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ANALYSIS OF SPRING WATERS FROM LESKO IN TERMS OF THEIR MEDICAL PROPERTIES

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ABSTRACT

Aim of the study

The aim of the study was to demonstrate the medical properties of spring waters from Lesko based on their physicochemical analysis.

Material and methods

There are three active sulphide springs and one mineral spring in Lesko. In water samples from Lesko (1, 2, 3) sulphides and hydrogen sulphide (divalent sulphur) were determined. The sulphide and hydrogen sulphide concentration in the springs was determined with iodometric, photometric and thiomercurimetric methods. All samples were checked for the presence of 7 heavy metals with the AAS method. In all examined waters, an additional quantitative analysis of such components as metaboric acid, orthosilicic acid, sulphur, bromine, iodine was carried out with two methods: the ICP-MS and the ICP-OES. Also, fluorine content was determined with ion chromatography.

Results and conclusions

All waters from Lesko, except mineral water, contain sulphides. No heavy metals, including mercury and arsenic, were detected in all spring waters. No lithium or significant amount of iron and manganese were found. In the waters (1, 2, 3) no selenium and molybdenum were found. In the examined waters (1, 2, 3, 4), metaboric acid, orthosilicic acid, fluorine and iodides were found

Keywords: ICP-OES, balneology, Lesko, sulphide springs, ORP

INTRODUCTION

There are numerous springs of sulphide waters in the entire Carpathian Mountains, including in Poland (Rajchel, 2000). They contain hydrogen sulphide quantities from 1 to 160 $mg \cdot dm^{-3}$, with mineralisation of 0.3 to 3.6 $g \cdot dm^{-3}$ but usually not exceeding $1 g \cdot dm^{-3}$. Three springs contain carbon dioxide, while in more than twenty springs metaboric acid (HBO_2) was found with a concentration above 5 $mg \cdot dm^{-3}$ (Paczyński and Sadurski, 2007). The origin of hydrogen sulphide is commonly associated with pyrite dispersed in rocks (Rajchel et al., 2005). However, the preliminary isotope studies do not exclude that the gas could originate from the Earth's mantle in several cases (Rajchel et al., 2002). Springs of sulphide waters have characteristic sediments, consisting of various colonies of sulphur bacteria (Rajchel et al., 2000) and white sediment of

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elemental sulphur. Naturally, sulphur occurs in reduced form as hydrogen sulphide (H_2S) and sulphides (HS^-, S^{2-}), in molecular form (S°) and in oxidised form as sulphates (VI) (SO_4^{2-}) (Paluch, 1973). In other forms of oxidation, it can occur only temporarily as stages of oxidation–reduction reactions (sulphur biogeochemical cycle) (Paluch, 1973). In the Carpathian province that covers the external Carpathian region, sulphide waters occur in the town of Wapienne (Paczyński and Sadurski, 2007). In this town, sulphide waters and mud are the basic medical raw materials (Tchórzewska-Cieślak and Rak, 2006). Wapienne near Gorlice is the smallest and the only Carpathian health resort with healing sulphide waters (Chowaniec et al., 2013).

The place where the sulphide springs are located is the town of Lesko (Łach, 2005; Kozak, 2016). The town has a rich tradition associated with the healing properties of several sulphide and mineral springs. The basic components of mineral waters that determine its degree of mineralisation include: chloride, bicarbonate and sulphate (VI) anions; as well as sodium, potassium, calcium and magnesium cations. This qualification is complemented by the introduction of specific ingredients which are chemical elements or compounds with a proven therapeutic effect (Tchórzewska-Cieślak and Rak, 2005). Waters in Lesko springs are HCO_3 – Ca – (Mg), H_2S type waters in which hydrogen sulphide is the specific component. The resources of the above mentioned waters were estimated at 0.2 $m^3 \cdot h^{-1}$ (Paczyński and Sadurski, 2007). The aim of the study was to demonstrate the healing properties of spring waters from Lesko.

