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RESEARCH OF PHYSICO CHEMICAL PARAMETERS BEFORE AND AFTER THE USE OF THERMAL WATER IN THE PEJA BATH

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Abstract

With the development and growth of the population, the demand for quality and safe water increases. The desire for a healthy body, at the same time to cure various health problems and to enjoy the natural beauty pushed one for the sources of thermal water springs, mostly natural and rich in innumerable healing properties for each disease. The purpose of this study is to investigate the physicochemical parameters of thermal water in Banja e Pejes, where sampling sites are located at inlet water sources, during use and at some exit points after thermal water has been used by the hospital for the treatment of several different diseases. A total of 12 samples were taken in this paper. dated: 23.12 2020, where samples are in three time frames 4 samples are taken at 8:00 am, the other 4 samples were taken at 11:00 am, and the last 4 samples were taken at 16:00 pm. The assays were performed with the most advanced methods at the University of Mitrovica Laboratory, we used spectrophotometric method, comparative method and in very rare cases standard classical method of analysis. In this case we have determined: temperature, dissolved oxygen, pH, electrical fluidity, odor, taste, turbidity, nitrates and nitrite. The purpose of this research is to analyze thermal waters before and after use by the Banja e Pejes and their discharge into the environment where it can have consequences for both flora and fauna may also have an impact on the waters used for drinking where the day by day is further reduced.

Keywords*:* *water terminal, physic chemical analysis, quality of various diseases, health treatment.*

Introduction

It is estimated that about 25 to 40 % of rainfall and other rainfall in temperate regions is absorbed (penetrates) into the soil. On the way to the groundwater, groundwater loses a lot of organic matter and at the same time digests more or less minerals such as: sodium, calcium, magnesium, CO_2 [1-3].

The deeper the water penetrates the more amount of matter it will digest. Water under high pressure is a strong solvent. Groundwater with the highest content of dissolved mineral salts is called mineral water. Water from mineral springs is often named after some special ingredient, which is dissolved in water, or from the locality of the spring. Groundwater which contains large amounts of salts and carbonic acid is mineral water [4-6]. Groundwater can contain some natural impurities or pollutants even without the impact of human activities. Natural pollutants are usually dissolved salts of alkali Na and K and alkaline-earth metals Ca and Mg [7]. Some groundwater contains harmful elements such as arsenic, or radon, a gas formed by the natural decomposition of radioactive uranium in the earth [8].

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The territory of Kosovo is rich in thermal and mineral water resources, where so far there has been very little research to identify and study the values of these springs [9-10]. According to the data so far in Kosovo are registered about 30 springs of thermal and mineral waters. More detailed research has been conducted only for the waters of Peja, Kllokot and Banjska Spas, which function as thermal healing baths. In addition to the healing aspect, Kosovo's thermal waters can also be used for the production of thermal energy, but so far there has been no detailed study to analyze the production potential of these waters. In general, the temperature of Kosovo thermo-mineral waters ranges from 17-54 °C, while the degree of mineralization from 2-5 g/L. Thermal and mineral water springs in Kosovo contain sulfates, hydrocarbons, calcium and magnesium [11].

Thermal waters are very rare but very precious around the world, in Kosovo there are several thermal springs among which the most famous are: Thermal water in Peja Spa "ONIX", Kllokot Spa "Mother Naile", and Dobërqan Spa [16]. It dates from 1936 when the first hotel was built (Ilingja). As a rehabilitation institution which uses natural hot mineral water from its source, where it was expanded with three other hotels to provide rehabilitation medical services and physical therapy. The new enterprise covers a land area of approximately 26 hectares including about 38000 m^2 area of facilities. Peja Spa is located in the western part of Kosovo, where it presents an impressive environment not only as a natural value, as a landscape with a suitable continental climate, but also with the resources it has and which make it be valued as a natural wonder, as the most unique bath in the whole Balkans [17]. Peja Spa lies at an altitude of 540 m and has a mild continental climate characterized by a Mediterranean climate. Winters are short and mild, while summers are long and warm with mild coolness. Of all the climatic elements, the air temperature has the greatest influence, where this more than any other factor, determines the length and quality of the tourist season, whether it is summer or winter. Peja Spa is very little affected by the release of carbon dioxide gases and other engine noise [18].

