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STUDY OF BIOLOGICALLY ACTIVE IONS IN THE WATERS OF THE SPRINGS IN LASURIASHI AND MAKHASHI VILLAGES, TSAGERI MUNICIPALITY, GEORGIA

Abstract: *The first hydrological and chemical investigation of the spring waters from Lasuriashi and Makhashi villages in Tsageri Municipality was conducted at the Hydrochemistry Laboratory of Akaki Tsereteli State University. The biologically active ions analyzed include: pH, water hardness, calcium, magnesium, chloride, bromide, bicarbonate, and ammonium ions, total hardness, permanganate oxidizability, dissolved oxygen, biochemical oxygen demand (BOD5), and carbon dioxide content. The analysis was performed using well-tested, simple, rapid, and* *reliable chemical, physicochemical, and photometric methods. Among the biogenic substances, nitrite ions were determined using the photometric method.*

Based on the experimental data, it was found that the water from the studied springs is low in mineralization, making its pH nearly neutral. The concentration of the above-mentioned ions in the studied waters is within the normative range and in compliance with the Georgian drinking water technical regulations, with some exceptions. The total iron content in the Lasuriashi and Gharis springs is within the norm, while in the Batoni Kalo spring, it is 0.036 mg/L, exceeding the standard regulation. The bromide ion content in the studied waters exceeds the standard norm, with a concentration of 0.336 mg/L in the Lasuriashi spring. As for the total hardness, it is within the norm at 0.029 mg/L in the Gharis spring, but a higher concentration of total hardness is recorded in the Batoni Kalo and Lasuriashi springs, at 0.041 and 0.038 mg/L, respectively.

Since the total iron, bromide ion, and total hardness content in some samples slightly exceed the standard limits, their use for drinking and household purposes is recommended, but should be approached with caution. Analytical samples were also tested for NO_2 content using the Gris reagent. Only the Gharis spring exhibited a reddish-purple coloration, confirming the presence of nitrite ions. The hydrological and chemical study of the spring waters from Lasuriashi and Makhashi villages, Tsageri Municipality, continues.

Objective: The objective of the study was to examine the chemical composition of the spring waters of Lasuriashi and Makhashi villages in the Cageri municipality. To this end, a hydrochemical analysis of the spring waters was conducted. The significance of this study lies in the fact that for the first time, the hydrochemical composition of these waters has been determined, for which highly sensitive methods were selected. The analyses were carried out in the Hydrochemistry Laboratory named after Iason Moseshvili at the Department of Chemistry, Faculty of Exact and Natural Sciences, Akaki Tsereteli State University.

Key words: *Lasuriashi, Makhashi, Ghar, Gativra, Indicator, Water, Spring, Methodology, Salts, Hardness.*

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Introduction

Water is an invaluable resource. During rainfall, most of the water penetrates into the soil, first passing through the soft layers, and then deeper into the ground. It filters through sand, pebbles, and stones – this is how the water gets purified. Eventually, it reaches a layer that does not allow water to pass through. Sometimes the underground layer is inclined, causing the water to flow through it, and eventually, it may even rise to the surface. This process forms a spring. A spring is cold and clean.

Pic.1. Cageri Municipality

A spring is a natural exit point for underground water to surface. People use spring water for drinking. During its movement through the soil crust, water absorbs many substances, including salts, which results in the formation of a defined composition. The amount of salts in the water varies widely, with their total concentration, i.e., mineralization, being relatively low in surface waters and significantly higher in underground waters.

Water is widely and diversely used. Modern humans can influence the biosphere and utilize its resources to develop production and create material well-being.

The content of calcium and magnesium salts gives natural water its hardness. When water containing CO_2 comes into contact with limestone layers, carbonates are converted into bicarbonates, which dissolve well in water. Water has some chemical anomalies, which are especially evident in its density.

It is known that, starting from 1000 C, as water cools, its density gradually increases and reaches a maximum at +4°C. If water did not have this property, it would freeze at the surface of water bodies in winter and eventually freeze through the entire depth, causing the death of all living organisms. This anomaly is caused by the arrangement of water molecules – a specific "structure" that changes with temperature. The structure of the molecules in ice is the least dense. When ice melts, the molecular structure is disrupted and becomes denser, which is why water has a greater density than ice.

The anomalies of water are influenced by dissolved salts, so the temperature variations in seawater change its density in a unique way. As the temperature decreases, the density of seawater increases, and it continues in one direction. Unlike pure water, seawater does not have the +4°C density limit. During winter, the surface water cools down and becomes denser, which causes the colder surface water to sink into the deeper layers, carrying dissolved oxygen necessary for marine animals. Due to the high concentration of salts, seawater does not freeze at 0°C, like pure water, but at a significantly lower temperature.