MATERIAL AND METHODS

Area of research

Lesko is a town located on the San river in south-eastern Poland, in the Podkarpackie Voivodeship (see: Fig. 1). Already before World War I, there was a spa at the present Źródlana street, and in the inter-war period, a natural medical institution was located there (Kozak, 2016). The springs, mostly hydrogen sulphide, were rebuilt in the form of reinforced wells and covered with concrete slabs (see: Fig. 2). The wells were only 2 meters deep. In 1936, a water pump room was established and it was planned to build bathrooms. The Voivodeship Office in Lviv oversaw the development of the spa, which in the future was to become a new resort in the Polish Carpathians.

To the south-east of Lesko, signs of arsenic-mercury mineralisation were found. Arsenic mineralisation occurs in the Central Carpathians. Anomalous concentrations of mercury and arsenic were detected in the weathering zone of flysch sediments near Baligród (Bystre, Rabe) (Jaworski, 1979). Arsenic-mercury mineralisation also applies to Lesko, and it was noticed before World War II (Kamieński, 1937). Today, arsenic has been found in groundwater in the Rabe 1 bore in the town of Rabe (Łach and Pasztyła, 2013; Chorostyński et al., 2016).

Methodology

There are 4 springs in Lesko, and their geographical coordinates (see: Table 1) and altitude were determined. Sulphide springs were marked with (1, 2, 3), and mineral spring that does not contain hydrogen sulphide with (4). For comparison, the Jan sulphide spring (5) in the spa town of Rymanów Zdrój in the Jasło-Ustrzyki sub region was included (Paczyński and Sadurski, 2007). The water analysis from this spring was performed by the Szczawna-Zdrój Balneoprojekt laboratory (Jaworski and Uliasz, 2006), and by the authors of the study.

Measurements and analyses of all parameters of water samples taken in spring, summer and autumn were carried out in accredited research laboratories or independently using applicable Polish standards, methodologies or validated testing procedures based on them. The measuring equipment used in the field was calibrated before measurements on the day of their performance.

For spring waters (2, 3, 4, 5) physicochemical measurements (see: Table 2) of following parameters were carried out: pH, oxidation-reduction potential (ORP), conductivity and temperature.

In water samples from Lesko (1, 2, 3) with a characteristic smell of “rotten eggs”, sulphides and hydrogen sulphide were determined. In the water from the spring (1), sulphides were determined using the iodometric method at first (Chorostyński et al., 2018). Now more accurate thiomercurimetric determining was performed in an accredited research laboratory using PN – 82/C – 04566.03. Determining of sulphides in the spring (2) was carried out based on the Mache-

