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THE ANALYSIS OF TRACE ELEMENTS INCLUDING URANIUM CONCENTRATION IN SPRING WATERS FROM LESKO WITH THE PROSPECT OF THEIR BALNEOLOGICAL USE

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ABSTRACT

Aim of the study

The aim of the study was to analyse trace elements including uranium concentration in spring waters in Lesko area. Our additional objective was to demonstrate that the increased concentration of uranium in these spring waters gives grounds for the assumption that we could be dealing with "specific healing radon water".

Material and methods

On the northern edge of Lesko town, there are springs of healing waters. The springs contain low-mineralised sulphide waters with a low redox potential (ORP) and a slight alkaline reaction. The efficiency of these sources is within 2–3 litres per minute.

The paper presents the results of the analysis of elements and trace elements in the above mentioned spring waters, using the following methods: AAS, IC, ICP-MS, and ICP-OES. The statistical method of Student's t-test was used to process the results.

Results and conclusions

The statistical research showed that the concentration of uranium in the waters of Lesko is higher than the corresponding concentration in the sulphide water from Rymanów Zdrój. Based on literature in the field of geology, it has been demonstrated that in the vicinity of Bezmiechowa – Monasterzec – Lesko, there are concentrations of uranium in rocks of low value, albeit sufficient for spring (underground) water to contain trace amounts of uranium in ionized form. The increased uranium concentration suggests the presence of radon in the tested waters. If it is proven that radon is present in an appropriate concentration in low-mineralized spring waters, this will allow the use of the above-mentioned waters as radon waters for balneological purposes.

Keywords: Lesko, AAS, ICP-OES, uranium, radon, spring waters, healing waters.

INTRODUCTION

A spring is a spontaneous and concentrated outflow of groundwater to the surface. Springs occur in places where the topographic surface intersects the aquifer or the static groundwater table. (Bajkiewicz-Grabowska and Mikulski, 2017).

There is a group of micronutrients found in groundwater in amounts of the order of $\mu g \cdot dm^{-3}$, which have a beneficial or even therapeutic effect (Szmytówna,

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2007). These elements are of particular biological importance due to their participation in the structure of certain enzymes or due to their catalytic properties in biochemical transformations. These are the so-called biocatalysts. The group of these elements includes vanadium, chromium, manganese, cobalt, copper, zinc, molybdenum, selenium and others. It should be assumed that with progress in the fields of biology, medicine and balneology the list of micronutrients with healing properties will be extended further (Macioszczyk and Dobrzyński, 2007; Piech and Baszak, 2016).

Groundwaters may owe their healing properties to a specific composition of macronutrients, sub-ingredients or micronutrients. We recognise, for example, ferric or boron healing waters. Healing properties may also be associated with the presence of gases (sorrels, sulphide waters), or with the occurrence of certain physical properties (thermal, radioactive waters) (Macioszczyk and Dobrzyński, 2007).

In the region of Podkarpacie, there are brine waters, such as petroleum brines of the Iwonicz Anticline, including mineral waters in Iwonicz Zdrój and Rymanów Zdrój (Paczyński and Sadurski, 2007). These localities, including Polańczyk, abound in medicinal bicarbonate-chloride-sodium waters (Tchórzewska-Cieślak and Rak, 2005; Tchórzewska-Cieslak and Rak, 2006).

Lesko is a town that possesses all the characteristics of a health resort. Three sulphide springs and one mineral spring are located here. In the earlier studies focused on Lesko area, it was shown that there are "specific healing sulphide waters" showing low mineralization, low ORP, and light alkalinity (Chorostyński et al., 2018; Chorostyński et al., 2019). The Lesko Foothills are part of the Eastern Carpathians (Kondracki, 2002). In the region, sulphide springs are of greater value as opposed to brine springs, due to the fact that chloride springs are widespread (health resorts), while sulphide springs are still practically undiscovered, whereas in terms of healing properties the latter are not inferior to the former (Chorostyński et al., 2018). It should be noted that sulphide waters are also available, although to a lesser extent, e.g. Jan's water in Rymanów Zdrój (Jaworski and Uliasz, 2006).

