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PHYSICOCHEMICAL PARAMETERS AND BACTERIOLOGY OF MINERAL AND SULPHATE WATERS DISCOVERED AROUND SANOK AND LESKO, AND THE PROSPECTS FOR THEIR MEDICAL USE

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ABSTRACT

The study included water samples from 10 test points located in the northern parts of Sanok and Lesko counties. The following analytical methods have been used: AAS (FAAS, CVAAS, HGAAS), ICP-MS, ICP-OES, Ion chromatography, Acid-base titration, argentometry, turbidimetry and also bacteriological tests. Two sources were identified as "natural mineral hard medium-mineralised waters" with low iron content. Four sulphide springs have been found. The Lesko source can be characterized as "a specific therapeutic sulphide water" with a content of divalent sulphur, determined iodometrically, above 1 mg · dm^{-3} and without any bacteriological concerns. Water from Lesko, apart from small amounts of metaboric and orthosilicic acid, is slightly alkaline with a strong negative ORP potential (–230 mV), which makes it healthy (an antioxidant that eliminates free radicals). In all waters the presence of heavy metals, arsenic, lithium, iron, manganese, alkali metals and alkaline earth metals has been indicated. The influence on the human body of analytically marked substances has been described.

Keywords: spring waters, arsenic, heavy metals, balneology

INTRODUCTION

Bieszczady Mountains are part of Outer Eastern Carpathians, often referred to as Flysch Carpathians. Polish Flysch Carpathians abound in mineralized and specific waters, often with healing properties. Chloride, bicarbonate and iodide waters with a minaralisation of 0.2–2.2% are utilized for therapeutic purposes form springs and wells in the subregion between Jasło and Ustrzyki (Rymanów Zdrój, Iwonicz Zdrój, Polańczyk) (Paczyński and Sadurski 2007). Particularly noteworthy is the only spa resort in the Bieszczady Mountains – Polańczyk. According to Polish legislation, the word "zdrój" (meaning in Polish "spa" or "spring") can be added to the locality's name, within which administrative area a spa is located, only if therapeutic waters are the basis of spa treatment. The boreholes in Polańczyk contain bicarbonate-chloride-bromide and iodide (unexploited) waters. In 1999 the town was declared a health resort – a category given to a town with natural factors like mineral water and climate. Another condition for becoming a health resort are notable natural values. Mineral waters are used in therapeutic baths and drinking cures, and climate features are applied in climatotherapy (Gołębiewski 2002).

The locality in Bieszczady that could turn into a health resort founded on its water resources was Rabe near Baligród (Łach and Pasztyła 2013, Chorostyński et al. 2016). Unfortunately, tapped waters need to meet additional criteria, i.e. keep a constant chem-

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ical composition. Also, Rabe's water contains small amounts of arsenic. Whether arsenic can appear in healing waters is debatable, especially lately, because of the fact that there is only a slight difference between therapeutic and toxic concentration of arsenic – which can be carcinogenic.

The third locality that has the makings of a spa is Lesko. Lesko does not lie exactly in the Bieszczady Mountains, but rather at their gateway – more precisely, in the Eastern Carpathians. There are four sulfide sources (not all are active) in Lesko.

On the regional scale, sulphide sources are more valuable than the chloride-bicarbonate-iodide sources, and that is because the chloride sources are widespread (health resorts), while the sulphide sources are practically undiscovered, and in terms of treatment the latter grant the same as the former. It should be noted that sulphide waters are also available, although to a lesser extent, like for example, Jan's water in Rymanów Zdrój.

The reason for carrying out this research was to provide the experimental documentation of the chemical composition and the medical properties of not one, but several such sources in a small area. A comprehensive analysis of spring waters can at the same time uncover one or more groundwater outflows that qualify for being mineral water. For both mineral and healing waters have to observe the regulation of the Ministry of Health – an additional research must be performed.

It is obvious that the better the location, the possibilities of creating a spa are all the greater. The chances increased in the case of towns with already available partly-developed infrastructure.

The aim of the study was to locate an occurrence of (spring) mineral waters in the Sanok Basin and the Lesko Foothills, and to conduct a comprehensive research of their physicochemical composition and to assess the possibilities of their medical application.

