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ANALYSIS OF SELECTED PHYSICO-CHEMICAL PARAMETERS IN BOTTLED WATERS AVAILABLE ON THE POLISH MARKET

Agnieszka Włodyka-Bergier, Tomasz Bergier, Dominika Gajewska, Emilia Stańkowska
AGH University of Science and Technology in Krakow

Abstract

Water is a significant source of macro – and microelements, necessary for the proper functioning of a human body. The purpose of this article was to analyze the quality of the selected bottled waters available on the Polish market in terms of the physico-chemical parameters (pH, conductivity, chloride ions, bromide ions), macroelements (sodium, potassium, calcium, magnesium) and trace elements (lead, nickel, antimony, arsenic). 17 brands of the bottled waters available on the Polish market were investigated within the study presented in the article (8 natural mineral waters, 6 spring waters and 3 therapeutic waters). The bottled waters, which were analyzed in the article, characterized with a large diversity of chemical composition. In two samples of therapeutic waters the permissible concentration of nickel was exceeded.

Key words: bottled waters quality, mineral waters, spring waters, therapeutic waters, trace elements

INTRODUCTION

Water is an extremely valuable resource, essential for the proper functioning of the human body, it is also considered as one of the significant sources of micro – and macroelements (Cidu *et al.,* 2010; Birke *et al.,* 2010). One of the possibilities of water consumption is the selection of commercially available bottled waters. The industry of these waters is constantly growing, which makes it an important sector of the economy in European Union countries (Bityukova and Petersell, 2010; Luo *et al.,* 2018; Michalski *et al.,* 2018). According to the European Federation of Bottled Water (EFBW), the average bottle water consumption in Europe in 2017 was 117 litres per capita. The country, in which the consumption of water per citizen was the largest, turned out to be Italy with an average consumption of 188 litres. However, according to the Federation data, a statistical Pole drank 99 litres of bottled water (EFBW, 2019). Currently, four types of bottled water are commonly available on the international market: natural mineral water, spring water, table water and therapeutic water. In Poland, the detailed requirements to be met by natural mineral waters, spring waters and table water are specified in the regulation of Minister of Health of March 31, 2011 (Minister of Health, 2011). The requirements that therapeutic water should meet are set by the regulation of Minister of Health of April 13, 2006 (Minister of Health, 2006).

The public's general opinion on bottled water is rather positive. The trend of increasing consumption of this type of water in recent years reflects the anxiety of the population about the quality of tap water (Vantarakis *et al.,* 2013). A large group of consumers perceive bottled water as a better alternative in terms of biological and chemical safety, flavor or aroma (Luo *et al.,* 2018; Diduch *et al.,* 2015; Ward *et al*., 2009). Many people oppose the unpleasant smell of chlorine, which is often felt during intake of tap water (Güler and Alpaslan, 2009; Kokkinakis *et al.,* 2008). However, the global consumption of bottled water is constantly growing even in countries where the quality of tap water is described as excellent. This increase is related to lifestyle changes and nutritional habits integrated with economic growth (Carlucci *et al.,* 2016; Etale *et al*., 2017).

An important issue, which due to the noticeable increase in the consumption of bottled water, should be taken into consideration, is the impact of bottled water industry on the natural environment. The society's growing knowledge of sustainable development makes that in the literature there are available more and more information about the negative impact of this industry on the ecosystems. The process of producing bottled water is very often criticized e.g. for the huge consumption of energy during the extraction stage, then processing and bottling of water. As a result of the production of 1 liter of bottled water, approximately 1kg of CO_2 is emitted into the atmosphere. Another issue is the distribution of bottled water. Its transport, usually over long distances, requires the consumption of enormous amounts of fossil fuels. Water is most often sold in bottles of polyethylene terephthalate (PET), which is derived from oil. During the combustion of plastic bottles, the very harmful gases and dusts containing heavy metals (cadmium, mercury, lead, nickel) are emitted, which additionally intensifies the negative effect of this sector on the natural environment (Kłos, 2016; Rani *et al.,* 2012; Varrica *et al.,* 2013).