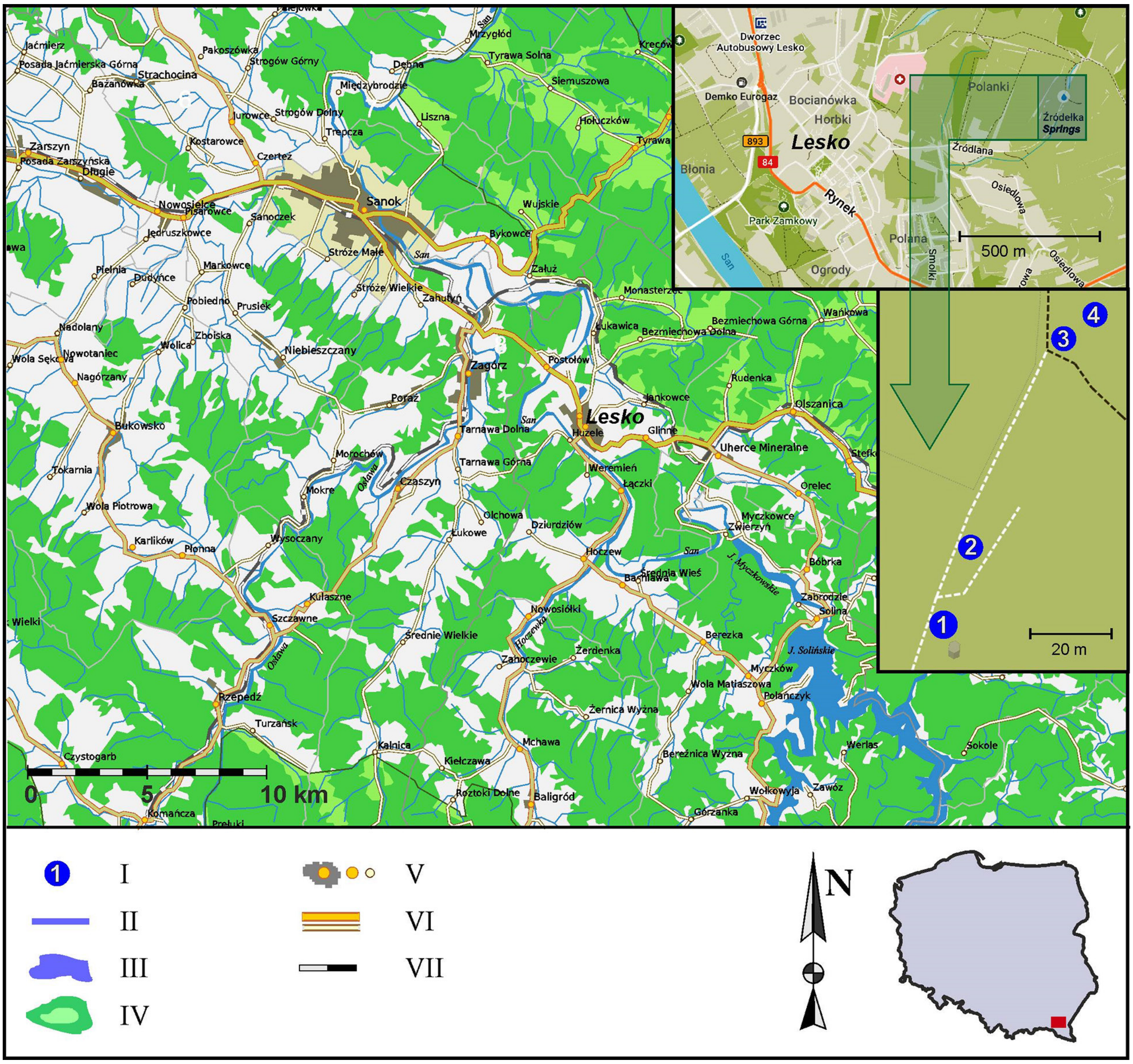

Fig. 1. Location of springs in Lesko, I – spring number; II – rivers, streams; III – lakes, water reservoirs; IV – forests; V – cities, towns; VI – national, local roads; VII – railway lines

Source: Author's own studies based on cartographic materials supplied by the State Forests and GPS MAPS.ME offline maps

rey–Nagel TEST in an accredited environmental testing laboratory. Sulphides and hydrogen sulphide in the spring (3) were determined iodometrically according to the method given by Minczewski and Marczenko (Minczewski and Marczenko, 2011). The Lesko spring (4) is a mineral spring free of sulphides and hydrogen sulphide (no characteristic odour and taste – the sensitivity of the organoleptic method is comparable to that of instrumental methods). The concentration of hydrogen sulphide (see: Table 2) in the Jan water in Rymanów Zdrój – water (5) was based on literature (Jaworski and Uliasz, 2006).

Fig. 2. View of enclosed springs in Lesko: 1, 2, 3, 4 – wells with spring water (photos taken by the authors)

Table 1. Location of tested springs

Parameter / Town/Place	Spring code	Spring and sample number	GPS N	GPS E	Position m a.s.l.	Scent type	Water type
LESKO	LE	1	49°28,380′	22°20,554′	373	"rotten eggs"	sulphide
LESKO	LK	2	49°28,378′	22°20,550′	382	"rotten eggs"	sulphide
LESKO	LO	3	49°28,403′	22°20,570′	387	"rotten eggs"	sulphide
LESKO	CM	4	49°28,416′	22°20,586′	390	no scent	mineral
Rymanów Zdrój health resort	X	5	49°32,890′	21°51,160′	156	"rotten eggs"	sulphide

Table 2. Concentration of sulphides as well as physical and bacteriological properties of water