MATERIALS AND METHODS

Research area

The environs of three towns: Sanok, Zagórze and Lesko, were the main area of exploration. The Sanok Basin is connected to three mesoregions: the Sanok-Turka Mountains from the east, Dynowskie Foothills from the north and the Bukowskie Foothills from the west and the south, and it should be included in the latter. The Lesko Foothills, which is situated between Osława and San, until now has not been acknowledged in the regional division of Poland. The humps of the foothill exceed 500 m in height. It cannot be included in neither the Western Bieszczady nor the Sanok-Turka Mountains, but due to the widely accepted macroregional division into Western and the South-East Carpathians along the valleys of San and Osława, the Lesko Foothills are part of the Eastern Carpathians, instead of the Bukowskie Foothills, although the geological structures and landscape types are similar (Kondracki 2002). Waters of arsenic-mercury mineralisation can be found in the Lesko area as well as to the south-east of the town (Kamieński 1937). The arsenic mineralisation in the Central Carpathians in the region of Baligród were studied for the first time in 1937. In the years 1954–1955 these areas were a subject to field and laboratory research (Ostrowicki 1958). Arsenic mineralization appears in lgota beds (Bystre, Rabe by Baligród) and in upper istebna beds (Rabe), which lie above lgota beds (Kita-Badak 1971). Anomalous concentrations of mercury and arsenic were detected in a zone of aeration of flysch sediments near Baligród (Jaworski 1979). The mineralisation of arsenic-mercury waters spreads up to Lesko (Kamieński 1937).

Methodology

The paper includes the analysis of samples from all the mineral water intakes located in the studied area (see: Fig. 1). The geographic coordinates of the research points in the area were determined, too (see: Table 1). Detailed research covered 10 sites, which were most often used as sources or intakes of groundwater, extracted with a manual pump. Sources located in sites of religious worship are called "miraculous sources" (Chowaniec 2007).

The observations also regarded sediment precipitation. Then, basic physicochemical indicators of water samples, i.e. pH, redox potential and temperature were tested. Due to arsenic-mercury mineralisation of the Lesko area, the concentration of seven heavy metals: zinc, cadmium, copper, lead, nickel, chromium and mercury was measured in all water samples. They were also analysed for the presence of arsenic, lithium and manganese. To determine the rate of general hardness and mineralisation, the concentration of sodium,