The water of Baja e Pejës has pH = 6.9. Since 1957, the Belgrade Medical Institute has conducted in-depth analyzes of thermal water and identified that water can treat diseases such as: rheumatism, sciatica, some skin diseases, some nerve diseases, some bone diseases, some chronic diseases of women, as well as helps to heal injured bones, moreover, within the lake many therapeutic physical surgeries of rehabilitative medicine are enabled through bathing, gymnastics, massage and other practices [13-15]. This water has been used extensively as a bath for external use, and very little is known for drinking. But recent analyzes and reports from internationally renowned institutes and laboratories such as the Institute for Analysis, Fresenius based in Berlin, and Balneological Reports for thermo-mineral waters in Europe, report that the thermal water of Peja Spa can also be used for drinking for treatment of some diseases as well as for inhalation. The water of Peja Spa has aroused great interest from many institutions not only European but also beyond. Thermal water can be used for health purposes such as drinking, inhaling and bathing. Services performed in Baja e Pejës are: full board accommodation, diagnosis by specialist doctors, banjotherapy, thermotherapy, electrotherapy, physical therapy, massage [12].

Banja e Pejës has a professional medical team with many years of experience. This team consists of specialist physiatrists, rheumatologists, physiotherapists, masseurs, nurses, laborers and pharmacists. The thermal water of this bath belongs to the group of healing waters of calcium and magnesium bicarbonate.

Its temperature is 48 °C with a capacity of 18 L/sec. The thermal water of this Bath is compared to over 500 other healing waters in the world and recent reports of international experts emphasize that this water is quite unique and special in chemical content

Experiment and Methods

The experimental part of this paper was performed in the laboratory of the University of Mitrovica, at the Faculty of Food Technology. During the research work and physic chemical analysis of thermal water in Peja Spa, different physic chemical methods of analysis have been applied such as: (turb, pH-meter, conduct meter and spectrophotometry). The place where the thermal water samples are taken for analysis depends on the quality of the source at the outlet points at which the samples are analyzed.

For the realization of this work, we have used modern methods of determining the parameters, such as: spectrophotometric method, comparative method, and in very rare cases the standard methods of analysis. To determine the parameters of thermal water samples in Peja Spa we have used the following apparatus and instruments:

- Jen Measurement of Dissolved Oxygen with Oxygen meter.
- Measurement of electrical conductivity where the Conductor Meter is used,
- We measured the pH with a pH meter,
- Nitrates and Nitrites with Spectrophotometer 0R-900.
- We measured the Turbidity with a Turbometer, Thermo Scientific.

Sampling was done in Peja Spa where there is a source of thermal water called rehabilitation water and cures for many different diseases, called Special Hospital for General Rehabilitation "ONIX SPALLCE", where 12 samples were taken at different time intervals so we analyzed the change of physic chemical parameters of thermal waters. The first sample was taken at springs before being taken for use by the hospital, the second sample was taken at the first exit after being used by the hospital, the third and fourth samples were taken at a distance of 100 m from each other. All samples were taken within one day on 23.12.2020 at different time intervals, where the first 4 samples were taken at 8:00 in the morning, the other 4 at 11:00 and at 16:00 4 were taken. recent samples.

The water temperature is also variable (depending on the annual period), which is also hygienically appropriate. As a result of the presence of these compounds may appear unpleasant taste, odor and color of water.

For the collection and treatment of water samples was acted according to the standards for water sampling of the Water Center which are defined by Administrative Instruction AI- No.16 / 2012 On the quality of water for human consumption, approved by the Government of Kosovo in December / 2012, and the sampling procedure according to ISO 5667-5: 2006 in accordance with ISO 17025 as well as Guidelines from the World Health Organization, WHO (WHO, 1997).

The method of sampling is as important as the analysis, so maximum care should be taken not to contaminate the sample during sampling and transport to the laboratory are:

- *Step first* - taking 3 samples from 1L where the water is taken in clean bottles which before filling are rinsed two or three times with the same water that will be analyzed;
- *Step two* - After sampling, the bottle is closed with a cap, which indicates the place of sampling, date, time, water and air temperature;
- *Step three* - Sending samples to the laboratory for the determination of physic chemical analyzes and for the determination of heavy metals.