The concept of trace analysis, i.e. the derived concepts such as ultra-trace analysis, cannot be defined in a strict and invariable manner. Several decades ago, it could be relatively strictly said that trace analysis concerns the determination of ingredients whose content does not exceed 10^{-2}%. Currently, such terms as microtraces, nanotraces, and even picotraces (10^{-14} – 10^{-17}%) are used (Hulanicki, 2001).

Trace analysis is currently one of the most important fields of analytics. Performing trace analysis requires taking special measures to avoid false results due to the environment of a sample or the process of its preparation and processing. Thus, one works in clean rooms or clean boxes with laminar flow of purified air (Danzer et al., 1980).

The aim of the study was to analyse trace elements including uranium concentration in spring waters in Lesko. In addition, it was necessary to show that the increased concentration of uranium in these spring waters gives grounds for the assumption that we could be dealing with "specific healing radon water" (Eckertová et al., 2019).

MATERIAL AND METHODS

Study area

Lesko is a county town situated on the right bank of the San River, on the slope of the scenic Baszta (421 m) (Orłowski, 2010)

For the three sulphide springs and one mineral spring (not containing hydrogen sulphide) in Lesko and for the Jan sulphide spring in Rymanów Zdrój (compar ative spring), the geographical coordinates and location above sea level were determined, which are presented in Table 1. Each spring has been given a number and a two-letter code.

The local springs have been known for a very long time. They formed naturally at the bottom of the structural basin and were used by the inhabitants as helpful in various ailments. The springs contain slightly mineralized sulphide waters with a capacity of 2–3 litres per minute. They are used in the treatment of gastrointestinal, rheumatic, skin and metabolic diseases. They can be used in both drinking and bathing therapies. In 1979, they were officially recognized as healing waters (Kłos, 2014).

Methodology

Water samples for analysis from the studied springs were taken in accordance with the PN-ISO 5667-11: 2017-10, PN-87 / C-04632 / 01-02 and PN-88 / C-04632/03

Table 1. Location of the tested springs

Parameter / Town/Place	Spring code	Spring and sample number	GPS N	GPS E	ASL position	Scent type	Water type
LESKO	LE	1	49º28,380’	22º20,554’	373	“rotten eggs”	sulphide
LESKO	LK	2	49º28,378	22º20,550’	382	“rotten eggs”	sulphide
LESKO	LO	3	49º28,403	22º20,570’	387	“rotten eggs”	sulphide
LESKO	CM	4	49º28,416	22º20,586’	390	no scent	mineral
Rymanów Zdrój health-resort	X	5	49º32,890’	21º51,160’	156	“rotten eggs”	sulphide

standards, taking into account the rules of water sampling for drilled wells in continuous operation. The samples were taken with the use of a flow-filter set in a way that minimized the contact time of water with the atmospheric air. At the same time, the samples were subjected to filtration with a flow filter of a pore size of 0.45 µm in order to avoid mineral and biological contamination. The containers, the method of processing the sample in the field, the method of preserving the sample, the preservation temperature, and the permissible storage time of the samples were in accordance with the guidelines provided in the PN-EN ISO 5667-3: 2018-08 standard and the recommendations in this regard specified by Witczak and Adamczyk (Witczak and Adamczyk 1994, 1995).

A publication by Chorostyński et al. (2019) presents the results of the determination of macroelements, microelements and heavy metals in spring waters (1–5) from Lesko and Rymanów Zdrój, using by the AAS (Atomic Absorption Spectrometry) method (Szczepanik, 2002). Fluorine content was determined using the IC (Ion Chromatography) method. The ICP-OES and ICP-MS methods were applied to determine the content of non-metals in the waters (1–4) from Lesko, and in Jan’s water (5) from Rymanów Zdrój (comparative water).

In the present study, all the elements analysed previously with the AAS method were determined. This time, the two methods were applied: ICP-OES (Inductively Coupled Plasma – Optial Emission Spectroscopy) and ICP-MS (Inductively Coupled Plasma – Mass Spectrometry) (see: Tables 2–5).

