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Bromate in Bottled Water – Potential Hazard for Human Health[2]

Abstract: In the International Agency for Research on Cancer (IARC) classification, bromates (by-products of water treatment) are categorized as Class 2B carcinogens; i.e., substances that are possibly carcinogenic to humans. The maximal concentration of bromate in drinking water must not be higher than 10 μg/L, while the WHO recommends that bromate levels should be as low as possible. Investigations undertaken in several countries have revealed the presence of bromate in bottled water, too. The main factor responsible for the presence of bromate is ozonation during the manufacturing process or bromate-contaminated substances used in the water disinfection.

The regulations currently in force in Poland forbid the addition of bacteriostatic agents and the application of treatment processes that alter the microflora in water. On the other hand, raw water can be filtered, aerated, or treated with air enriched in ozone – although only in the amounts required to remove iron, manganese, arsenic compounds, and sulfides. However, during the manufacturing process, bottled water may be exposed to ozone from electric-powered ionizers used in the process of the dry-cleaning of bottles or PET preforms. The maximal admissible bromate contents in bottled water is 3 μg/L. The current regulations in Poland effectively reduce hazards due to the presence of bromate in water. However, the results of investigations undertaken in other countries indicate that this aspect should be brought to the attention of both water manufacturers and regulatory bodies.

Keywords: bromate, bottle water, ozonation, water quality

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1. Introduction

Water disinfection has always been a significant factor that is responsible for lowering the risk hazards posed to human life and health. The introduction of disinfectants into the water treatment process used by water distribution systems led to a significant decrease in the number of deaths caused by disease agents and pathogenic organisms. The development of analytical methods and advances in the field of medicine brought about the recognition of negative phenomena involved in the disinfection process; i.e., the resultant formation of by-products – some of which that can have an adverse effect on human health. These by-products of the water disinfection process include THM (identified as a health risk in the 1970s) and bromate (identified in the 1990s, when ozonation started to be commonly used in water treatment plants).

Potable water is supplied through distribution systems, but drinking water is also sold in packaging. A growing interest in bottled water displayed by both consumers and producers causes their manufacture and consumption to be increasing steadily. The types of water available in unit packages differ in their levels of mineralization, including water containing similar or even lower total amounts of dissolved minerals when compared to tap water. Moreover, such water may be hardly distinguishable from tap water in terms of taste. In the water from distribution systems, by-products of water treatment can be present; however, the amounts of these products cannot exceed the applicable standards. The results of research into the quality of bottled water carried out in a number of different countries point out the fact that these products might contain mutagenic compounds. The aim of this paper is to discuss the problem of the potential presence of bromate in bottled water. In the International Agency for Research on Cancer (IARC) [1] classification, bromates (by-products of water treatment) are categorized as Class 2B carcinogens; i.e., substances possibly carcinogenic to humans. Despite the considerable interest in the quality assessment of bottled water (both among potential customers and the research community), this issue has yet to be addressed by the Polish scientific literature. Any published research results pertaining to the chemical composition of bottled water from different regions of the world indicate the presence of health risks.

2. Occurrence of Bromate in Bottled Water

Bromine is a chemical element that can occur in a few oxidation states (−1, 1, 3, 5, 7); however, the form that predominates in nature is an oxidation state of –1 (bromide). In the majority of the products participating in the water circulation cycle, the mass concentration of bromides is below the limit of quantification (LOQ), whereas they can occur in different concentrations in water with a higher mineral content

(depending on the type). Seawater contains 65 mg/L of Br^-, and brine contains a few, several, or even more than a thousand miligrams per liter of Br^-.