The significant impact of the bottled water industry on the natural environment does not change the fact that such water is a valuable source of minerals, which during its consumption in the daily diet can be easily supplemented. Natural mineral waters as groundwater mined are characterized by stable mineral composition, which may have a prophylactic or therapeutic effect. The properties of mineral waters and their taste depend on the content of cations, anions, trace elements and their mutual proportions. The content of individual minerals and chemicals in these waters is related to the composition of rocks, hydrodynamic properties of the aquifer and geochemical processes occurring within this layer (Salomon and Regulska-Ilow, 2013; Platikanov *et al.,* 2012). Calcium and magnesium are the important elements, abundantly found in many types of bottled natural mineral waters, fulfilling key physiological functions and playing a significant role in the processes taking place in the circulatory and nervous system (Rajchel, 2009).

In the case of spring waters, their composition does not have to meet such rigorous requirements regarding the chemical composition. They are also not assigned any therapeutic features, because the mineral composition of such waters and their general properties do not differ from the composition of tap water (Pawlak *et al.,* 2016; Minister of Health, 2017).

The purpose of this article was to analyze the quality of selected bottled waters available on the Polish market in terms of the following physico-chemical parameters: pH, conductivity, inorganic anions (chloride ions, bromide ions), macroelements (sodium, potassium, calcium, magnesium) and trace elements (lead, nickel, antimony, arsenic).

MATERIALS AND METHODS

The research involved the study of 17 bottled waters of the most popular brands commonly available on the Polish market. 6 of the selected waters were spring waters, 3 of which were sparkling waters (S1S, S2S, S3S) and 3 still ones (S4, S5, S6); 8 – natural mineral waters, 3 of which were sparkling waters (M1S, M2S, M3S) and 5 still ones (M4, M5, M6, M7, M8); 3 – therapeutic waters (H1–H3). The selected physico-chemical parameters were determined in the water samples. The analyzed physico-chemical parameters included: bromide concentration (by spectrophotometric method with chloramine T as an oxidizing agent and phenol red as an indicator), chlorides (according to PN-ISO 9297: 1994), pH (PN-EN ISO 10523: 2012), conductivity (PN-EN 27888: 1999). Determinations of the trace elements (Pb, Ni, Sb, As) were carried out using the graphite method of AAS (atomic absorption spectrometry), with atomization in a graphite cuvette using palladium matrix modifier with reference to the model solutions of the determined elements. These measurements were conducted with Hitachi Z-2000 atomic absorption spectrometer. The analysis of the samples in terms of the content of elements: K, Na, Mg, Ca was carried out with the flame technique with Zeeman correction, in reference to the patterns of the determined elements.

The analysis of Pearson's correlation was used to assess the relationship between individual water quality parameters. It was conducted using Statistica (ver. 13.0) by StatSoft.

RESULTS AND DISCUSSION

Fig. 1 presents the results of pH and conductivity measurements in the studied bottled waters. The examined waters were characterized by very high variability of these parameters. The pH values ranged from 5.3 to 8.2. The average pH value in all tested waters was 6.6 (the standard deviation value was 0.95). The average value for this parameter for spring waters was 6.4; for natural mineral waters was 7.0 and for therapeutic waters – 6.1. Conductivity ranged from 267 $\mu S \cdot cm^{-1}$ to 4635 $\mu S \cdot cm^{-1}$. The average conductivity value in all tested waters was 1113 $\mu S \cdot cm^{-1}$ (the standard deviation value was 1082 $\mu S \cdot cm^{-1}$). The average value for this parameter for spring waters was 587 $\mu S \cdot cm^{-1}$, for mineral waters was 931 $\mu S \cdot cm^{-1}$ and for therapeutic waters – 2648 $\mu S \cdot cm^{-1}$. The highest conductivity values were obtained for therapeutic waters H1 and H2. According to the Polish law regulating the quality of water intended for consumption by people (Minister of Health, 2017), the pH value should be in the range of 6.5–9.5, and the value of conductivity should not exceed 2500 $\mu S \cdot cm^{-1}$. However it is not required by Polish law to specify these two parameters on the labels of bottled waters (Minister of Health, 2011). High pH values do not pose a threat to human health, however, they can cause a negative reception of the water quality by a consumer, due to the unpleasant alkaline taste. Therefore, information on a water bottle label with the value of this parameter would be expected and appreciated by many consumers.