The Atomic Absorption Spectrophotometry (AAS) is highly selective, and it enables the determination of approximately 60 elements. One should bear in mind the so-called matrix effect that can be eliminated by background correction, or by adding matrix-modifying compounds (lanthanum, caesium salts). The “cold vapour” technique is used to determine mercury (Gertig and Przysławski, 2006). In elemental analysis, the so-called combined techniques, e.g. ICP-OES are gaining importance. Combined techniques are characterized by greater sensitivity and selectivity and a weaker matrix effect (Gertig and Przysławski, 2006). It is particularly important in the analysis of trace amounts of radioactive elements, including uranium that occurs in the lithosphere and hydrosphere (Singhal et al., 2011).

Additionally, the content of trace elements in all waters (1–5) (Lesko, Rymanów Zdrój) was determined by the ICP-OES method (see: Table 6). In Tables 2–6, for each element, the analytical method used for its determination is indicated. In Tables 2–5, the results (AAS, IC) were repeated by the ICP-OES and ICP-MS methods in order to increase the accuracy of the analyses performed.

ICP-MS research (PN-EN ISO 17294-2: 2006) was carried out at the Petro-Geo Wołomin Laboratory and Geological Services Company. ICP-MS tests (PN-EN ISO 17294-2: 2016-11) were carried out at the SGS Pszczyna Environmental Laboratory. The AAS tests (PN-EN ISO 7980: 2002) were performed on the Thermo Scientific S4 spectrometer, while the ICP-OES tests (PN-EN ISO 11885: 2009) were performed on the PerkinElmer Avio 200 spectrometer at the State University in Sanok. IC tests (PN-EN ISO 10304-1: 2009) were performed at the WSSE in Rzeszów, Laboratory Department in Sanok.

Table 2. The content of alkali metals and alkaline earth metals

Element mg · dm^{-3}	Ca	±%	Ca	±%	K	±%	K	±%	Li	Li	±%	Mg	±%	Mg	±%	Na	±%	Na	±%
Method / Sample	AAS	RSD	ICP-OES	RSD	AAS	RSD	ICP-OES	RSD	AAS	ICP-OES	RSD	AAS	RSD	ICP-OES	RSD	AAS	RSD	ICP-OES	RSD
1	74	3.0	61	4.4	2	1.7	2.0	2.8	< 0.1	0.01	4.0	22	2.4	23	2.4	22	1.8	24	2.5
2	66	2.8	56	2.5	1	1.7	1.6	2.9	< 0.1	0.03	3.9	21	3.5	17	2.1	5	1.2	7	3.5
3	72	1.4	53	3.1	2	2.9	1.3	3.7	< 0.1	0.08	4.7	24	1.1	18	2.4	29	2.1	22	3.1
4	88	1.5	57	3.2	3	3.2	1.8	4.0	< 0.1	0.05	4.8	27	1.6	21	3.2	30	1.9	26	2.0
5	133	1.2	102	4.1	8	2.2	9.9	4.3	< 0.1	0.37	3.2	27	1.5	18	3.0	330	2.3	307	1.9

RSD – relative standard deviation expressed as a percentage, at level of significance $p = 0.95$ $n = 3$

Table 3. The content of microelements

Element µg · dm^{-3}	As	As	Fe	±%	Fe	±%	Mn	±%	Mn	±%	Mo	±%	Mo	Se	Se	Se	±%
Method / Sample	AAS	ICP-OES	AAS	RSD	ICP-OES	RSD	AAS	RSD	ICP-OES	RSD	ICP-OES	RSD	ICP-MS	AAS	ICP-MS	ICP-OES	RSD
1	< 0.3	< LOQ	10	2.4	2	5.2	30	3.8	25	5.9	27	4.1	<5	<5	<5	458	7.1
2	< 0.3	< LOQ	10	3.3	3	7.4	10	3.4	1	6.0	15	5.5	<5	<5	<5	684	8.4
3	< 0.3	< LOQ	10	2.6	1	7.8	20	3.4	12	6.4	22	4.2	<5	<5	<5	146	6.3
4	< 0.3	< LOQ	20	3.1	5	6.5	30	2.7	2	5.3	18	3.6	–	–	–	231	7.7
5	< 0.3	< LOQ	10	2.5	20	5.1	10	2.9	153	7.9	30	4.4	–	–	–	479	6.5