Bromate (BrO_3^-) do not occur in natural water; however, cases of groundwater contamination have been reported regarding these compounds. This could have been caused by waste from the chemical plants that manufacture this compound [2]. Bromates are by-products of water disinfection – they are formed from the ozonation of water that contains bromides. This process can take place directly via molecular ozone or indirectly through radical reactions. Bromide's oxidation to bromates is a multi-stage process. The first product of the reactions of ozone molecules with bromates are hypobromites, which are a transient form. Due to the reaction with ozone, hypobromites change into bromides and bromates [3]. Depending on a number of factors (e.g., parameters of raw water [pH, organic matter content, temperature] and the process itself [the dose of ozone]), 5–30% of bromides change into bromate [4]. It has been determined that even a Br^- ion concentration of 0.05 mg/L can lead to the formation of BrO_3^- in quantities exceeding standard concentrations [3]. The maximum concentration of bromate in drinking water must not be than 10 μg/L, while the WHO recommends that the bromate content should be as low as possible. The maximum admissible levels are occasionally exceeded in water distribution systems. Studies that have been carried out in France, Germany, and the USA show that the cases of exceeding the admissible value refer to ca. 10% of drinking water that has undergone ozone-enriched air treatment [5]. The investigations into the quality of tap water in Poland that were conducted by the State Sanitary Inspectorate in 2007 detected BrO_3^- concentrations in excess of the maximum admissible levels in 8 out of 195 studied cases [6]. This can be confirmed by the number of published papers dealing with this topic [3, 4]. The number of publications devoted to BrO_3^- content in bottled water is significantly lower. The main area of interest in research papers referring to the situation in Poland is bromate found in water distribution systems. Papers on the quality of bottled water in Poland do not investigate the potential occurrence of BrO_3^- ions and their related hazards.

3. Bromate in Bottled Water – Examples from Other Countries

Research conducted on bottled water in a number of countries (the USA, Canada, South Korea, Sudan, Saudi Arabia, India, Thailand, China, and Kuwait) shows that, in some of the products under study (in several to several dozen percent of the samples), bromate has been detected. Bromide compounds have also been determined. Within the frame of some of these studies, the concentrations of bromide have also been determined. The relationships between the concentrations of BrO_3^- and Br^- ions have been analyzed, and the influence of the processes to which the water was subjected have been studied.

A vast majority of the published research results refer to countries with arid climates (e.g., Saudi Arabia). The research conducted on 50 different types of bottled water showed that the bromate content exceeded the levels recommended by the WHO in 70% of the investigated samples [7]. In the case of some studies, the limit of the quantification was substantially higher than the validated content (50 μg/L); thus, it was not possible to assess the potential risks posed by this factor in the case of parameters lower than 50 μg/L [8].

During the years of 1995–1997, detailed studies were conducted on the quality of mineral, spring, and other types of water sold in Canada [9]. Bromates were detected in 116 out of the 199 investigated samples. BrO_3^- ions were not detected in all of the water containing Br^- ions, and the determined contents of both forms of bromine did not indicate the existence of any correlation between them. Bromates were also detected in non-ozonated water. The research indicated that the water treatment processes affected the bromate content in bottled water more significantly than the concentrations of bromide. It was concluded that the application of hypochlorite (which is usually contaminated with BrO_3^-) might have been the factor that determined the occurrence of bromate [9]. In the USA, BrO_3^- ions were detected in a small number of samples of ozonated water (mostly in concentrations below 10 μg/L) [10, 11]; however, contents were also identified in excess of this value [12].

All of the studies point to ozonation as the main reason for the presence of BrO_3^- in bottled water. In South Korea, the detected contents of BrO_3^- ranged from 0.09–27.67 μg/L in natural mineral water samples subjected to ozonation [13]. In Saudi Arabia, the detected contents of BrO_3^- were significantly lower in water subjected to UV treatment than in water in which the concentrations of bromide compounds were lower, but they had been subjected to ozonation [14]. In the bottled water in Kuwait, bromates were detected in 50% of the studied samples. The detected concentrations of BrO_3^- exceeded the maximum acceptable levels (even by several orders of magnitude in some cases) [8]. The presented results concerning the water of the USA, Canada, Saudi Arabia, and Thailand refer to more than one group of samples (Fig. 1).