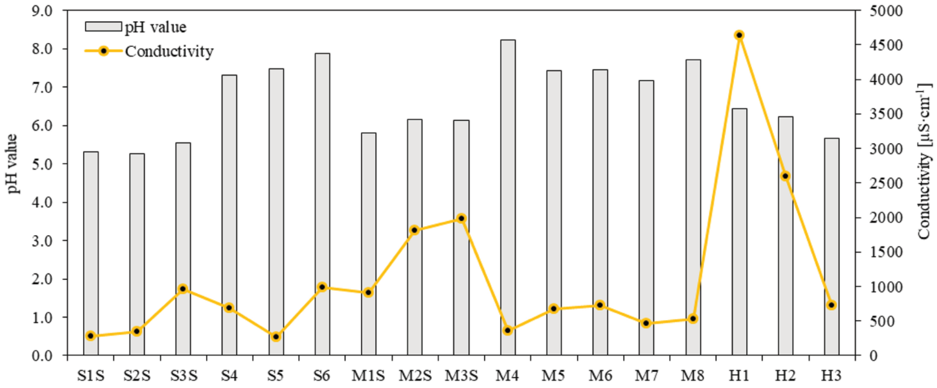

Figure 1. pH value and conductivity in the studied bottled waters

Fig. 2 presents the results of the concentration of four characteristic mineral components (sodium, potassium, calcium, magnesium) in the studied bottled waters. A large variation in the concentrations of the studied macrocomponents can be observed on the graph. The average sodium concentration in all tested waters was 129.8 mg·dm^{-3} (the standard deviation value was 270.4 mg·dm^{-3}), potassium concentration was 6.9 mg·dm^{-3} (the standard deviation value was 7.8 mg·dm^{-3}), calcium concentration was 111.5 mg·dm^{-3} (the standard deviation value was 79.6 mg·dm^{-3}) and magnesium concentration was 24.7 mg·dm^{-3} (the standard deviation value was 25.5 mg·dm^{-3}). The average sodium concentration for spring waters was 56.3 mg·dm^{-3}, for natural mineral waters was 32.1 mg·dm^{-3} and for therapeutic waters – 537.6 mg·dm^{-3}. The highest concentration of sodium was found in the therapeutic waters H1 and H2 (1112.6 mg·dm^{-3} and 482.6 mg·dm^{-3} respectively). The potassium concentration in the tested waters ranged from 0.9 mg·dm^{-3} to 28.5 mg·dm^{-3}. The average potassium concentration for spring waters was 3.7 mg·dm^{-3}, for natural mineral waters was 6.6 mg·dm^{-3} and for therapeutic waters – 14.3 mg·dm^{-3}. The recommended concentration of this element in drinking water is 300 mg·dm^{-3} (Śliwińska and Boszke, 2013). Thus, the values determined in the considered waters, despite the large variation, are in fact very low, not significantly affecting the functioning of the human body with optimal water consumption. One of the most important minerals present in water are calcium and magnesium. The average calcium concentration for spring waters was 61.5 mg·dm^{-3}, for natural mineral waters was 141.7 mg·dm^{-3} and for therapeutic waters – 130.9 mg·dm^{-3}. The highest calcium concentration was observed for sparkling natural mineral waters M1S, M2S and M3S, and it was 139.6 mg·dm^{-3}, 211.2 mg·dm^{-3} and 372.2 mg·dm^{-3} respectively. The average magnesium concentration for spring waters was 8.7 mg·dm^{-3}, for natural mineral waters was 36.4 mg·dm^{-3} and for therapeutic waters – 25.7 mg·dm^{-3}. Calcium and magnesium deficiencies, constituting about 30% of the daily requirement, can be supplemented by consuming water with a minimum magnesium content of 50 mg·dm^{-3} and calcium – 150 mg·dm^{-3} (Derkowska-Sitarz and Adamczyk-Lorenc, 2008). Among all the examined waters only two sparkling natural mineral waters (M2S and M3S) fulfilled such the condition.