< LOQ – result below the limit of quantification

Table 4. The content of heavy metals

Element µg · dm^{-3}	Cd	Cd	Cr	Cr	±%	Cu	Cu	Hg	Hg	±%	Ni	Ni	Pb	Pb	Zn	Zn	±%
Method / Sample	AAS	ICP-OES	AAS	ICP-OES	RSD	AAS	ICP-OES	AAS	ICP-OES	RSD	AAS	ICP-OES	AAS	ICP-OES	AAS	ICP-OES	RSD
1	< 1	< LOQ	< 5	4	4.4	< 10	< LOQ	< 0.08	0.6	5.7	< 5	4	< 4	< LOQ	< 10	3	4.9
2	< 1	< LOQ	< 5	3	4.8	< 10	< LOQ	< 0.08	0.7	6.4	< 5	6	< 4	< LOQ	< 10	< LOQ	–
3	< 1	< LOQ	< 5	3	5.3	< 10	< LOQ	< 0.08	0.4	5.5	< 5	3	< 4	< LOQ	< 10	2	5.4
4	< 1	< LOQ	< 5	3	5.6	< 10	< LOQ	< 0.08	< LOQ	–	< 5	< LOQ	< 4	< LOQ	< 10	< LOQ	–
5	< 1	< LOQ	< 5	9	3.1	< 10	< LOQ	< 0.08	0.3	6.9	< 5	7	< 4	< LOQ	< 10	< LOQ	–

< LOQ – result below the limit of quantification

Table 5. The content of non-metals

Element mg · dm^{-3}	B	±%	Br	±%	F	±%	I	±%	I	S	±%	Si	±%
Method / Sample	ICP-MS	RSD	ICP-MS	RSD	IC	RSD	ICP-OES	RSD	ICP-MS	ICP-OES	RSD	ICP-OES	RSD
1	0.135	2.7	< 0.1	–	0.2	2.2	0.25	3.5	< 0.05	4.6	2.0	6.7	3.6
2	0.084	3.3	< 0.1	–	0.11	2.7	0.18	2.2	–	10.4	3.1	11.3	3.0
3	0.058	3.2	< 0.1	–	0.17	3.4	0.22	3.6	–	5.1	2.7	10.7	4.4
4	0.027	2.6	< 0.1	–	0,.0	3.1	0.10	2.7	–	14.0	2.4	9.2	3.7
5	5.762	5.1	1.4	2.3	0.19	2.1	0.40	2.8	–	2.9	2.5	8.2	2.8

Table 6. The content of trace elements

Element µg · dm^{-3}	Ba	±%	Cs	±%	Ga	±%	Sb	±%	Sn	±%	Sr	±%	U	±%	V	±%	Zr	±%
Method / Sample	ICP-OES	RSD	ICP-OES	RSD	ICP-OES	RSD	ICP-OES	RSD	ICP-OES	RSD	ICP-OES	RSD	ICP-OES	RSD	ICP-OES	RSD	ICP-OES	RSD
1	63	4.0	94	3.9	11	3.2	77	3.1	158	5.4	181	5.3	15	3.6	14	3.3	102	5.6
2	7	4.1	19	4.3	9	3.3	32	3.0	161	4.6	122	4.4	13	3.1	15	3.4	119	2.1
3	25	5.0	75	3.7	8	4.4	67	4.0	165	3.6	260	5.7	13	4.5	15	4.7	95	5.8
4	13	3.8	36	2.2	16	4.5	69	4.2	202	5.5	123	5.3	18	4.8	17	4.7	94	4.3
5	2368	7.4	6179	6.8	14	4.6	281	5.1	211	5.7	895	6.0	9	3.2	15	3.4	390	6.2

In analytical practice, we often use the so called statistical hypothesis testing, which makes it possible to assess whether the difference between the obtained (calculated) results is small or large, whether it is significant or can be neglected. The testing methods enable us to determine whether the values that are found experimentally, while put into the formula for calculating a given testing criterion, remain within the assumed level of probability, within the limits of the so-called critical values for a given test. The critical values can be found in the relevant tables. The probability level is defined as the significance level α, for which the value found is compared with the value read from the table. In chemical analysis, we often use the t-test (Szczepaniak, 2019).