Temperature is one of the most important parameters. Temperature has an effect on most chemical reactions which occur in natural aquatic systems. Temperature also has a pronounced effect on the solubility of gases in water. Most chemical reactions involving the decomposition of solids are accelerated by raising the temperature. On the other hand, gas solubility decreases at high temperatures. Cold water contains more soluble oxygen than hot water. Temperature is important factors that affect the taste of thermal water. Thermometers are used to measure it. Temperature determination for all samples was done in the field during sampling, where after flow 3 to 5 minutes the temperature was measured.

Fragrance is determined immediately after sampling or within two hours. To evaluate the aroma and taste we use the evaluation system with 0 to 5 points. It is determined visually by raising the bottle high behind a white background to see if the sample is colored.

The determination of water taste is done before performing the analyzes. We should not consume food or drink anything sweet, salty or sour. To test the taste of water, take the amount of water for analysis and put it in the throat, where the throat is rinsed and then we hold it a little on the tongue, so in this form we determine the taste of the water. The determination of the pH is done in this way: in a laboratory glass with about 100 ml of distilled water we make the measurement, where it serves as a blind sample where then, in the water sample for analysis is placed the electrode of the pH-meter prepared for measure and read the pH value at its scale.

First, we do the verification of the instrument (conduct meter) by calibrating the instrument, where the electrode is immersed in a glass of distilled water that should have a conductivity of 1 to 3 μS/cm. The electrode or probe is taken from the distilled water and inserted into the water sample for analysis and the conductivity reading is done on the conduct meter scale.

Nitrites NO_2 and Nitrates NO_3 are worked on the photometer, the apparatus reads the result in the penetration of ultraviolet UV rays through the prepared solution. The photometer is a product of MERK and the reagents used for the analysis must be of the same company.

The instrument for measuring turbidity is called a turbid meter. First, the instrument (turbid meter) is activated where the standard solution is placed (polymer foramina is used as a standard for turbidity suspension) in the instrument housing with measuring unit 0.61 NTU or 10 NTU where the instrument calibration is performed. Then we take the container (cuvette) with a sample of 25 ml of water, the sample is mixed well, the air bubbles are expected to be removed, and the result is read, we also repeat the same action for all samples by re-reading the result.

The concentration of dissolved oxygen is an indicator of water quality. Water in contact with atmospheric oxygen, at a certain temperature, pressure and concentration of salts, absorbs a certain amount of atmospheric oxygen. If the water is contaminated with reducing substances, the oxygen concentration will decrease. The larger the difference between the expected oxygen concentration and the oxygen concentration found, the worse the water will be.

Chlorides are determined by the Mohr method, between neutral and weak basal, in the presence of potassium chromate as an indicator, as well as by the potentiometric method with ion-selective chloride electrode in the Titration DMF-785 potential graph of Mohr with the dynamic method of DET titration.

Water hardness is the total amount of alkaline-earth metals present in water. It is assumed that they are only salts of Ca and Mg, because there are no salts of other alkaline earth metals in the water. Water hardness is expressed in degrees of hardness: German degree °D, French degree °F or English degree °E.

During the experimental part, the physic chemical parameters of the thermal water in Peja Spa were determined. The obtained results are presented below in the Table 1, Table 2 and Table 3.

Table 1. Determination of physic chemical parameters at 08:00

Settings	Standard Method	Unit	Values	M1	M2	M3	M4
Temperature		^{O}C	8 - 12	48	37.8	29	23
Aroma				Smell the eggs	/	/	/
Taste				/	/	/	/
Turbidity	ISO 7027:1999	NTU	1.0 NTU	7.13	1.67	1.6	1.26
Color		Co - Pt	10 - 20	/	/	/	/
pH	ISO10523:2008	pH	$\geq$ 6.5 - $\leq$ 9.5	6.4	6.84	6.86	6.95
O_2 Cost	ISO71505:1986	mg/l	8 - 12	13.42	12.49	11.57	11.31
Chlorides	ISO 9297:1989	mg/l	5 - 250	2.83	3.54	6.67	6.38
NO_2	ISO 6777:1984	mg/l	0,50	/	/	/	/
NO_3	ISO78902:1988	mg/l	50	1.5	2.1	1.8	2.8
Electrical Conductivity	ISO27888:1985	$\mu S/cm^{-1}$	2500	1749	1406	1429	1277
Water hardness		^{O}dH	5 - 30	17.48	22.54	26	23.5

