Cudownego Źródełka” w Radoszycach (okolice) należy do wód miękkich (twardość = 10 stopni niemieckich) oraz niskozmineralizowanych (mineralizacja  $< 500 \text{ mg} \cdot \text{dm}^{-3}$ ). Oznaczono również biopierwiastki, które występują w wodach źródłanych w ilościach śladowych tj. jod  $< 0,3$  i fluor  $< 0,1$  [ $\text{mg} \cdot \text{dm}^{-3}$ ] oraz selen i wanad  $< 20$ , cynk i miedź  $< 10$ , chrom i nikiel  $< 5$ , molibden  $< 1$  [ $\mu\text{g} \cdot \text{dm}^{-3}$ ]. Analizy chemiczne wykonano następującymi metodami: ASA, ICP-OES, ICP-MS, IC, potencjometria (pH), konduktometria (EC), potencjał ORP, turbidymetria, argentometria, alkacymetria. Opisano wpływ na funkcjonowanie organizmu człowieka, niektórych biopierwiastków.

**Słowa kluczowe:**

źródła, biopierwiastki, wody mineralne, wody lecznicze, analiza śladowa, ASA, ICP-OES, ICP-MS, IC