RESULTS AND DISCUSSION

All the analyses were performed three times: in spring (May), summer (July) and autumn (September) 2017. The results (mean values) are given in Tables 2–6. We should add that for all the results, except inequality (<), and also excluding the measurements below the limit of quantification (< LOQ), for $n = 3$ and the significance level $p = 0.95$, the relative standard deviation expressed in per cent (% RSD) was given. The smallest standard deviation in per cent was 1.1% and it was related to the AAS method (see: Table 2) (magnesium). On the other hand, the highest % RSD was 8.4% and was characteristic of the quantifications made with the ICP-OES method (see: Table 3) (selenium).

The results in Table 2 obtained by the two methods (AAS, ICP-OES) are highly correlated, with the AAS concentration values being, in most cases, higher than the ICP-OES results. The results in Table 3 can be interpreted in a similar way, with one exception: the determination of selenium by the ICP-OES method seems to be burdened with a "gross error", because, firstly, the selenium content in spring waters in the amount of about 0.5 $mg \cdot dm^{-3}$ is quite unlikely, and, secondly, the two results obtained by AAS and ICP-MS methods (5 $\mu g \cdot dm^{-3}$) are the same. In Table 4, the situation is also similar: the values obtained by the AAS method are higher than the values determined by the ICP-OES method, although there is one exception. In the case of mercury, the AAS method produced the results that were lower by one order of magnitude (the cold vapour method was used). In the case of non-metals (see: Table 5), we should comment on the determination of iodine by the ICP-MS method, the result of which seems to be largely undervalued. The results in Table 6 were obtained using only one test method (ICP-OES). What may seem interesting is the concentration of barium and caesium in the water (5) from Rymanów Zdrój: in case of caesium it exceeded 6 $mg \cdot dm^{-3}$ (relatively high concentration). This value can be compared to the amount of sodium in the same water (5), as determined by two methods (AAS, ICP-OES), and found to exceed 300 $mg \cdot dm^{-3}$. The sodium content in the water from Rymanów Zdrój is clearly higher, for example, compared to the content of this element in spring waters (1–4) from Lesko. Therefore, it is not surprising that the content of caesium in water is increased (5), as this element, together with sodium, is in the same group of the periodic table (i.e. it has similar properties). The same analogy can be demonstrated by comparing the concentrations of calcium and barium (the concentration of Ca is higher than 100 $mg \cdot dm^{-3}$, and the concentration of barium is higher than 2 $mg \cdot dm^{-3}$) in the water from Rymanów Zdrój, and, of course, both elements belong to the same group of the periodic table.

In Table 7, the t-test was performed for the content (concentrations) of trace elements. The test shows that for the elements of gallium, selenium, tin, and vanadium, the difference between the concentrations in Lesko and Rymanów Zdrój is statistically insignificant (the concentrations are the same). The difference in concentrations is statistically significant for the following elements: chromium, molybdenum, nickel, antimony, strontium, zircon, and their concentration is higher for Jan's water from Rymanów Zdrój than in the water from Lesko. This phenomenon is natural, because Jan's water is classed as highly mineralized spa water (1650 $mg \cdot dm^{-3}$) (Chorostyński et al., 2019). There is one exception to this rule: the concentration of uranium (U) in the water from Lesko is the only one that is higher than in the water from Rymanów Zdrój (comparative water).

The results of the analyses and the t-test concerning uranium constitute a certain hydro-geochemical curiosity, as they suggest that mineralization of rocks in this region indicates increased uranium content.

The occurrence of rocks with increased uranium content was found for the first time in Bezmiechowa Górna near Lesko in 1956, during the studies on the bituminosity of menilite shales (Kita-Badak et al., 1965).

In groundwater, uranium usually occurs in insignificant amounts, most often not exceeding the concentration of 10 $\mu g \cdot dm^{-3}$ (usually 0.1–10.0 $\mu g \cdot dm^{-3}$) (Przylibski, 2005).

Radon is formed by the successive transformations of uranium, and it is found in small amounts in air, water and soil (Przylibski et al., 2014).

In Poland, the highest concentrations of radon in abyssal waters have been found so far in the Sudetes. All the healing and potentially healing waters of the Sudetes are of infiltration origin (Ciężkowski, 1990; Paczyński and Płochniewski, 1996). Low-mineralized waters with a dissolved salt concentration below 1000 $mg \cdot dm^{-3}$ and showing radioactive activity above 74 $Bq \cdot dm^{-3}$ are treated as "specific healing radon waters" (Regulation, 2006; Regulation, 2016; Świetlik and Malik, 2012).