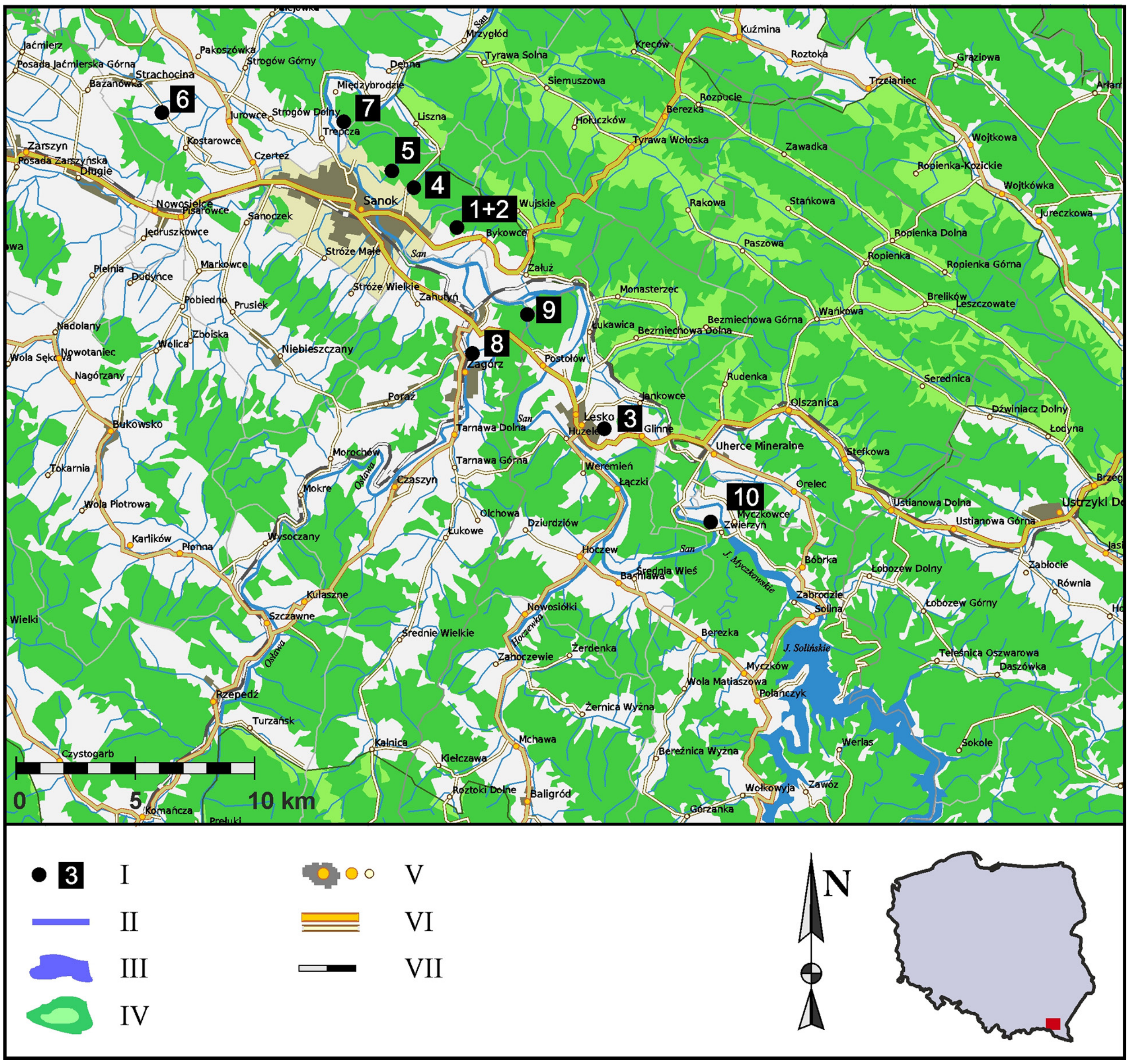

Fig. 1. Location of test points, I – test point with code number: 1 + 2 – Bykowce, 3 – Lesko, 4 – Olchowce, 5 – Sanok, 6 – Strachocina, 7 – Trepcza, 8 – Zagórz, 9 – Zasław, 10 – Zwierzyń; II – rivers, streams; III – lakes, water reservoirs; IV – forests; V – cities, towns; VI – national, local roads; VII – railway lines

Source: Author's own studies based on cartographic materials supplied by the State Forests

potassium, calcium and magnesium was recorded in the samples. Sulphide waters (1, 2, 3, 9), in which sulphides were detected by iodometric method, required bacteriological tests. In sulphide waters and in waters with the highest mineralisation (6, 7, 8) the concentration of carbon dioxide, and anions (bicarbonate, sulphates (VI), chlorides) were tested. Lesko waters (3) were subjected to additional quantitative analysis of following elements: metaboric acid, orthosilicic acid, fluorine, selenium, bromine, iodine (see: Fig. 1).

In Lesko there are both bicarbonate-calcium-magnesium and sulphide waters. Four sources (only one

Table 1. Identification of a research point

Parameter / Town/Place	Test point number	GPS N	GPS E	Position m a.s.l.	Outflow type	Type of sediment	Other qualities
Bykowce	1	49º32,970’	22º15,832’	323	spring	White	„pond”
Bykowce	2	49º32,976’	22º15,843’	323	spring	No sediment	
Lesko	3	49º28,380’	22º20,554’	373	spring	No sediment	
Olchowce	4	49º33,786’	22º14,130’	325	spring	No sediment	
Sanok	5	49º34,311’	22º13,554’	320	stream	No sediment	
Strachocina	6	49º35,824’	22º5,884’	313	well	No sediment	miraculous spring
Trepcza	7	49º35,279’	22º11,996’	288	spring	No sediment	
Zagórz	8	49º30,123’	22º15,861’	310	well	No sediment	
Zasław	9	49º31,089’	22º18,037’	314	spring	White	„pond”
Zwierzyń	10	49º26,146’	22º23,912’	349	spring	No sediment	miraculous spring

was tested) achieve a total capacity of 0.2 $m^3 \cdot h^{-1}$ (Paczyński and Sadurski 2007).

The content of heavy metals (see: Table 2), microelements (see: Table 3) and alkaline earth metals (see: Table 4) was determined using the Atomic Absorption Spectrometry (AAS) UNICAM SOLAAR 969 and THERMO SCIENTYFIC S4. For non-metal analysis an inductively coupled plasma mass spectrometry (ICP-MS) (PETROGEO 2015) and an inductively coupled plasma optical emission spectrometry (ICP-OES) (PETROGEO 2015) were used. The study included the determination of fluorine, sulphates (VI), chlorides, sulphides, bicarbonates ion through chromatography (WSSE 2015), turbidymetry (WSSE 2015), argentometry (WSSE 2015), iodometry, alkacimetry (WSSE 2015), respectively. Bacteriological test were also carried out (WSSE 2015), including for *Escherichia Coli*, bacteria of *Coli* group, Enterococcus and other bacteria. A portable device for measuring pH, ORP and temperature was available.

The formula for calculation of water hardness was used to develop data on the analysis of alkaline earth metals (calcium, magnesium):

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

where:

Two – general water hardness, $mmol \cdot dm^{-3}$,
c – concentration of metal cation, $mg \cdot dm^{-3}$,
m – multiplier of metal cation, $mmol \cdot mg^{-1}$.

The aim of research was to find water that met all the following (see: Tables 3, 4, 5) criteria:

- quotient Ca/Mg < 3 (relatively much magnesium),
- sum of Ca + Mg ≥ 3 $mmol \cdot dm^{-3}$,
- sum of cations > 120 $mg \cdot dm^{-3}$,
- sum of anions > 400 $mg \cdot dm^{-3}$,
- general hardness ≥ 20 German degrees (°dH),
- type of hardness – hard water,
- iron (Fe) content > 100 $\mu g \cdot dm^{-3}$ (0.1 $mg \cdot dm^{-3}$),
- mineralisation > 500 $mg \cdot dm^{-3}$,
- type of mineralisation – medium mineralisation.

All of these criteria are met by two water samples from Strachocina (6) and Zagórze (8).