PARAMETER / SAMPLE	Sulphides	pH	Redox	Conductivity	Temperature T	Coliform bacteria	Escherichia Coli	Faecal enterococci	Water suitable for consumption according to the Decree from 2010
UNIT	$mg \cdot dm^{-3}$	unitless	mV	$\mu s \cdot cm^{-1}$	°C	units · 100g cm^{-3} of water			
1	1.90	7.70	–230	540	9	0	0	0	Yes
2	0.10	7.30	–90	520	13	0	0	0	Yes
3	0.80	7.60	–180	600	12	0	0	0	Yes
4	no sulphides	6.90	+145	720	13	not tested	not tested	not tested	No data
5	1.40	7.20	+80	2340	16	0	0	0	Yes

Arsenic-mercury mineralisation around Lesko may be the reason for underground water enrichment with heavy metal ions as a result of water infiltration by rocks with increased mineralisation resulting from the presence of chemical compounds of these metals. Therefore, in all water samples, atomic absorption spectrometry (ASA) analysis of heavy metals: zinc, cadmium, copper, lead, nickel, chromium, mercury (see: Table 3), and arsenic (see: Table 4) (toxic and carcinogenic elements) (National Research Council, 2001; ATSDR, 2007, Dobrzyński i Stępień, 2009) was performed. Water samples were also analysed with this method for the presence of micronutrients: lithium, manganese, iron (see: Table 4) and for sodium, potassium, calcium and magnesium content (see: Table 5).

In the water samples, carbon dioxide content and concentration of anions: bicarbonates (acid–base titration), chlorides (argentometry), and sulphates (VI) (turbidimetry) were examined (see: Table 6). In the sulphide waters (1, 2, 3) in which sulphides were detected and determined, bacteriological determinations were carried out, including: Escherichia coli, coliform bacteria, faecal Enterococci (see: Table 2). The above parameters were determined by an accredited research laboratory of the State Sanitary Inspectorate (PIS).

In all examined waters, additional analysis of the following components was performed: boron, silicon, sulphur, bromine, iodine. Two methods were used: inductively coupled plasma mass spectrometry (ICP – MS), and inductively coupled plasma optical emission spectrometry (ICP – OES) (Table 8). The above-mentioned samples also have fluorine content determined with ion chromatography (see: Table 8), the analysis was carried out by the accredited PIS testing laboratory.

Table 3. The content of heavy metals

METAL / SAMPLE	Unit	Zinc Zn	Cadmium Cd	Copper Cu	Lead Pb	Nickel Ni	Chromium Cr	Mercury Hg
1, 2, 3, 4, 5 ASA traceability	$\mu g \cdot dm^{-3}$	< 10	< 1	< 10	< 4	< 5	< 5	< 0.08
Norm according to the Regulation by the Minister for Public Health	$\mu g \cdot dm^{-3}$	3000	5	2000	10	20	50	1

Table 4. The content of microelements

Element $\mu g \cdot dm^{-3}$ / Sample	Fe (og) Iron	Mn (og) Manganese	Li Lithium	As (og) Arsenic	Se (og) Selenium	Mo Molybdenum
1	10	20	< 100	< 0.3	< 5 < 5 ASA ICP–MS	< 5 ICP–MS
2	10	10	< 100	< 0.3	< 5 < 5	< 5
3	10	20	< 100	< 0.3	< 5 < 5	< 5
4	20	30	< 100	< 0.3	not tested	not tested
5	10	10	< 100	< 0.3	not tested	not tested
Norm according to the Regulation by the Minister for Public Health	200	50	–	10	–	–

Table 5. The content of alkali metals and alkaline earth metals

Type of metal / Sample	Unit	Na Sodium	K Potassium	Ca Calcium	Mg Magnesium	Sum of cations
1	$mg \cdot dm^{-3}$	22	2	74	22	120
2	$mg \cdot dm^{-3}$	5	1	66	21	93
3	$mg \cdot dm^{-3}$	29	2	72	24	127
4	$mg \cdot dm^{-3}$	30	3	88	27	147
5	$mg \cdot dm^{-3}$	330	8	133	27	498

Table 6. Content of anions and carbon dioxide

ANION mg · dm^{-3} / Sample	CO_2 carbon dioxide	HCO_3^- bicarbonates	Cl^- chlorides	SO_4^{2-} sulphates	Sum of anions	Mineralisation (anions+cations)	Type of mineralisation
1	103	366	13	9	388	508	moderately mineralised
2	115	311	5	30	346	439	low mineralised
3	98	327	11	14	351	478	low mineralised
4	26	329	23	42	394	541	moderately mineralised
5	127	752	395	4	1151	1649	highly mineralised

