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Original scientific paper

DETERMINATION OF MINERALS IN SPRING WATER IN SOUTHWESTERN AND PELAGONIA REGION OF NORTH MACEDONIA

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ABSTRACT

Spring water quality can vary widely with geography, geology, and proximity of pollution sources. In the rural area, the population more often consumes spring water then in urban area. Because of that, there is a need to make a regular assessment of the water quality and prevent its consumption in the case of presence of mineral and organic species in concentrations that are higher than those recommended by the World Health Organization (WHO). In this work spring water from 5 springs in southwestern and Pelagonia region was analyzed for mineral content (Ca, K, Mg, Mn, Fe, Cu) by Atomic Absorption Spectrometry. The obtained results point out that the concentration of manganese in each sample is higher than the maximum acceptable concentration for manganese in drinking water (0.05 mg/L). Especially in the sample 5, where the concentration of manganese is 1.73 mg/L. In this water sample, also the concentration of potassium (80.22 mg/L) is very high compared with the other samples. The concentration of iron is in the range of acceptable values, except for the sample 5 where its concentration is 6.41 mg/L which compared with the maximum acceptable concentration for iron (0.2 mg/L) is very high. The pH value for all samples was in the allowed range.

Key words: atomic absorption spectrometry, mineral content, spring water, water.

INTRODUCTION

Water is a life sustaining drink and it is essential for the survival of all organisms. The assessment of drinking water quality and its continuous monitoring it is tremendously important (Kullar et al., 2019). The primary sources of drinking water are groundwater and surface water. Another source of water for individual water supply is natural springs. A spring is groundwater that reaches the surface because of the natural contours of the land. The quality of the water depends on the source. Surface water (lakes, reservoirs, streams, and rivers), is generally of poor quality and requires extensive treatment. Groundwater, is of better quality, while spring water is of varying levels of quality.

Public water supplies are monitored by Food and Veterinary Agency of North Macedonia. Private drinking water systems and mountain springs are not monitored frequently and it is up to the owner or consumer to test and treat their water. Trace metals are required by the body in small amount for various metabolic activities, but at high concentrations, they can cause adverse effects to the body. Calcium (Ca) is one of the most abundant minerals in water. Ca is present in all water samples, but the concentration varies depending on the source. There is no evidence that the calcium in water is harmful to human health.

In fact, some studies have shown that calcium from water may actually be beneficial (Cormick et al., 2020). Potassium (K) is an essential element in humans and it is seldom found in drinking water at levels that could be a concern for human's health. However, the potassium content in spring water should be monitored because increased exposure to potassium could result in significant health effects in people with kidney disease or other conditions, such as heart disease, coronary artery disease, hypertension and diabetes (Arega, 2020). Drinking water can contain moderate to high levels of magnesium (Mg). In some studies, it was found that magnesium could potentially prevent 4.5 million heart disease and stroke deaths per year, worldwide (Rosanoff, 2013). Manganese (Mn) is commonly present in air, soil, food, and water. It is an essential nutrient, but in excess can also interfere with the normal function of the nervous system (Avila et al., 2013). At low concentrations, iron (Fe) plays an important role in metabolic and fermentation processes, as an enzyme activator, stabilizer and functional component of proteins. At higher concentrations, however, iron can be toxic (Tautkus et al., 2004). Copper (Cu) enters the environment via different human and natural activities. Cu is a heavy metal required by the body in very small amounts. When people are exposed to Cu at high levels it causes health problems like vomiting, nausea, blood cell damage, and kidney failure (Zhong et al., 2016). Thus determination of trace amounts of copper in different matrices is of great significance (Bagherian et al., 2019).

Another important parameter which should be addressed in the case of the drinking water is its hardness. Hard water is high in dissolved minerals. The simple definition of water hardness is the amount of dissolved calcium and magnesium in the water. Hardness is most commonly expressed as milligrams of calcium carbonate equivalent per liter. Water containing calcium carbonate at concentrations below 60 mg/L is generally considered as soft, 60–120 mg/L, moderately hard, 120–180 mg/L, hard, and more than 180 mg/L, very hard (McGowan & Harrison, 2000). Flame atomic absorption spectrometry (FAAS) is one of the most used techniques for determining various elements in water with significant precision and accuracy. This analytical technique is remarkable for its selectivity, speed and relatively low operational cost. The aim of this work was to assess spring water quality in rural area by means of FAAS.

MATERIAL AND METHODS

Materials

In this work various spring water samples were analyzed. Water samples were collected from five springs in southwestern and Pelagonia region of North Macedonia (Figure 1). The samples were collected and stored in the dark in plastic bottles.

Figure 1. Location of the springs

The stock standard solutions for each metal were purchased from sigma Aldrich. In the preparation of working standards of analytes, proper dilutions were done by 1.0 mol/L nitric acid from the stock solutions of Ca, K, Mg, Mn, Fe and Cu (1000 mg/L). Solution of 1.0 mol/L nitric acid was used as a blank probe.

The standard solutions were prepared from the stock solutions by dilution. A 3% HNO_3 was employed as a solvent. The 3% HNO_3 solution was prepared with dilution of concentrated HNO_3 (70%). The HNO_3 with high purity (≥ 99.999%) was employed for this purpose.

Methods

The analysis of spring water for the presence of Ca, K, Mg, Mn, Fe and Cu was carried out using the atomic absorption spectrometer (PerkinElmer AANALYST 700). A flame atomic absorption spectrometry mode was employed. The sample was aspirated into a flame and the metals were atomized. A cathode lamps composed of each element was used for the analysis. The working wavelength for each metal and the standard solutions concentrations are given in Table 1. The calibration standards were prepared prior to the measurement by dilution from the stock solutions.