Hydrogen sulphide H2S is a colourless gas with a strong, characteristic odour of “rotten eggs”. It is easy to recognise organoleptically, by taste and smell. The sensitivity of an organoleptic method is very high and comparable to sensitive instrumental methods. For this reason, detection of hydrogen sulphide or its salts – alkali metal sulphides – by smell (taste), is considered very reliable. This method has been used to select sulphide springs from 10 different intakes. It turned out that there are four sources of such water (1, 2, 3, 9). Also, sulphides were determined iodometrically in these waters (selection proved to be correct) (see: Tables 6, 7). These water samples were collected in three locations: (1, 2) – Bykowce, (3) – Lesko, (9) – Zasław (see: Table 1). These localities are situated at the Gate of Bieszczady Mountains (Lesko). In a relatively small area four of the studied sulphide sources were discovered, which on one hand may be related to the geological structure of the terrain, and on the other hand, it may be an attractive site for a health resort. Especially, when taken into consideration that two of the sulphide sources lie in Zasław, with only one tested (9), while in Lesko there are four suphide sources and here too only one was tested (3). In Bykowce there are two sulphide sources, both of which were tested (1, 2).

Taking into account the results of the indication of sulphides, sulphates(VI) and the total amount of sulphur, a relative error of sulphur indication has been calculated. In Table 7 the contents of various forms of sulphur were listed and converted into clean sulphur. The table includes three different research methods: iodometry (sulphides), turbidimetry (sulphates(VI)), an inductively coupled plasma mass spectrometry (ICP-MS) (pure sulphur). The comparison of an indication of different forms of sulphur using three methods (including two instrumental) with the maximum indication error amounting to 7.7% (the titration-iodometric method can introduce the biggest error) is considered satisfactory.

RESULTS AND DISCUSSION

Results

No trace concentrations of heavy metals were detected in the 10 tested samples, including mercury. Two samples (3, 10) from the vicinity of Lesko did not contain either mercury (above detection limit of 0.08 $\mu g \cdot dm^{-3}$) (see: Table 2) and arsenic (above the detection limit of the 0.3 $\mu g \cdot dm^{-3}$) (see: Table 3). None of the samples contained lithium, even not in the sample (6) from the vicinity of Wzdów, where its presence could have been expected. Two sources (1, 9), which formed a "pond", and also precipitated a white sediment, showed a concentration of manganese 50 $\mu g \cdot dm^{-3}$, giving the highest result for this element (see: Tables 1, 3). An elevated level of iron was registered, 220 $\mu g \cdot dm^{-3}$ in the sample (6), and 110 $\mu g \cdot dm^{-3}$ in sample (8) (see: Table 3) – these samples turned out to be "natural mineral hard medium-mineralised waters" (see: Tables 4, 5). Quantitative indication included sodium, potassium, calcium, magnesium in all waters in order to determine the hardness of water (calcium, magnesium – in German degree of hardness) (see: Table 4) and mineralisation (see: Table 5). The divalent sulphur was marked in four water samples (1, 2, 3, 9), of which the highest content of sulphide was found in the sample from Lesko (3), approximately 1.1 mg $S^{2-} \cdot dm^{-3}$. At the same time, this sample did not raise any concerns of bacteriological kind, like the sample (2), both were fit for consumption (see: Table 6). The measurement of hydrogen ion exponent for water from Lesko evaluated the reaction as pH = 7.70, and the potential as ORP –230 mV (see: Tables 6, 7), both were taken at 9°C. Water (3) contained

Table 2. The content of heavy metals

Metal / Sample	Unit	Zn Zinc	Cd Cadmium	Cu Copper	Pb Lead	Ni Nickel	Cr Chromium	Hg Mercury
1, 2, 3, 4, 5, 6, 7, 8, 9, 10 Traceability ASA	$\mu g \cdot dm^{-3}$	< 10	< 1	< 10	< 4	< 5	< 5	< 0,08
Norm according to Regulation by the Minister of Health	$\mu g \cdot dm^{-3}$	3000	5	2000	10	20	50	1

small amounts of orthosilicic and metaboric acid, without any bromides, iodides and selenium – only a trace of fluorine was found (see: Table 8).

Discussion

The most of heavy metals are toxic and their permissible rate is defined by the Regulation of Minister of Health (Rozporządzenie… 2010 and 2000). However, some traces of heavy metals, for example copper or chromium, are not only acceptable, but even desirable in healing waters. Regarding determination of heavy metals, the analysis of two samples drawn from the vicinity of Lesko (3, 10) – arsenic-mercury mineralization (see: Table 2), which showed lack of even trace amounts of arsenic and mercury in these (mineral) groundwaters was of particular significance. Probably the arsenic-mercury mineralization of groundwaters does not reach up to Lesko.