In Figure 1, the maximum admissible concentrations of BrO_3^- in water intended for human consumption (binding in a majority of countries worldwide) and the maximum values applicable to water bottled in Poland are marked.

It should be noted that the correlated research results (Figs. 1, 2) concerned different numbers of samples and different types of packaged water being sold.

On the basis of the presented data, it can be concluded that concentrations of bromate in excess of the admissible levels are not so rare. In some cases, the maximum registered BrO_3^- concentrations exceed the acceptable level several-fold. In the countries with scarce water resources, the average and median values are also over 10 μg/L. A small body of data meets the applicable standards for bottled water in Poland (3 μg/L). The lack of published research results on the content of BrO_3^- in water bottled in Poland might be indicative of the fact that such research has not been conducted.

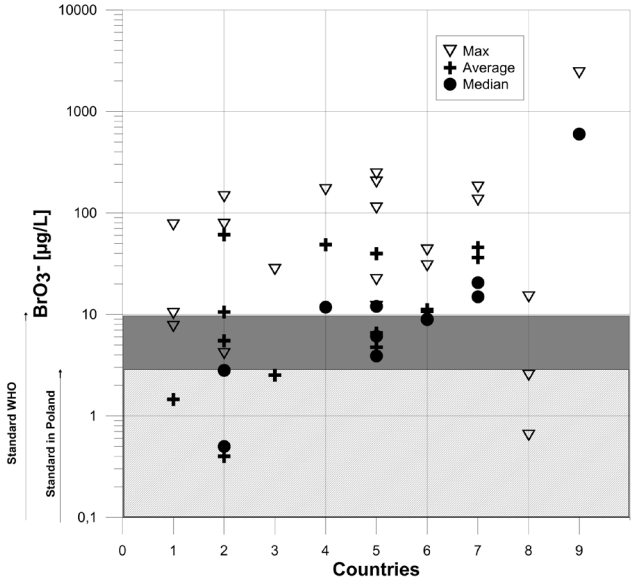

Fig. 1. Bromate in bottled water – maximum, average, and median values:
1 – USA [10–12], 2 – Canada [9], 3 – South Korea [13], 4 – Sudan [15], 5 – Saudi Arabia [7, 14, 16–18], 6 – India [19, 20], 7 – Thailand [21], 8 – China [22, 23], 9 – Kuwait [8]

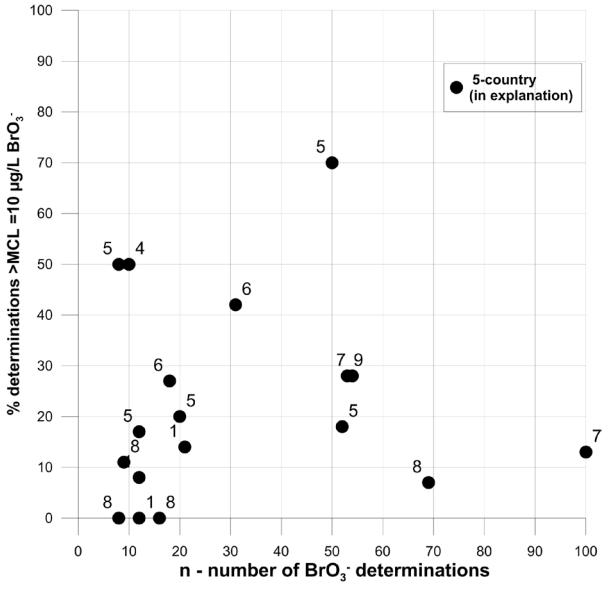

Fig. 2. Bromate in bottled water – percentage of the exceeded standards according to WHO (MCL = 10 µg/L) in comparison with all determinations.