There was a statistically significant correlation ($p < 0,05$) between sodium and potassium concentration ($r = 0,743$) as well as calcium and magnesium concentration ($r = 0,784$).

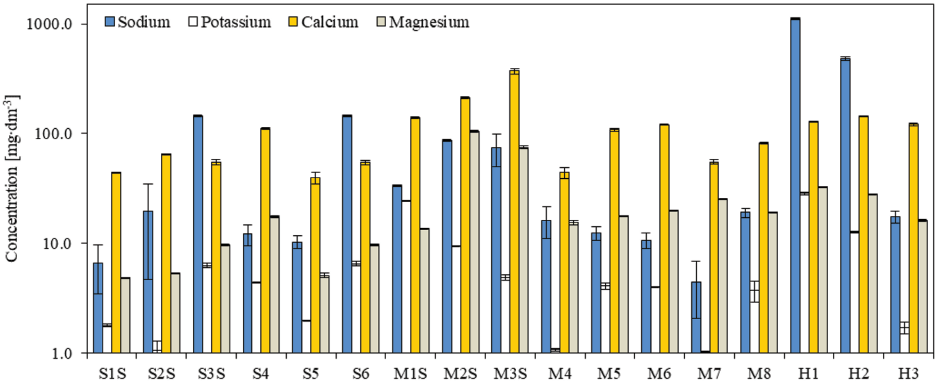

Figure 2. Sodium, potassium, calcium and magnesium in the studied bottled waters

Fig. 3 presents the results of the examination of chloride and bromide ions content in the analyzed bottled waters. In the most of considered waters, the presence of chloride ions was found at an average level of 13.3 mg·dm^{-3}. The values significantly higher were observed for sparkling spring water S3S (166.9 mg·dm^{-3}), the non-sparkling spring water S6 (163.3 mg·dm^{-3}) and therapeutic waters H1 and H2 (507.7 mg·dm^{-3} and 245.0 mg·dm^{-3} respectively). Water with an optimal content of chloride ions is characterized with the concentration of this anion at the level not exceeding the value of 200 mg·dm^{-3} (Śliwińska and Boszke, 2013). Too high chlorides concentration (above 250 mg·dm^{-3}) causes the water salty taste, which probably is not an incentive for the consumer to buy such water (Kończyk *et al.,* 2019). The average bromide ions concentration in all tested waters was 0,32 mg·dm^{-3} (the standard deviation value was 0.24 mg·dm^{-3}). The average value for this parameter for spring waters was 0,18 mg·dm^{-3}, for mineral waters was 0,31 mg·dm^{-3} and for therapeutic waters – 0,66 mg·dm^{-3}. Among the examined waters, the highest concentrations of bromide ions were observed in the therapeutic waters H1 and H2 (0.84 mg·dm^{-3} and 0.97 mg·dm^{-3} respectively), and the sparkling natural mineral water M2S (0.56 mg·dm^{-3}). For the other waters, the average concentration of this anion was close to the value of

0.22 mg·dm^{-3}. Bromide ions are a natural component of all waters. The concentration of these ions in surface and underground waters varies from a few to about 800 mg·dm^{-3}. Bromide ions do not adversely affect human health, however they are precursors of toxic bromates (V) that may appear in water when it undergoes an ozonation process. The maximum permissible concentration of bromates in drinking water is 10 µg·dm^{-3} (Kończyk *et al.,* 2019; Łakomska and Wiśniewski, 2012).