Presence of mercury in water is definitely inadvisable. Mercury is a heavy metal with a high toxicity, being a part of the so-called group of death metals (Cyran 2013). it is more complicated as to arsenic, because it is an undesirable component in drinking water, due to its toxic and carcinogenic properties (USNRC 2001, Toxicological 2007, Dobrzyński and Stępień 2009), whereby arsenic (III) demonstrates greater toxicity than arsenic (V). Currently, arsenic is being removed from the spa waters, so it meets the limits indicated by the Minister of Health, i.e. 10 $\mu g \cdot dm^{-3}$ for drinking water (Rozporządzenie... 2010) and up to 50 $\mu g \cdot dm^{-3}$ of arsenic (III + V) in water for drinking cures (Rozporządzenie... 2006). Typical amount of arsenic is 10––30 $\mu g \cdot dm^{-3}$ (Łach and Paształa 2013, Chorostyński et al. 2016). Presence of arsenic was indicated, a.o., in two samples (3, 10) (see: Table 3), for which there was a valid suspicion that traces of this element may be detected. Arsenic can be found in the spring waters in the Bieszczady Mountains in Bystre and Rabe to the south-east of Lesko.

The second element possibly present in the examined waters was lithium. There was some probability of detecting it in the sample (6). This sample was extracted from sites located to the west of Sanok, near Wzdów. The publications on soils of the region indicated a high (28.4 $mg \cdot kg^{-1}$ in 2000) content of lithium in soils, where the average level was 6 $mg \cdot kg^{-1}$ in light soils and 15 $mg \cdot kg^{-1}$ in heavier ones (Oleszek and Siebielec 2012). Water, through infiltration, should enrich itself in this element. Unfortunately, there is no literature on the content of lithium in groundwater in this region. The discussed element in large quantities shows toxic activity, but at low concentrations it helps to treat alcoholism, depression and neurosis.

The first reports of cases of chronic manganese poisoning were already described in the 80s of the 19th century, but it was not until recently that researchers drew attention to possible toxic effects of manganese compounds on an organism (Hundnell 1999). According to the present state of knowledge, chronic exposure to manganese compounds leads to symptoms similar to Parkinson's syndrome (Zawadzki et al. 2008). Manganese, unlike the other elements with toxic activity (e.g. lead or cadmium), is present physiologically in

Table 3. The content of microelements

Nr punktu badawczego / Element $\mu g \cdot dm^{-3}$	1	2	3	4	5	6	7	8	9	10
Fe (og) Iron	10	70	10	8	60	220	20	110	160	10
Mn (og) Manganese	50	10	30	10	13	10	10	10	50	10
As (og) Arsenic	< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	< 0,3	< 0,3
Li Lithium	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100

the organism and necessary for its proper functioning. Hypomanganemia primarily affects disorders of motor coordination, damage the osteoarticular system and cause osteoporosis (Zawadzki et al. 2008).

The maximum concentration of manganese in drinking water cannot exceed 50 µg · dm^{-3} (1, 9) as stated by the Minister of Health (Rozporządzenie… 2010). The permissible amount of iron in water fit for human consumption (Rozporządzenie…. 2010) is 200 µg · dm^{-3}. Iron was marked, among others, in two samples (6, 8) with the highest concentrations (see: Table 3). Iron takes part in oxidation processes – with its deficiency the level of hemoglobin in blood drops, causing anaemia.

Sodium, potassium, calcium and magnesium (see: Table 4) were recorded in 10 of the tested samples. Water hardness is a function of cations of calcium (Ca^{2+}), magnesium (Mg^{2+}) and optionally iron(II) (Fe^{2+}) and manganese(II) (Mn^{2+}) concentrations (Dardel and Arden 2005).

With the calcium and magnesium content in mg · dm^{-3}, water hardness was calculated in German degrees (°dH) (see: Table 4). As far as mineralisation is concerned, a new classification of natural mineral waters by a rate of dissolved minerals is currently in force (Rozporządzenie…. 2003). Low-mineralised waters – below 500 mg · dm^{-3}, medium-mineralised waters – from 500 to 1500 mg · dm^{-3}, high-mineralised waters – above 1500 mg · dm^{-3}. Two water sources were selected: from Strachocina (6) and Zagórze (8), because they met the criteria of hardness (above 20 German degrees) – hard waters (see: Table 4), and the criteria of mineralisation (above 500 mg · dm^{-3} of dissolved minerals) – medium-mineralised waters (see: Table 5).

In the area between Bykowce (1, 2), Lesko (3) and Zasław (9) eight sulphide sources were registered, four of which were analysed, especially the sample (3). The analysis proved two water sources (2, 3) out of four fit for consumption (no bacteriological concerns) (see: Table 6). Pharmacodynamic factors are applied for an assessment of the properties of therapeutic waters (Rozporządzenie... 2006). These coefficients are the minimum content of selected chemical components (the so-called specific components) or the minimum value of physical properties of water that cause their therapeutic effect (Michalski 2006). In the case of sulphide waters, if the content of sulphides (divalent sulphur) marked iodometrically (Minczewski and Marczenko 1978) exceeds 1 mg · dm^{-3}, they can be regarded as therapeutic waters. Out of the two sulphide waters (2, 3) only the sample from Lesko (3) meets this condition. The sulphide content in this source is approximately 1.1 mg S^{2-} · dm^{-3}.