Explanation: countries as in Figure 1

The presented literature data suggest that this issue is more relevant for countries affected by the scarcity of fresh (salt-free) water. Nevertheless, studies carried out in developed countries (e.g., Canada) also show that some of the bottled water does not comply with the officially binding standards for bromate. A wide range of processed water that is sold in packaging is subjected to is still another issue. This problem currently refers mostly to countries affected by a shortage of weakly mineralized high-quality water (countries with arid and semi-arid climatic conditions) and may affect larger regions all over the world in the future. The development of desalination technologies may lead to their more widespread applications. It should be borne in mind that, due to the origin and treatment processes to which it is subjected, this water will inevitably contain bromate. Health awareness and technological advances will probably lead to the elimination of this hazard, but it will entail economic costs. Thus, it will create additional problems for developing countries and, more importantly, for consumers.

4. Regulations Pertaining to Bottled Water Sold in Poland Regarding Potential Occurrence of Bromate

The production and distribution of water that is available in unit packages is subject to the provisions of an act on food and nutrition safety [24]. In Poland, three types of bottled water are available on the market: natural mineral water, spring water, and table water. These all originate from underground water obtained from one or several wells. Natural mineral water and spring water are originally clean regarding their chemistry and microbiology. The differences between natural mineral water and those supplied by the distribution system lie in their stable mineral composition and therapeutic properties. Table water is obtained by supplementing spring water with natural mineral water or mineral salts with at least one component that produces physiological effects. Spring water is originally pure in the chemical and microbiological sense and it does not differ in terms of its properties and mineral composition from water intended for human consumption in accordance with the ordinance of the Minister of Health [25]. Table water is obtained by supplementing spring water with natural mineral water or mineral salts with at least one component that produces physiological effects [26].

The specific requirements with which natural mineral water, spring water, and table water must comply are laid out in the ordinance of the Minister of Health [27]. The regulations currently in force in Poland forbid the addition of bacteriostatic agents and the application of treatment processes that alter the microflora in water. On the other hand, raw water can be filtered, aerated, or treated with air enriched with ozone, though only in the amounts required to remove iron, manganese, arsenic compounds, and sulfides. The addition of ozone accelerates the oxidation of these

compounds, which are subsequently removed during filtration. The conditions of the use of ozone-enriched air treatment is that it must not have a bacteriostatic effect and cannot lead to the formation of constituents that are harmful to human health in concentrations exceeding admissible levels. As regards bromate, this level is 3 μg/L. The amount of the applied ozone has to be calculated using stoichiometry on the basis of the reactions that occur, leading to the removal of the above-mentioned constituents. A producer of water in unit packaging who uses ozone treatment in the production process should notify a competent district sanitary inspector about it. Water that has been treated with ozone-enriched air during the production process shall bear the words: 'water subjected to an authorized ozone-enriched air oxidation technique' on the label next to the information on the characteristic mineral constituents [27].

5. Production Processes of Bottled Water Sold in Poland and Bromate-Related Hazards

An analysis of the legal regulations referring to the quality of bottled water shows that the risk connected with the presence of undesirable constituents in such water is unlikely. The presence of BrO_3^- ions in water is due to disinfection processes, the application of which not being permitted in the production of bottled water in Poland. Specifying the maximum permissible BrO_3^- content in bottled water at a lower level than that in other kinds for water intended for consumption is another factor that protects against this risk. In the case of bottled water, the main bromate risk-inducing factor is ozone. An additional important element is the presence of bromides in the raw water. Therefore, the processes in which ozone is applied should not be used in water containing Br^- ions. The possibility of water contacting ozone during the process of preparing (cleaning) preforms or bottles cannot be excluded. A vast majority of the water sold in packaging is available in PET-type bottles. Then, a preform blower forms the first stage of the process line (in some water-bottling plants, the preforms are manufactured; alternatively, injection-molding machines for the preforms are combined with preform blowers). Any bottles carried by the handling equipment are rinsed with clean water or blown with ionized sterile air; then, they are filled with water and sealed. Another method used is to clean the preforms prior to blowing them with air. The dry-method system of cleaning consists of subjecting a preform/bottle to ionized air. Electric ionizers emit small quantities of ozone. The dry system of cleaning is considered to be more effective than rinsing with water [28].