There was a statistically significant correlation ($p < 0,05$) between bromide and chloride ions concentration ($r = 0,681$) as well as bromide ions and sodium concentration ($r = 0,769$) and chloride ions and potassium concentration ($r = 0,689$).

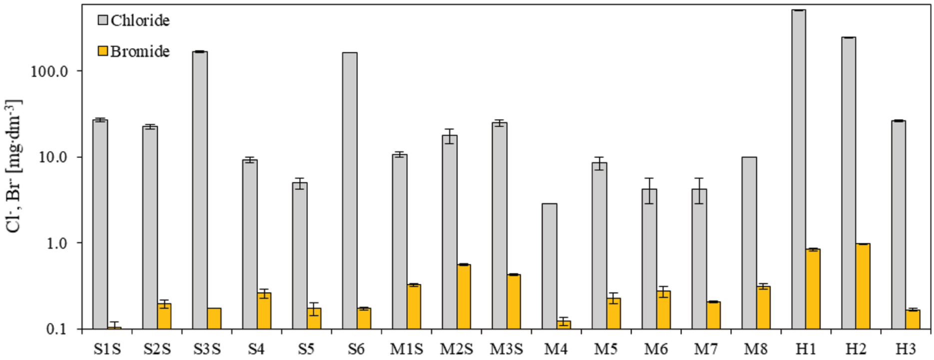

Figure 3. Chloride and bromide ions in the studied bottled waters

Fig. 4 presents the average concentration, minimum and maximum values of four trace elements (lead, nickel, antimony, arsenic) in the studied natural mineral, spring and therapeutic waters. The average lead concentration in spring and mineral waters was 2.1 µg·dm^{-3}. Its maximum content was found in the therapeutic waters at the level of 10.7 µg·dm^{-3}. In studies carried out by Krachler and Shotyk (2009), who determined trace elements in 132 brands of bottled water from 28 countries, the maximum concentration of lead was markedly lower than in this work (0.76 µg·dm^{-3}). A similar value was obtained by the team of Peh, Šorša and Halamić (2010), investigating the concentration of trace elements in Croatian bottled waters. The maximum concentration of lead which they determined was 0.65 µg·dm^{-3}. The average nickel concentration in the analyzed spring waters was 1.5 µg·dm^{-3}. In the case of mineral waters, it was 2.9 µg·dm^{-3}, while in the therapeutic waters – 26.0 µg·dm^{-3}. The highest acceptable content of nickel in therapeutic waters can be 0.03 mg·dm^{-3} (Minister of Health, 2006). Exceeding this value was observed in two samples of the same brand of therapeutic water. Nickel concentration in these samples was respectively 75.1 µg·dm^{-3} and 44.9 µg·dm^{-3}. Peh with the team (2010), in the waters they tested, observed the maximum concentration of nickel at the level of 5.28 $\mu g \cdot dm^{-3}$. The maximum concentration of antimony in the waters considered in this article was determined in one of the spring waters (2.1 $\mu g \cdot dm^{-3}$). The similar content of this element (2.57 $\mu g \cdot dm^{-3}$) was also detected by Krachler and Shotyk (2009). The analyzed waters were characterized by an average arsenic content of 0.6 $\mu g \cdot dm^{-3}$. Cicchella *et al*. (2010), investigating trace elements in Italian bottled waters, detected this element in a concentration of 0.89 $\mu g \cdot dm^{-3}$.

There was a statistically significant correlation ($p < 0,05$) between bromide ions and nickel concentration ($r = 0,621$).