This brings up the question, in what form divalent sulphur (hydrogen sulphide) actually occurs in water. Apparently, it depends on the pH. In the pH range = 5–7, most commonly found in natural waters is either H_2S gas or hydrogen sulphide ion (HS^-) (see: Table 7) (Kowal and Świderska-Bróż 2000). At pH > 7, recorded in the studied waters, the balance shifts towards hydrogen sulphide ion (HS^-).

If the water contains alkali metal sulphides (hydrosulphides), and that is the case of waters from Lesko (3), they dissociate in aqueous environment producing HS^- hydrosulphides and S^{2-} sulphides (see: Table 7). In turn, the replaced ions are hydrolysed to form hydrogen sulphide and hydroxyl ions $HS^- + H_2O = H_2S + OH^-$, which provide water with a base reaction. All sulphide waters have a slight alkaline reaction, for example (3) has a pH = 7.70 (see: Table 6).

Empirically selected sulphide waters (3) from Lesko has a very low redox potential ORP (Suslow 2004), equal to (minus) –230 mV (see: Table 6), which results, among other, from the sulphide reduction properties. Other sulphide waters also have a negative ORP potential, namely, water (1) –72mV, water (9) –50 mV, and water (2) –20 mV.

Sulphides (iodometry) (Minczewski and Marchenko 1978), hydrogen sulphide (see: Table 7), in the presence of the calcium cation reduce the level of sugar in blood and urine, have a positive impact on insulin activity, are desensitizing, detoxifying, stimulating the secretion of bile and pancreatic juice, apply in poisoning with metals (Kochański 2002).

Silicon (ICP-OES) (orthosilicic acid) (see: Table 8) is involved in building the skeleton, cartilaginous tissues and teeth.

Boron (ICP-MS) (metaboric acid) (see: Table 8) is a trace element and affects human body, mainly, the skeleton. It is believed that it is necessary for proper calcium economy of the body. Together with calcium, magnesium and vitamin D_3 it regulates the metabolism, growth and development of bone tissue. Its deficiency causes loss of calcium and bone demineral-

Table 4. The content of alkali metals and alkaline earth metals

Type of metal	Test point number	1	2	3	4	5	6	7	8	9	10
Na, Sodium	$mg \cdot dm^{-3}$	25,53	3,52	21,69	6,76	21,08	4,19	40,83	11,48	11,8	6,36
K, Potassium	$mg \cdot dm^{-3}$	4,09	1,86	1,77	1,47	2,63	1,54	1,35	2,35	1,48	1,21
Ca, Calcium	$mg \cdot dm^{-3}$	79,15	80,55	74,24	88,35	63,70	84,93	97,20	110,86	48,53	73,42
Mg, Magnesium	$mg \cdot dm^{-3}$	14,62	11,24	22,51	6,75	8,53	33,71	13,08	37,45	13,71	20,46
Ca multiplier	$mmol \cdot mg^{-1}$	0,02495	0,02495	0,02495	0,02495	0,02495	0,02495	0,02495	0,02495	0,02495	0,02495
Mg multiplier	$mmol \cdot mg^{-1}$	0,04114	0,04114	0,04114	0,04114	0,04114	0,04114	0,04114	0,04114	0,04114	0,04114
Ca+Mg sum	$mmol \cdot dm^{-3}$	2,576	2,471	2,778	2,482	1,940	3,506	2,963	4,307	1,775	2,674
Ca/Mg quotient	unitless	5,41	7,16	3,29	13,08	7,46	2,52	7,43	2,96	3,54	3,59
Sum of cations	$mg \cdot dm^{-3}$	123	97	120	103	96	124	153	162	75	101
Hardness	°dH	14	14	16	14	11	20	17	24	10	15
Type of water hardness	–	medium hard	medium hard	medium hard	medium hard	soft	hard	medium hard	hard	soft	medium hard

Table 5. Content of anions and carbon dioxide

Test site number / Anion	Unit	1	2	3	6	7	8
CO_2	$mg \cdot dm^{-3}$	88	121	103	37	29	55
HCO^{3-}	$mg \cdot dm^{-3}$	342	305	366	427	390	403
Cl^-	$mg \cdot dm^{-3}$	1	2	13	4	5	7
SO_4^{2-}	$mg \cdot dm^{-3}$	1,2	30	9	29	67	65
Sum of anions	$mg \cdot dm^{-3}$	345	337	388	460	462	475
Mineralization (anions + cations)	$mg \cdot dm^{-3}$	468	434	508	584	615	637
Type of mineralization	–	low-mineralised	low-mineralised	medium-mineralised	medium-mineralised	medium-mineralised	medium-mineralised

Table 6. Concentration of sulphides as well as physical and bacteriological properties of water