Table 7. Zawartość siarki, siarkowodoru, siarczków, siarczanów VI

PARAMETER / SAMPLE	pH pH	SULPHUR FORM	SULPHIDES mg · dm^{-3}		SULPHUR FORM	SULPHATES VI mg·dm^{-3}	SULPHUR CONCENTRATION mg S · dm^{-3}				DETERMINATION ERROR
			RESULT	APPROXIMATION			sulphides	sulphates VI turbidimetrically	total ICP–OES	total calculated	
							1	2	3	4 = 1 + 2	
1	7.70	H_2S HS^-	1.920	1.9	SO_4^{2-}	9.0	1.9	3.0	4.6	4.9	6.5%
2	7.30	H_2S HS^-	0.097	0.1	SO_4^{2-}	30.0	0.1	10.0	10.4	10.1	2.9%
3	7.60	H_2S HS^-	0.830	0.8	SO_4^{2-}	14.0	0.8	4.7	5.1	5.5	7.8%
5	7.20	H_2S HS^-	1.400	1.4	SO_4^{2-}	4.0	1.4	1.3	2.9	2.7	6.9%

Table 8. Contents of non–metals

Non-metal mg · dm^{-3} / Sample	Boron B	HBO_2 Metaboric acid (calculated)	Silicon Si	H_2SiO_3 Orthosilicic acid (calculated)	S Sulphur	F Fluorine	Br Bromine	I Iodine
1	0.135	0.547	6.7	18.6	4.6	0.20	< 0.1	0.25
2	0.084	0.340	11.3	31.4	10.4	0.11	< 0.1	0.18
3	0.058	0.235	10.7	29.7	5.1	0.17	< 0.1	0.22
4	0.027	0.109	9.2	25.5	14.0	0.10	< 0.1	0.10
5	5.762	23.350	8.2	22.8	2.9	0.19	1.4	0.40

The method of atomic absorption spectrometry (ASA) was also used to determine the content of selenium in waters (1, 2, 3) (see: Table 4). The selenium determination was repeated (checked) with inductively coupled plasma mass spectrometry (ICP–MS). In an environmental research laboratory, the ICP – MS method was used to determine the concentration of a trace element (a micronutrient) molybdenum (a bio element) in the same waters.

All physicochemical measurements such as: pH, ORP, conductivity, temperature were made “at the source” using portable instruments (Łach, 2011) by the authors of the work. Also, all ASA analyses (Na, K, Mg, Ca, Mn, Fe, Zn, Cu, Pb, Cd, Ni, Cr, Hg, As, Se) and some ICP analyses – MS i ICP – OES (B, Si, I, Br, S) were performed by the authors of the work.

Knowing the results of the determination of sulphides, sulphates (VI), and the total amount of sulphur, the relative error of sulphur determination was calculated. In Table 7 the content of various forms of sulphur was balanced and converted to pure sulphur. The table includes three different test methods for the determination of sulphides: thiomercurimetry, photometry (instrumental analysis – TEST Macherey-Nagel), iodometry, and the instrumental method for the determination of sulphates (VI) – turbidimetry and determination of pure sulphur – inductively coupled plasma excitation emission spectrometry (ICP-OES). Comparison of the determination of various forms of sulphur using 5 methods (including three instrumental ones) with a maximum error of 7.8% is considered satisfactory (Chorostyński et al., 2018).

RESULTS AND CONCLUSIONS

The results were included in Tables 1–8. There was a slight variation between the results of the determination of the same parameters of individual analysed spring waters at different times of the year. The smallest standard percentage deviation – % RSD (Relative Standard Deviations) was 2–3% and concerned the measurement of pH value. The highest % RSD was 7–8% and was characteristic for determinations made with titration methods and ICP-OES method. The recorded values of percentage standard deviations for individual parameters of the same spring water did not exceed the coefficients of variation of the test methods used for their determination. The results of physicochemical measurements of sulphide water from Lesko (1) were taken from the article (Chorostyński et al., 2018).