Cageri Municipality

To the west, Cageri Municipality borders Martvili, to the north, Lentekhi, to the east, Ambrolauri, and to the south, the municipalities of Tskaltubo and Khoni. The territory of the municipality corresponds to the Cageri Basin, which is surrounded by mountains of varying heights, including the eastern part of the Egrisi Range—comprising the Tsekuris, Sazamtros, and Sakheris massifs. These massifs are characterized by old glacial formations and deeply fragmented rocky reliefs. On the western side, the eastern branches of the Askhi Massif are raised. In the southern part of the municipality, between the Rioni and Tskhenistskali river valleys, Khvamli is located on the southern extension of the Nakerala Ridge. Its southern slope is steep and rocky.

Along the Rioni River, low to medium-height mountains, separated by deep valleys, stretch out. The extensive Cageri Basin, which is crossed by the Tskhenistskali River, begins from the Muri Cliff and extends southward to the Saretskeli Cliff. Both cliffs are cut into solid, tough limestone. The eastern boundary of the Cageri Basin is formed by the middle Lechkhumi Ridge, which separates it from the Orbeli Basin. To the east, the Rioni River creates the Tvishi Cliff within the limestone layers. The basin's floor is covered with alluvial soils, while its mountain slopes are dominated by forested and cordian-carbonate soils. The higher mountains have an upper belt of alpine forest with sparse and disturbed forested areas, as well as cordian and cordian-peat alpine meadow soils. Steep, rocky areas are completely devoid of a soil cover.

The municipality belongs to the humid subtropical maritime climate zone, where air temperature and atmospheric precipitation vary significantly with altitude. The maximum precipitation occurs in autumn, while the minimum occurs in summer. In the mountainous areas, air temperature decreases, and precipitation increases. The main rivers are the Rioni and Tskhenistskali. The largest tributary of the Rioni is the Jonoulula, and the largest of the Tskhenistskali is the Lajanura. The rivers are fed by rain, snow, and groundwater. The Tskhenistskali and Rioni also receive water from glacier melt in their upper reaches. Some smaller rivers exhibit karstic behavior, while others show flash-flood characteristics. The rivers experience flooding in spring, with higher water flow in summer and autumn.

Experiment Review: In the spring waters of Lasuriashi and Makhashi villages in Cageri Municipality, for the first time, the following were determined: pH, water hardness, Mg2+, Ca2+, total iron, Cu2+, HCO3-, Br-, total chloride, permanganate oxidation, dissolved oxygen, BOD5, and free carbon dioxide levels, using chemical and photochemical methods. The analysis results are presented in Table N 1.

Table 1. Results of Hydrochemical Analysis of the Spring Waters of Lasuriashi and Makhashi in the Cageri Municipality

N	Angular name of spring waters	pH	mg-eq./L	mg/L														
			Water hardness	Mg^{2+}	Ca^{2+}	Common iron	Cu^{2+}	Cl^-	Br^-	HCO_3^-	SO_4	Free CO_2	Open oxygen	SBM5	Oxidation of permanganate 02	NH_4^+	Common arsenic
1	Baton-Kalos	7,2	4,76	11.71	76,00	0,036	-	23,57	0,127	5,23	0,248	1,06	2,88	21,63	2,16	-	0,041
2	Lasuriashi	7,3	4,08	11,72	62,40	0,142	0.002	13,06	0,335	4,34	0,320	2,22	2,11	19,20	4,00	-	0,038
3	Gharis	7,0	3,53	8,88	56,00	0.014	-	15,05	0.205	5,96	0,182	1,10	2,08	23,36	1,28	0.46	0,029

The pH of the investigated spring waters ranges from 7.0 to 7.3.

The hardness of the water is relatively higher in the Bato-Kalos spring, with 4.76 mg/L. The hardness is lower in the Gharis spring, with 3.53 mg/L.

The magnesium ion concentration is highest in the Lasuriashi spring, at 11.72 mg/L. The lowest concentration is found in the Gharis spring, at 3.53 mg/L.

The ion concentration also varies. The higher concentration was recorded in the Bato-Kalos spring, with 76.00 mg/L, while the lowest concentration was found in the Gharis spring at 56.00 mg/L.

The total iron concentration is higher in the Bato-Kalos spring at 0.036 mg/L, and lower in the Gharis spring at 0.014 mg/L.

Cu^{2+} was found in the Lasuriashi spring at 0.002 mg/L.

The chloride ion concentration is higher in the Bato-Kalos spring at 23.57 mg/L, while it is lower in the Lasuriashi spring at 13.06 mg/L.

The bromide ions are more concentrated in the Lasuriashi spring, with 0.335 mg/L, while they are less in the Bato-Kalos spring, with 0.127 mg/L.

The highest concentration of bicarbonate ions was found in the Gharis spring at 5.96 mg/L, while the lowest concentration was recorded in the Lasuriashi spring at 4.34 mg/L.

The sulfate ions have a relatively high concentration in the spring lasuriash waters, with a maximum of 0.320 mg/L.ow concentrations of sulfate ions are found in the Gharis spring 0,182 mg/L .