Table 2. Determination of physic chemical parameters at 11:00

Settings	Standard Method	Unit	Values	M1	M2	M3	M4
Temperature		^{O}C	8 - 12	48	35.2	27	22.4
Aroma				Smell the eggs	/	/	/
Taste				/	/	/	/
Turbidity	ISO 7027:1999	NTU	1.0 NTU	7.13	2.66	1.52	1.68
Color		Co - Pt	10 - 20	/	/	/	/
pH	ISO10523:2008	pH	≥ 6.5 - ≤ 9.5	6.4	7.13	7.31	7.14
O_2 Cost	ISO71505:1986	mg/l	8 - 12	13.42	8.49	8.92	9.40
Chlorides	ISO 9297:1989	mg/l	5 - 250	2.83	2.83	2.12	2.12
NO_2	ISO 6777:1984	mg/l	0,50	/	0.001	/	0.001
NO3	ISO78902:1988	mg/l	50	1.5	3.1	2.7	3.2
Electrical Conductivity	ISO27888:1985	$\mu S/cm^{-1}$	2500	1749	1725	1530	1325
Water hardness		^{O}dH	5 - 30	17.4	27.4	30.13	42.8

Table 3. Determination of physic chemical parameters at 16:00

Settings	Standard Method	Unit	Values	M1	M2	M3	M4
Temperature		^{O}C	8 - 12	48	35.8	27	22.4
Aroma				Smell the eggs	/	/	/
Taste				/	/	/	/
Turbidity	ISO 7027:1999	NTU	1.0 NTU	7.13	1.49	1.66	1.10
Color		Co - Pt	10 - 20	/	/	/	/
pH	ISO10523:2008	pH	≥ 6.5 - ≤ 9.5	6.4	7.09	7.20	7.10
O_2 Cost	ISO71505:1986	mg/l	8 - 12	13.42	10.10	10.23	10.35
Chlorides	ISO 9297:1989	mg/l	5 - 250	2.83	3.54	4.25	4.25
NO_2	ISO 6777:1984	mg/l	0,50	/	/	/	/
NO_3	ISO78902:1988	mg/l	50	1.5	2.3	2.3	2.5
Electrical Conductivity	ISO27888:1985	$\mu S/cm^{-1}$	2500	1749	1771	1626	1346
Water hardness		^{O}dH	5 - 30	17.48	36.1	39.3	42.8

Results and Discussions

In the part of the experimental work during the drafting of this paper, a total of 12 samples of thermal water were taken in the Peja Spa. Samples were taken in three-time frames: 8:00 in the morning at 11:00 and 16:00 on 23.12.2020. From the obtained result, the assessment of the condition of the thermal water quality was made.

Temperature from the results obtained during the experimental work we notice that the temperature in the first three samples M1, M1, M1 did not change, while in the other subsequent samples (M2, M3, M4) in the three-time intervals we have a decrease in temperature.

Aroma from all samples taken we noticed that only at the source the first samples (M1, M1, M1), had a smell of rotten eggs while the other outgoing samples did not smell Aroma. Blur in terms of visibility we noticed that in the first samples M1, M1, M1 the transparency does not change, while in the following samples (M2, M3, M4) in the three different time frames the transparency values decrease.

pH- In the first three samples M1, M1, M1 in time frame the pH value is the same as corresponding to a degree of weak acidity, while in the samples M2, M3, M4 in different time intervals pH values have a steady increase in light that responds to a weakly acidic environment by switching to a strong basic environment.

Oxygen consumption, in terms of elemental oxygen O2 in the first three-time intervals the first samples M1, M1, M1 are unchanged. While in the samples M2, M3, M4 that belong to the time period of 11:00 we have a decrease of oxygen, while the samples M2, M3, M4 of 16:00 we have a decrease of oxygen compared to the samples of the hour 8:00 while we have oxygen increase compared to 11:00 samples.