The bivalent sulphur content in the water sample (1) from Lesko, ($1.9\ mg \cdot dm^{-3}$) allows to state that it is sulphide water with a bivalent sulphur content above $1\ mg \cdot dm^{-3}$, therefore it meets the criterion to be classified as a healing water. Pharmacodynamic coefficients are the minimum contents of selected chemical components (so-called specific components) or the minimum value of physical properties of water, causing their therapeutic effect (Regulation, 2006; Michalski, 2006). Considering the coefficients, it can be shown that water (1) is “specific healing sulphide water”. Also, healing water (5) with a divalent sulphur content of $1.4\ mg \cdot dm^{-3}$ (H_2S) is this kind of water. In the pH range of 5–7, which is the most commonly found in natural waters, both gaseous H_2S and hydrosulphide ion (HS^-) may be present (Kowal and Świderska-Bróż, 2000). At pH > 7, which happens in the waters we study, the equilibrium shifts towards the hydrosulphide ion (HS^-) (see: Table 7).

The oxidation-reduction potential (ORP), also known as the redox potential of any fluid, depends on the activity of electrons (Suslow 2004). Sulphide waters (1, 3) from Lesko have a very low redox potential (see: Table 2) which results from, among others, reduction properties of sulphides (Chorostyński and in., 2018). The more negative the redox potential (expressed in millivolts), the greater the water’s reducing (anti-oxidative) properties (Hanaoka et al., 2004). Negative ORP water can have a positive effect on our health because, having reducing properties, it is an antioxidant that causes “neutralisation” of free radicals (Ignacio et al., 2012).

The prolonged state of the disturbed acid-base balance leads to adverse health consequences, the clinical symptoms of which are acidosis (a condition in which the acid-base balance is shifted towards lower pH values), fatigue, lack of appetite, migraine, drowsiness, increased urinary excretion of minerals (Na, Ca, Mg) leading to kidney stones, increased blood pressure (Gertig and Przysławski, 2006). All sulphide waters are slightly alkaline e.g. water (1, 2, 3) (see: Table 2), therefore, it is advisable to drink them in case of disturbed acid-base balance (acidosis, excess stomach

Table 9. Sulphide waters of Carpathian province (selected hydrogeochemical data) (Paczyński and Sadurski, 2007)

Town/Place	Number of springs	Resources $m^3 \cdot h^{-1}$	H_2S $mg \cdot dm^{-3}$	Mineralisation $g \cdot dm^{-3}$	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

acid). Water alkalinity may result not only from the presence of alkali metals (sodium, potassium, calcium, magnesium). If the water contains sulphides (hydrosulphides) of alkali metals, they dissociate in the aqueous environment. In turn, ions hydrolyse, resulting in the formation of hydrogen sulphide and hydroxyl ions $HS^- + H_2O = H_2S + OH^-$, which give the water an alkaline reaction (Chorostyński et al., 2018).

Sulphide waters from Lesko (1, 2, 3) were bacteriologically tested (Escherichia Coli, coliform bacteria, faecal enterococci), all were drinkable (no pathogenic bacteria) (see: Table 2).

In the examined waters, no heavy metals, arsenic or mercury were detected. It has been shown that in spring waters, mercury and arsenic are not present even in trace amounts, which makes the water fit for consumption (Regulation, 2017; Michalski, 2007).

Water from Lesko consists iron and manganese in trace amounts. Thanks to this, the extracted water is clear, does not precipitate sediments of $Fe(OH)_3$ (brown, colloidal sediment) or MnO_2 (manganese(IV) oxide – brown sediment). The maximum value of manganese concentration in drinking water allowed by the Minister of Health (Regulation, 2017) may not exceed 50 $\mu g \cdot dm^{-3}$, while the iron concentration 200 $\mu g \cdot dm^{-3}$ (see: Table 4). Manganese deficiency is mainly expressed in the form of impaired motor coordination, osteoarticular damage and osteoporosis (Zawadzki et al., 2008). Anaemia is a classic symptom of iron deficiency in the body that is confirmed by a decrease in haemoglobin below normal for a given age and sex (Gertig and Przysławski, 2006).