An indispensable factor in eliminating risks to water quality is controlling not only the chemical composition but also the work flow of the technological processes applied in water-bottling plants. This control should take the specific character of

these processes into account; in addition, it should include the specific character of the process (ozone dosing), the justification of its application, and the labelling of products formed due to chemical reaction of bromate and bromomethane compounds in the case of aeration with ozone.

6. Summary

The processes employed in the production of bottled water in various countries might be different from those permitted by the provisions that are legally binding in Poland. This results in lowering the quality of the bottled water and the appearance of undesirable mutagenic constituents in such water. The main factor leading to the formation of bromate in bottled water is water ozonation. Any Br^- ions that occur in water are transformed into BrO_3^- ions as a result of reactions with ozone. The occurrence of bromate in water where Br^- ions have not been detected might be due to the application of disinfectants polluted by BrO_3^- ions. Current regulations in Poland that are relevant to bottled water do not permit disinfection, and the application of ozone is subject to strict regulations. This is an extremely important factor that effectively reduces the hazards connected with the presence of bromate in water. However, the results of investigations undertaken in other countries indicate that this aspect should be brought to the attention of both water manufacturers and regulatory bodies. A global analysis of the hazards posed by bromates shows that, being faced with a shortage of good-quality water with low mineral content as well as advances in desalination technologies, the problem of the presence of bromate in water intended for human consumption (including that which is commercially distributed) may become more serious over time. In numerous countries, public health protection may require the introduction of strict legal procedures guaranteeing the appropriate standards and effective tools for water quality management.

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Bromiany(V) w wodach butelkowanych – potencjalne zagrożenie zdrowia

Streszczenie: Bromiany(V), uboczny produkt dezynfekcji wód, zostały zakwalifikowane przez Międzynarodową Agencję Badań nad Rakiem do grupy 2B, substancji, których rakotwórcze działanie na człowieka jest możliwe. Wartość parametryczna stężenia jonów BrO_3^- w wodach przeznaczonych do spożycia, wynosi 10 μg/L, niemniej jednak zgodnie z zaleceniami WHO należy dążyć do jak najmniejszej ich zawartości. Badania przeprowadzone na terenie kilku krajów wskazują, że bromiany(V) są wykrywane w wodach butelkowanych. Głównym czynnikiem decydującym o obecności tych związków jest stosowanie ozonu w procesie produkcji, ale przyczyną ich obecności mogą być także zanieczyszczone jonami BrO_3^- substancje stosowane w dezynfekcji wód.
Wody butelkowane w Polsce podlegają przepisom, które zabraniają dodawania do tych wód środków bakteriostatycznych i stosowania zabiegów, które mogą zmienić mikroflorę wód. Możliwe natomiast jest poddawanie wody surowej procesom filtracji, napowietrzania, a także traktowanie wody powietrzem wzbogaconym w ozon, ale tylko w ilości niezbędnej do przeprowadzenia procesu usuwania związków żelaza, manganu, siarki(II) i arsenu. Maksymalna dopuszczalna zawartość bromianów(V) w wodach butelkowanych wynosi 3 μg/L. W procesie produkcyjnym nie można wykluczyć kontaktu wody z ozonem pochodzącym z jonizatora elektrycznego stosowanego w procesie suchego czyszczenia butelek lub preform PET. Obowiązujące w Polsce przepisy dotyczące wód butelkowanych sprzyjają ograniczeniu zagrożenia związanego z obecnością bromianów(V) w tych wodach. Zważywszy na wyniki badań z innych krajów, zarówno producenci, jak i organy kontroli powinni mieć na uwadze potencjalne niebezpieczeństwo pojawienia się bromianów w wodach butelkowanych.

Słowa kluczowe: bromiany(V), wody butelkowane, ozonowanie, jakość wód