Parameter / Sample	Sulphides	Hydrogen ion exponent pH	Potential redox ORP	Temperature *T*	Coliform bacteria	Escherichia coli	Faecal enterococci	Other bacteria	Water suitable for consumption according to the Decree from 2010
Unit	mg · dm^{-3}	unitless	mV	°C	units · 100 g cm^{-3} of water				
3	1,080	7,70	–230	9	0	0	0	0	Yes
2	0,746	7,48	–20	6	0	0	0	0	Yes
1	1,010	7,58	–72	5	0	0	0	Present	No
9	0,906	7,62	–50	7	Present	Present	Present	Present	No

Table 7. Content of sulphur, sulfuretted hydrogen, sulphides, sulphates(VI)

Parameter / Sample	pH	Sulphur form	Sulphides mg · dm^{-3} Result	Sulphides mg · dm^{-3} Approximation	Sulphur form	Sulphates(VI) mg · dm^{-3}	Sulphur concetration mg S · dm^{-3}: sulphides iodometrically	sulphates(VI) turbidimetrically	Total ICP-OES	total counted	Marking error
							1	2	3	4 = 1 + 2	
1	7,58	H_2S HS	1,010	1,0	SO_4^{2-}	1,2	1,0	0,4	1,5	1,4	7,7%
2	7,48	H_2S HS	0,746	0,75	SO_4^{2-}	30,0	0,75	10,0	10,5	10,75	2,4%
3	7,70	H_2S HS	1,080	1,1	SO_4^{2-}	9,0	1,1	3,0	4,3	4,1	4,6%

Table 8. Contents of non-metals

Non-metal mg · dm^{-3} / Sample	Boron	HBO_2 Metaboric acid (calculated)	Si Silicon	H_2SiO_3 Orthosilicic acid (calculated)	Se Selenium	F Fluorine	Br Bromine	I Iodine
3	0,135	0,547	6,7	18,6	< 0,005	0,20	< 0,1	< 0,05
2	0,133	0,539	4,4	12,2	–	0,14	< 0,1	–
1	0,712	2,884	4,6	12,8	–	0,23	< 0,1	–

isation. However, positive influence of boron on the human body is debatable. Boric acid and borates have a dehydrating effect on cellular protoplasm that cause metabolic disorders and lead to changes in the electrolyte economy and acid-base balance. Drobnik and Latour (2001), in the study of pharmacodynamic properties of the solution H_3BO_3 found significant changes in the fat and mineral metabolism. However, not until the concentration reaches 100 mg $HBO_2 \cdot dm^{-3}$ it causes problems for the body (see: Table 8).

Fluoride (ion chromatography) (see: Table 8) is a component of bones and teeth, strengthens an enamel, dentin, prevents an occurrence of dental caries and reduces the solubility of enamel. Fluoride deficiency causes demineralisation bone as well as brittleness and susceptibility of teeth to decay. Constant consumption of waters containing over 1.5 mg · dm^{-3} advances fluorosis development, a disorder that manifests itself through spots on teeth enamel and their fragility. However, only the daily dose of fluorides within 20–40 mg causes formation of severe skeletal system fluorosis, leading to disability (Drinking water and health 1977, Kowal and Świderska-Bróż 2000).

In the region of the Outer Carpathians, sulphide waters can be found in the village of Wapienne and in the area of the Carpathian Foredeep, in localities of Krzeszowice, Hyżne-Nieborów and Lesko – with its sulphide sources (see: Table 9) (Paczyński and Sadurski 2007). Wapienne near Gorlice is the smallest and the only Carpathian health resort with therapeutic waters of sulphide type (Chowaniec et al. 2013). These waters, with mineralisation between 437–536 mg · dm^{-3}, has been included into category of specific and sulphide waters (H_2S over 1 mg · dm^{-3}).

As satisfactory should be considered the fact that empirical data obtained in the research is consistent with the selected hydrogeochemical data (see: Table 9) for Lesko. The studies have shown presence of hydrogen sulphide H_2S in the amount of 1.08 mg · dm^{-3}, and the data predicted the range of 1.0–2.5 mg · dm^{-3}, while mineralisation of Lesko (3) waters based on chemical analyses was estimated at 0.508 g · dm^{-3}, and hydrogeochemical data assume mineralisation between 0.4––0.5 g · dm^{-3}.

The performance 0.2 m^3 · h^{-1} of four sources in Lesko (see: Table 9), compared with other sulphide sources (Krzeszowice, Hyżne-Nieborów, Wapienne) is low. The type of water in Lesko (bicarbonate-calcium-magnesium, sulphide) HCO_3-Ca-(Mg), H_2S, is the closest to the sulphide waters of Wapienne.