Mineral water spring in Lesko (4) does not contain sulphides but has a relatively elevated content of sodium, potassium, calcium and magnesium (in regard of sulphide waters of Lesko). Determination of the concentration of these elements and the concentration of anions in all waters allowed the calculation of mineralisation (sum of solid components) (see: Table 6). Water (1, 4) turned out to be medium mineralised, water (2, 3) was low mineralised, and comparative water (5) was highly mineralised (Regulation, 2003).

The content of boron (HBO_2), silicon (H_2SiO_3), iodine and fluorine was determined in the examined waters (Table 8). The quantities of elements were compared with pharmacodynamic coefficients (Regulation, 2006; Michalski, 2006) and there is no element present in a quantity that allows naming the water (except sulphides) as a "specific water".

The capacity of 0.2 $m^3 \cdot h^{-1}$ (Paczyński and Sadurski 2007) of sulphide springs in Lesko (Table 9) is low in comparison with other sulphide springs (Krzeszowice, Hyżne-Nieborów, Wapienne). The Lesko water (bicarbonate-calcium-magnesium, sulphide type) HCO_3 – Ca – (Mg), H_2S is the closest to sulphide waters in Wapienne (Chowaniec et al., 2013; Chorostyński et al., 2018).

CONCLUSIONS

1. Spring water from Lesko (1) with a hydrogen sulphide concentration of 1.9 $mg \cdot dm^{-3}$ is a "specific healing sulphide" water.
2. Sulphide waters are slightly alkaline and their alkalinity results from the hydrolysis of sulphide ions.
3. Sulphide waters from Lesko have low oxidation-reduction potential (ORP) (they have reducing properties), i.e. they are antioxidants.
4. No heavy metals, including mercury and arsenic, were detected in all waters. The lack of trace amounts of these elements makes these waters fit for consumption. It is significant since there are

underground waters containing arsenic (Rabe, Bystre) south–east of Lesko.

5. Sulphide waters were bacteriologically tested, no pathogenic bacteria were detected.
6. The Lesko sulphide spring (1.9 mg · dm^{-3} H_2S) has a higher concentration of hydrogen sulphide than the Jan sulphide spring in Rymanów Zdrój. However, water from Rymanów has higher specific conductivity and mineralisation (highly mineralised water).
7. Considering the conclusions, it should be stated that the springs, despite their low efficiency, are suitable for use as healing waters.

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ANALIZA WÓD ŹRÓDLANYCH Z LESKA W ASPEKCIE ICH LECZNICZYCH WŁAŚCIWOŚCI

ABSTRAKT

Cel pracy

Celem pracy było wykazanie właściwości leczniczych wód źródlanych z Leska na podstawie ich analizy fizykochemicznej.

Materiał i metody

W Lesku znajdują się trzy aktywne źródła siarczkowe, oraz jedno mineralne. W próbkach wody z Leska (1, 2, 3) oznaczono siarczki i siarkowodór (siarka dwuwartościowa). Stężenie siarczków i siarkowodoru w źródłach, określono metodami: jodometryczną, fotometryczną i tiomercurymetryczną. We wszystkich próbkach wody sprawdzono obecność 7 metali ciężkich metodą ASA. We wszystkich badanych wodach dodatkowo przeprowadzono analizę ilościową takich składników jak: kwas metaborowy, kwas ortokrzemowy, siarka, brom, jod dwoma metodami: ICP-MS oraz ICP-OES. Oznaczono również zawartość fluoru metodą chromatografii jonowej.

Wyniki i wnioski

Wszystkie wody z Leska oprócz wody mineralnej zawierają siarczki. We wszystkich wodach źródlanych nie wykryto metali ciężkich w tym rtęci oraz arsenu. Nie stwierdzono obecności litu oraz większej ilości żelaza i manganu. W wodach (1, 2, 3) nie wykryto obecności selenu i molibdenu. W badanych wodach (1, 2, 3, 4) stwierdzono obecność kwasu metaborowego, kwasu ortokrzemowego, fluoru i jodków.

Słowa kluczowe: ICP-OES, balneologia, Lesko, źródła siarczkowe, ORP