Due to the presence of uranium, the spring waters of Lesko may also contain radon (Eckertová et al., 2019), which gives them the potential to be used for balneological purposes.

Balneological treatments (in the form of baths, showers, inhalations, direct consumption) with the use of radon are applied, for example, in the treatment of rheumatic diseases, atherosclerosis, arterial hyperten-

Table 7. Trace elements: STUDENT's T-TEST

Element µg · dm^{-3} / Sample		Cr	Ga	Mo	Ni	Sb	Se	Sn	Sr	U	V	Zr
	1 (Xi) Lesko	4	11	27	4	77	458	158	181	15	14	102
	2 (Xi) Lesko	3	9	15	6	32	684	161	122	13	15	119
	3 (Xi) Lesko	3	8	22	3	67	146	165	260	13	15	95
	4 (Xi) Lesko	3	16	18	3	69	231	202	123	18	17	94
$\bar{X}$ (1–4) arithmetic mean		3.25	11	20.5	4	61.2	380	171	171	14.7	15.2	102
5 Rymanów Zdrój (RZ)		9	14	30	7	281	479	211	895	9	15	390
$S\bar{X}$ Standard deviation		0.25	1.78	2.59	0.70	9.00	121	105	21.7	1.18	0.63	5.78
µ real value	(RZ)	9	14	30	7	281	479	211	895	9	15	390
P trust level ν	the number of degrees of freedom	$p = 0.95$					ν = 3			($ν = n - 1$)		
t_{KR} critical value							$t_{KR} = 3.182$					
t (calculated)		–23.00	–1.68	–3.67	–4.28	–24,.2	–0.82	–0.37	–33.27	4.87	0.39	–49.73
definition of the interval		a) (–∞;–3.182] · [+3.182;+∞)						b) (–3.182;+3.182)				
statistical difference between	$\bar{X}$, µ	a) statistically significant difference						b) a statistically insignificant difference				
section		a) left	b)	a) left	a) left	a) left	b)	b)	a) left	a) right	b)	a) left
concentration	L – Lesko RZ – Rymanów Zdrój	L < RZ	L = RZ	L < RZ	L < RZ	L < RZ	L = RZ	L = RZ	L < RZ	L > RZ	L = RZ	L < RZ

sion, ischemic heart diseases, bronchial asthma and some dermatological diseases (Pachocki, 1995; Kochański, 2002; Pachocki, 2009). Healing treatments with radon for balneo-therapeutic treatments are used by the following health resorts: Świeradów Zdrój, Lądek Zdrój, and Szczawno Zdrój.

CONCLUSIONS

In the earlier studies focused on Lesko area, it had been demonstrated that there are "specific healing sulphide waters" showing low mineralization, low ORP, and light alkalinity. In this latest study, the measurements for the analysis of the elements were repeated, and the new data was interpreted, with particular reference to the differences that resulted from the applied analytical methods.

The following analytical methods were used in the research: AAS and ICP-OES. The Atomic Absorption Spectrophotometry (AAS) method is characterized by high selectivity, while also being burdened with the so-called matrix effect, which however can be eliminated by background correction or by adding matrix modifying compounds (lanthanum, caesium salts). In the analysis of elements, combined techniques such as ICP-OES are often used. Combined techniques are characterized by greater sensitivity and selectivity and a weaker matrix effect, which has a positive impact on increasing the accuracy of the obtained test results.