CONCLUSIONS

1) Four out of 10 tested waters (1, 2, 3, 9) are springs with sulphide content, where divalent sulphur's content ranges from 0.746 to 1.080 mg · dm^{-3}, while two waters (6, 8) are characterized by an elevated amount of calcium and magnesium, with their hardness exceeding 20 German degrees.
2) The research indicated concentrations of heavy metals, manganese (50 µg · dm^{-3}) and arsenic in tested waters did not go beyond the highest permissible concentration set by the Regulation of The Minister of Health, which in the case of arsenic in water for drinking cures is 50 µg · dm^{-3}, and for water fit for human consumption is 10 µg · dm^{-3}.
3) A slightly elevated level of iron concentration was recorded in two samples – pursuant to the guidelines of the Minister of Health (200 µg · dm^{-3}), the concentration levels of lithium in the tested waters were below the limit of detection (100 µg · dm^{-3}).
4) On the basis of new Regulations of the Minister of Health (Rozporządzenie… 2003, Rozporządzenie... 2011) and the European Union guidelines (Dyrektywa 2009), waters from outflows (6, 8) can be named "natural mineral waters of medium mineralization" with small iron content. The selected sources (6, 8) show – considering the levels of hardness – that hard waters have a similar chemical composition to known and popular waters of medium mineralization available in trade in Poland.

Table 9. Sulfide waters of Carpathian province (selected hydrogeochemical data)

Town/Place	Number of springs	Resources m^3 · h^{-1}	H_2S mg · dm^{-3}	Mineralization g · dm^{-3}	Type of water
Krzeszowice	1	6,61	3,7–7,8	2,1–3,1	SO_4-Ca-Mg,H_2S
Hyżne – Nieborów	4	1,3	3,7–15,6	1,4–3,6	(Cl)-(HCO_3)-Na-Ca,H_2S,B
Lesko	4	0,2	1,0–2,5	0,4–0,5	HCO_3-Ca-(Mg), H_2S
Wapienne	2	2,92	0,5–10,5	0,2–0,53	HCO_3-Ca-Mg-(Na), H_2S

Source: Paczyński and Sadurski (2007)

5) All sulphide waters have negative ORP potential, with source from Lesko (3) having –230 mV and other waters respectively: (1) –72 mV, (9) –50 mV, (2) –20 mV.
6) The sample from Lesko (3) does not give rise to any bacteriological concerns (*Escherichia coli*, Enterococci, Coli bacteria and other), containing sulphides indicated iodometrically in an amount slightly over 1 mg $S^{2-} \cdot dm^{-3}$, which makes it "a specific therapeutic water due to sulphides". These waters can be determined – according to its alkaline water properties – as weakly alkaline (pH = 7.70), providing qualities good for health. In addition, it has a very low ORP potential, measured *in situ*, which makes it a valuable healing water (an antioxidant, eliminates free radicals).
7) The sample from Lesko (3) contains small concentrations of orthosilic and metaboric acid and fluorine, which have a positive effect on the body. It is water of medium mineralisation, from 500 to 1500 mg $\cdot$ dm^{-3}.
8) In the source from Lesko (3) no bromides (< 0.1 mg $\cdot$ dm^{-3}) nor selenium (< 0.005 mg $\cdot$ dm^{-3}) was registered.
9) The efficiency of sources in Lesko, comparing with other sulphide sources of the Carpathian province, is low. However, this is the only shortcoming of the region's sources, apart from that – they seem interesting, with a great potential for therapeutic use.

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PARAMETRY FIZYKOCHEMICZNE I BAKTERIOLOGIA ODKRYTYCH WÓD MINERALNYCH I SIARCZKOWYCH W OKOLICACH SANOKA I LESKA ORAZ MOŻLIWOŚCI LECZNICZEGO WYKORZYSTANIA TYCH WÓD

ABSTRAKT

Przebadano wodę z 10 punktów badawczych zlokalizowanych w północnej części powiatów Sanok i Lesko następującymi metodami analitycznymi: ASA (FAAS, CVAAS, HGAAS), ICP-MS, ICP-OES, chromatografia jonowa, alkacymetria, argentometria, turbidymetria oraz wykonano badania bakteriologiczne. Rozpoznano dwie „naturalne wody mineralne twarde średniozmineralizowane” z niewielką zawartością żelaza. Odkryto cztery źródła siarczkowe z czego źródło w Lesku cechuje woda „swoista lecznicza siarczkowa” o zawartości dwuwartościowej siarki oznaczonej jodometrycznie powyżej 1 mg · dm^{-3}, nie budząca zastrzeżeń bakteriologicznych. Woda z Leska oprócz małych ilości kwasu metaborowego i ortokrzemowego, jest wodą słabo alkaliczną, o silnie ujemnym potencjale ORP (–230 mV) co czyni ją prozdrowotną (antyoksydant, który likwiduje wolne rodniki). We wszystkich wodach sprawdzono obecność metali ciężkich, arsenu, litu, żelaza, manganu, metali alkalicznych i ziem alkalicznych. Opisano wpływ na organizm człowieka oznaczonych analitycznie substancji.

Słowa kluczowe: wody źródlane, arsen, metale ciężkie, balneologia