The highest concentration of free carbon dioxide is found in the Lasuriashi spring at 2.22 mg/L. The lowest concentration of free carbon dioxide is found in the Bato-Kalos spring at 1.06 mg/L.

Dissolved oxygen concentration is higher in the Bato-Kalos spring at 2.88 mg/L, while a relatively low concentration is found in the Amalion spring at 1.34 mg/L.

The BOD_5 is highest in the Gharis spring at 23.36 mg/L, and lower in the Lasuriashi spring at 19.20 mg/L.

The permanganate oxidation demand is highest in the Lasuriashi spring at 4.00 mg/L, with a lower concentration in the Gharis spring at 1.28 mg/L.

The total dissolved salts concentration is highest in the Bato-Kalos spring at 0.041 mg/L, while it is lower in the Gharis spring at 0.029 mg/L.

The NH_4^+ concentration was detected only in the Gharis spring, with 0.46 mg/L.

Experimental Part. Methodology for Determining Chemical Elements in Water

The analysis was conducted at the Analytical Chemistry Laboratory of Akaki Tsereteli State University in Kutaisi. The methods used in this study are validated in hydrochemical practice [5,6,7,8].

The pH was measured using the potentiometric method.

The concentrations of Ca^{2+} and Mg^{2+} ions, as well as the total water hardness, were determined by complexometric titration using a 0.01N complexone III solution. For magnesium ion determination, Eriochrome black T was used as an indicator, and ammonia buffer was prepared to create the recommended reaction area. Calcium ions were determined using Merexide as an indicator, and a 2N sodium hydroxide solution was used to prepare the alkaline solution.

The total iron concentration was determined by spectrophotometric method, following preliminary oxidation in an alkaline medium (using the photometric reagent Sulfosalicylic acid).

Cu^{2+} was determined using the spectrophotometric method in an alkaline solution (with ammonia) using sodium N,N-diethylthiocarbamate as a reagent.

Bicarbonate ions (HCO_3^-) were determined using the acidimetric method, with a titrant of 0.1-0.01N and methyl orange as the indicator.

Chloride ions (Cl^-) were determined by the mercurometric method, using a 0.01N titrant and diphenylcarbazole as the indicator.

Sulfate ions (SO_4^{2-}) were determined by classical gravimetric method, with the precipitate forming a solid form.

The total dissolved salts were determined by iodometric titration, using a 0.05N iodine solution and starch as the indicator.

The NH_4^+ ion concentration was determined using the alkalimetric method, by adding formaldehyde in a neutral solution, followed by titration with 0.1N NaOH solution until a weak reddish color appeared (with phenolphthalein as the indicator).

Free carbon dioxide was determined using the alkalimetric method, with titrant concentrations of 0.1-0.01N. The sample was treated with small amounts of segment salt and phenolphthalein as an indicator.

The oxidation demand was determined using the permanganometric method (with a 0.01N oxidizing agent in an acidic solution).

Dissolved oxygen and BOD_5 were determined by iodometric method, using a 0.01N titrant in an alkaline medium. Oxygen in water reacts with manganate ions and forms a compound that is oxidized under acidic conditions, generating a yellow color. [6, 9, 10]

Bromide ions were determined by iodometric method, using sodium hydrophosphate, sodium hypochlorite, and sodium formate. The sample was heated, cooled, and then treated with potassium iodide, sulfuric acid, and ammonium molybdate. A 0.01N titrant was used, with starch as an indicator. Bromide ions were oxidized to bromate ions.

NO_2^- ions were detected using a characteristic reaction with Gris's reagent, producing a reddish-violet color under acidic conditions (using universal indicator paper). [5]

Conclusion:

The results of the hydrochemical analysis of the spring waters in the villages of Lasuriashi and Makhashi in Cageri Municipality show that the pH, water hardness, calcium, magnesium, chloride, bicarbonate, permanganate oxidation demand, dissolved oxygen, BOD_5, and free carbon dioxide levels are in line with the technical regulations for drinking water in Georgia, with some exceptions.

The total iron concentration in both the Lasuriashi and Gharis springs is within the normal range. However, the concentration of total iron in the Bato-Kalos spring (0.036 mg/L) exceeds the technical regulation limits.

The bromide ion concentration exceeds the standard in the Lasuriashi spring (0.336 mg/L).

Regarding total dissolved salts, the concentrations in the Gharis spring (0.029 mg/L) are within the standard range, while the concentrations in the Bato-Kalos and Lasuriashi springs (0.041 mg/L and 0.038 mg/L, respectively) are slightly above the norm.

Due to the slight exceedance of the iron, bromide, and total dissolved salts concentrations in some samples, their use for drinking and agricultural purposes is still considered acceptable.

Only in the Gharis spring was the presence of nitrite ions detected, as confirmed by the appearance of a reddish-violet color using Gris's reagent.

The hydrochemical investigation of the spring waters of Lasuriashi and Makhashi in Cageri Municipality continues.

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