Table 1. Experimental conditions

water sample	wavelength [nm]	calibration standards [mg/L]
Ca	422.67	0.1, 0.5, 1, 2.5, 5, 10
K	766.49	0.1, 0.5, 1, 2.5, 5, 10
Mg	285.21	0.5, 1, 2.5, 5, 10, 25
Mn	279.49	0.01, 0.02, 0.03, 0.04, 0.05
Fe	248.33	0.1, 0.5, 1, 2.5, 5, 10
Cu	324.75	0.1, 0.5, 1, 2.5, 5, 10

Hardness, sulfate and chloride content was determined by Lovibond EN Method Reference handbook 1.0 (Lovibond). According to this method all three parameters are determined by means of UV-Vis spectrophotometry. For this purpose spectrophotometer XD 7500 was used. pH was measured on Seven Excellence pH meter S400 pH meter. To avoid any contamination, all glassware was rinsed with concentrated nitric acid in then with deionized water before use. Water was purified with a double distilled deionization system and has a specific resistance of 12 mega ohms/cm. This water was used for preparations of standard solutions.

RESULTS AND DISCUSSION

There has been a growing concern about the spring water quality in the rural area of North Macedonia. In these areas the most common source of drinking water for the inhabitants are the springs. Therefore, the monitoring of the mineral content in the spring water is a very important. In this work the mineral content (Ca, K, Mg, Mn, Fe and Cu) of water samples from five natural springs in southwestern region of North Macedonia was evaluated by means of FAAS. This techniques is one of the most extensively used for the determination of various elements in water samples. It is also remarkable for its selectivity, speed and fairly low operational cost.

The water samples were analyzed according to Standard Methods for Examination of Water and Wastewater (Carranzo, 2012). The concentration of obtained by FAAS are presented in Table 2.

Table 2. Results for metal determination in water samples

water sample	Ca [mg/L]	K [mg/L]	Mg [mg/L]	Mn [mg/L]	Fe [mg/L]	Cu [mg/L]
sample 1	70	0.02	7.75	0.12	0.42	0.09
sample 2	125.4	1.16	8.04	0.12	0.08	0.09
sample 3	63.01	0.523	6.17	0.11	0.06	0.06
sample4	50.97	0.253	7	0.12	0.10	0.09
sample 5	111.9	80.22	8.11	1.73	6.41	0.09
certified [mg/L]				0.05	0.2	2

As can been seen from the Table 2, all water samples have relatively elevated Ca concentration. Its concentration is higher in the case of samples 2 and 5. The potassium concentration is elevated only in the case of the sample 5. For potassium content the difference between the sample 5 and the other samples is very significant. Potassium is present in the water as potassium chloride. In Table 3 are presented the results obtained for sulfate and chloride anions. According to the results presented in table 3, the concentration of chloride anions for sample 5 is significantly higher in comparison to the other samples. In the similar manner, the conductivity of the sample 5 has also an elevated value in comparison with the other samples (Table 4). The electrical conductivity reflects the amount of the total dissolved solids in the drinking water.

All samples have presented slightly elevated level of manganese. Mn is an essential element found in the earth's crust. Water percolating through soil and rock can dissolve minerals containing Mn. Elevated Mn concentrations in drinking water that surpass the recommended value of 0.05 mg/L have been reported in studies from around the world (Frisbie et al., 2012).

Table 3. Concentration of sulfate and chloride anions in the spring water samples

water sample	sulfate [mg/L]	chloride [mg/L]
sample 1	7	34
sample 2	2	24
sample 3	5	29
sample 4	5	21
sample 5	> 100	> 200
certified [mg/L]	250	250

The Fe concentration was in the acceptable range, except for sample 5 where its concentration is significantly higher than that recommended by WHO. High concentration of Fe was also obvious from the color near the spring (reddish brown color). Iron is mainly present in water in two forms: either the soluble ferrous iron or the insoluble ferric iron. The sample 5 is clear and colorless because the iron is completely dissolved. This indicates that it is rich with ferrous iron. After some time, the water turns cloudy and a reddish brown precipitate begins to form. This sediment is the oxidized or ferric form of iron that will not dissolve in water. Dissolved ferrous iron gives water a disagreeable metallic taste. This water is not suitable for drinking. The Cu concentration of all samples is in the allowed range.

Table 4. Conductivity, hardness and pH value of the spring water samples

water sample	EC [µS/cm]	hardness [mg/L $CaCO_3$]	pH
sample 1	692	27.5	7.1
sample 2	1965	< 2	6.6
sample 3	457	31.2	7.1
sample4	346	>50	8.1
sample 5	4600	26.3	6.9
certified [mg/L]		< 60 mg/L	6.5 - 9.5

pH is a term used universally to express the intensity of the acid or alkaline condition of a solution. According to the results presented in table 4, the pH values of the water samples was in the range of 6.6 to 8.1. All the values are in the allowed range. The lowest pH value 6.6 was recorded in the water sample number 2, while the maximum value of 8.1 was recorded in the water sample 4.

CONCLUSION

In this work 5 spring water samples were analyzed for mineral content. The pH value was also determined. According to the presented results, all water samples contain slightly elevated manganese concentration and one water sample (sample 5) besides elevated concentration of manganese, also contain high concentration of iron and potassium and it is not safe for drinking. Sample 5 is also water rich with iron. According to the results obtained in this study, the water sample 5 is not suitable for drinking.

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