Chlorides also in the first three samples M1, M1, M1 in three different time frames the value of chlorides is unchanged. While M2, M3, M4 chloride values start to fall in the samples at 11:00, while in the samples at 16:00 the chloride values have a slight increase compared to the samples at 11:00.

Nitrates NO3 in three-time frames in the first three samples M1, M1, M1 their values are the same, while in the samples M2, M3, M4 belonging to 11:00 the values of Nitrates are higher than the samples belonging to 8:00 and 16:00.

Electrical conductivity, electrical conductivity values in samples M1, M1, M1 in three-time intervals is unchanged, while samples M2, M3, M4 belonging to the time period 8:00 their values are smaller than compared to 11:00 and 16:00 samples.

The strength of thermal water in the three samples M1, M1, M1 of different time periods are the same, while the values of the samples M2, M3, M4 belonging to the time period 16:00 are higher compared to the values of samples at 11:00 and 8:00.

Conclusion

During the research work in this study, 12 samples of thermal waters were taken in Peja Spa, where we made the analysis of physic chemical parameters. After the analysis, the results obtained were compared with the values analyzed at three different time intervals. Where we came to the conclusion that the samples at the springs in the three-time intervals have not changed the proven parameters as the source is isolated and there is no factor which allows the water to have any change in the physic chemical parameters.

Samples taken at the exit points at three-time intervals after the water was used by the hospital for the treatment of many diseases cured by thermal water, we noticed changes in physic chemical parameters at the three points of the place of sampling. During the research of the samples in three-time intervals 8:00, 11:00, 16:00, we came to the conclusion that the biggest changes in the three-time frames are those of 11:00 and 16:00, as the number of visitors or patients who use thermal water for the treatment of many diseases and for this reason affects the change of physic chemical parameters, while at 8:00 the number of visitors is lower in the Onyx hospital in Peja Spa compared to the other two-time intervals.

From the obtained analyzes we see that the quality of thermal water at the exit points factor of change of parameters are the treatments which are used to cure many diseases, thermal water after use by the hospital it is thrown out of the pipe which is directly discharged into the environment where there may be Adverse effects on flora and fauna but may also be found in drinking water as this water belongs to the group of waters which contain: Calcium and Magnesium bicarbonates.

References

[1] Dakoli, H. and Xhemalaj, Xh. *Hydrogeology,* 1997, Tirana, Albania, pp. 45-65.

[2] Hoxha B. *Analytical chemistry - the practical part*, 1999 Pristina, Kosovo, pp. 25-28.

[3] Dalmacia, B. *Kontrolla kvaliteta voda*, 2000, Novi Sad, Serbia, pp. 67-70.

[4] Korça B. *Chemical Analysis of Water*, 2001, Pristina, Kosovo, p 32-39.

[5] Çullaj, A. *Environmental Chemistry*, 2003, Tirana, Albania, pp. 85-97.

[6] Korça, B. *Chemical Analysis of Water*, 2003, Tirana, Albania, pp. 17-32.

[7] Çullaj, A. *Instrumental methods of chemical analysis,* 2004, Tirana, Albania, pp. 37-40.

[8] Davis, M.L. and Masten, S. *Principles of Environmental Engineering and Science*, USA, 2004.
[9] *Kosovo Environmental Action Plan 2006-2010*, MMPH/REC, 2006 Pristina, Kosovo.
[10] MMPH, *State of the environment report 2006/2007*, 2008, Pristina, Kosovo.
[11] REC, *Progress monitoring report*, 2008, Pristina, Kosovo.
[12] Simunic, A. *Geotermalne i mineralne vode*, 2008, Zagreb, Republic of Croatia, pp. 182-193.
[13] Cullaj, A. *Environmental Chemistry*, 2010, Tirana, Albania, pp. 125-128.
[14] Shallari, S. *Environmental Assessment and Management*, 2013, Tirana, Albania.
[15] Frashëri, A. *Geothermal Atlas of Albania*, 2013, Tirana, Albania, pp. 83-85.
[16] http://onixspa.com.
[17] http://www.nenanaile.com.
[18] https://bajaedoberqanit.weebly.com/sheumlrimet-e-bajeumls.html.

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