The most important part of the study is the analysis of trace elements concerning spring waters from Lesko and Rymanów Zdrój. The obtained results, including the results of the t-test used for their processing, showed that the water from Lesko contains more uranium (14.7 $\mu g \cdot dm^{-3}$) than the comparative water (9 $\mu g \cdot dm^{-3}$) from Rymanów Zdrój, despite the fact that the sulphide water from the health resort is characterized by a much higher mineralization and a lower concentration of hydrogen sulphide. For the analysis of both waters (Lesko, Rymanów), the same research method was used (determination of uranium concentration by ICP-OES method). Based on the literature in the field of geology, the paper reports that uranium deposits with low concentrations have been detected in the region of Lesko, not far from Lesko town (in Bezmiechowa-Manasterzec). The uranium concentration is too low for the deposit to be of industrial value. However, it may be sufficient for groundwater (spring) to contain uranium ions. Uranium is a radioactive element, and radon-222 (a noble gas) is in the radioactive sequence of its decay. In Lesko, where uranium is present, radon should be present as well. Unfortunately, in order to detect radon and prove that a spring is radioactive, it would be necessary to use radiological analysis and check whether its radioactive activity is higher than 74 $Bq \cdot dm^{-3}$ ("specific healing radon water"). The likelihood of this happening is small, due to the low concentration of uranium in the rocks. Measurement of activity would be advisable (in the form of trace detector) if the issue was to be taken up in a new study.

SUMMARY

This is already the third study on spring waters from Lesko area. In this work, three sulphide springs and one mineral spring (not containing hydrogen sulphide) from Lesko, and Jan's sulphide spring (comparative) from Rymanów Zdrój had been examined. The results of the previous analyses performed with the use of AAS and IC methods were taken into account, and, additionally, all the analysed elements (including trace elements) were determined using ICP-OES and ICP-MS. The t-test was applied for statistical analysis, which demonstrated that the concentrations of almost all trace elements in the water from Rymanów Zdrój are higher than the concentrations of these elements in the spring waters from Lesko. There was one exception: uranium concentration is higher in the waters of Lesko. Attention was drawn to the geological structure of the Bezmiechowa – Monasterzec – Lesko region, where geologists found increased uranium mineralization in the rocks. The mineralization is not so high as to be of industrial value, but it is sufficient to increase the concentration of uranium ions in the groundwater in this area. Traces of uranium can cause the presence of traces of radon-222 (radon water). Radon is in the natural radioactive decay series of uranium. The presence of even trace amounts of radon in the spring waters of Lesko may give these waters the characteristics of radon water. It is possible that the concentration of the Rn-222 radon isotope will ultimately be deemed too low for the water to meet the conditions of "specific radon water", but the issue requires further re-

search. The last section of the paper describes the healing properties of radon waters and their occurrence in health resorts.

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ANALIZA PIERWIASTKÓW ŚLADOWYCH Z ZAWARTOŚCIĄ URANU W WODACH ŹRÓDLANYCH Z LESKA Z PERSPEKTYWĄ ICH BALNEOLOGICZNEGO ZASTOSOWANIA

ABSTRAKT

Cel pracy

Celem pracy było wykonanie analizy pierwiastków śladowych – w tym stężenia uranu – w wodach źródlanych w miejscowości Lesko. Dodatkowo należało wykazać, iż podwyższone stężenie uranu w omawianych wodach źródlanych jest podstawą do przepuszczeń, że możemy mieć do czynienia z „wodą swoistą leczniczą radonową".

Materiał i metody

Na północnym skraju miasta znajdują się źródła wód leczniczych. Źródła zawierają słabo zmineralizowane wody siarczkowe o niskim potencjale redox (ORP) i lekkim odczynie alkalicznym. Wydajność tych źródeł mieści się w granicach 2–3 litrów na minutę. Stężenia pierwiastków i pierwiastków śladowych w wyżej wymienionych wodach źródlanych analizowano metodami: AAS, IC, ICP-MS, ICP-OES. Do przetwarzania wyników zastosowano statystyczną metodę testu t-Studenta.

Wyniki i wnioski

Badania statystyczne wykazują, że stężenie uranu w wodach Leska jest wyższe niż w wodach siarczkowych z Rymanowa Zdroju. Na podstawie literatury z zakresu geologii wykazano, że w okolicach miejscowości Bezmiechowa – Monasterzec – Lesko występują niskie stężenia uranu w skałach, które wystarczają, aby wody źródlane zawierały śladowe ilości uranu w postaci zjonizowanej. Podwyższone stężenie uranu sugeruje obecność radonu w badanych wodach. W przypadku udowodnienia, że radon w wodach źródlanych występuje w odpowiednim stężeniu, pozwoli to na stosowanie w/w wód jako radonowych do celów balneologicznych.

Słowa kluczowe: radon, ICP-OES, uran, wody źródlane, Lesko