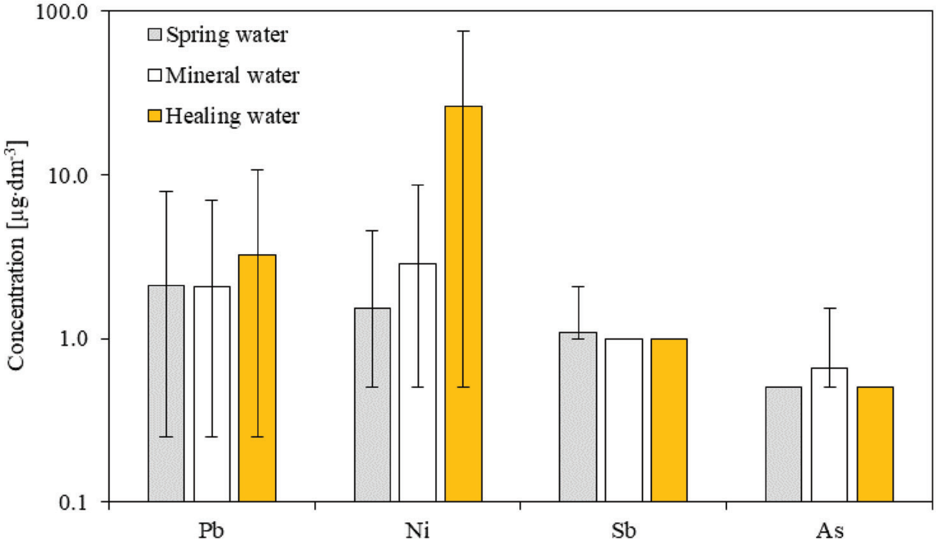

Figure 4. The average concentration of trace elements in the studied bottled waters

CONCLUSION

The consumption of bottled water is one of the possibilities to supplement the deficit of basic minerals, necessary for the proper functioning of the human body. It is also a quick and easily available method of satisfying thirst, hence the analysis of individual physico-chemical and microbiological parameters of bottled waters available on the market is so important.

The natural mineral waters, spring waters and therapeutic waters analyzed in the article, were characterized by a large diversity of chemical composition. For most bottled waters pH value was in the most optimal range 6.5–9.5. The highest mineralization was observed in therapeutic waters, which was confirmed by the results of conductivity. In the case of four basic mineral components (sodium, potassium, calcium, magnesium): the highest sodium concentration was detected in therapeutic waters; potassium – in one therapeutic water and one natural sparkling mineral water; calcium – in one natural sparkling mineral water, in which the value of this element was determined almost twice as high as the average value obtained for the remaining waters. Also, in two mineral waters a significantly higher concentration of magnesium was observed, compared to the results from the other waters. When analyzing the content of trace elements, the content of nickel was exceeded in two samples of therapeutic water.

Large variation in the aspect of the chemical composition of bottled waters available on the Polish market makes were observed as the result of the conducted studies, thus the consumer has a wide possibility of choice for most suitable water for themselves, water with the most favorable content of individual mineral components.

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Corresponding author: Eng. Dominika Gajewska, MSc
AGH University of Science and Technology
Faculty of Mining Surveying and Environmental Engineering,
al. Mickiewicza 30
PL 30-059 Krakow
Tel. (+48) 12 617 47 57
Email: gajewska@agh.edu.pl

Eng. Agnieszka Włodyka-Bergier, DSc, PhD
AGH University of Science and Technology
Faculty of Mining Surveying and Environmental Engineering,
al. Mickiewicza 30
PL 30-059 Krakow
Tel. (+48) 12 617 47 57
Email: wlodyka@agh.edu.pl

Eng. Tomasz Bergier, DSc, PhD
AGH University of Science and Technology
Faculty of Mining Surveying and Environmental Engineering,
al. Mickiewicza 30
PL 30-059 Krakow
Tel. (+48) 12 617 47 57
Email: tbergier@agh.edu.pl

Eng. Emilia Stańkowska, MSc
AGH University of Science and Technology
Faculty of Mining Surveying and Environmental Engineering,
al. Mickiewicza 30
PL 30-059 Krakow
Tel. (+48) 12 617 47 57
Email: stankowska@agh.edu.pl

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