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# DETERMINATION OF BARIUM IN NATURAL WATERS BY ICP-OES TECHNIQUE. PART II: ASSESSMENT OF HUMAN EXPOSURE TO BARIUM IN BOTTLED MINERAL AND SPRING WATERS PRODUCED IN POLAND

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## ABSTRACT

**Background.** A method of the classification of natural mineral and spring waters and maximum admissible concentration (MAC) levels of metals present in such types of waters are regulated by Commission Directive 2003/40/EC, Directive 2009/54/EC of the European Parliament and of the Council and Ordinance of Minister of Health of 30 March 2011 on the natural mineral waters, spring waters and potable waters. MAC of barium in natural mineral and spring waters was set at 1.0 mg/l, while World Health Organization determined the Ba guideline value in water intended for human consumption at the level of 0.7 mg/l.

**Objective.** The aims of the study were: the determination of barium in natural mineral and spring waters (carbonated, non-carbonated and medium-carbonated waters) produced and bottled on the area of Poland, and assessment of human exposure to this metal presents in the above-mentioned types of waters.

**Material and method.** The study concerning barium determinations in 23 types of bottled natural mineral waters and 15 types of bottled spring waters (bought in Polish retail outlets) was conducted in 2010. The analyses were performed by validated method of determination of barium in water based on inductively coupled plasma optical emission spectrometry, using modern internal quality control scheme.

**Results.** Concentrations of barium determined in natural mineral and spring waters were in the ranges from 0.0136 mg/l to 1.12 mg/l and from 0.0044 mg/l to 0.43 mg/l, respectively. Only in the single case of natural mineral water the concentration of barium (1.12 mg/l), exceeded above-mentioned MAC for this metal, which is obligatory in Poland and the European Union - 1.0 mg/l. The long-term monitoring of barium concentration in another natural mineral water (2006 - 2010), in which incidental exceeding MAC was observed in 2006, was conducted. All measured barium concentrations in this water were lower than 1.0 mg/l and therefore, it is possible to state that the proper method of mixing waters taken from six independent groundwater intakes applied during production is actually used. The estimated Hazard Quotient indices were in the ranges: 0.0019 - 0.16 (natural mineral waters) and 0.00063 - 0.061 (natural spring waters), respectively.

**Conclusions.** The natural mineral waters are usually characterized by higher Ba concentrations than those observed in the cases of natural spring waters. The presence of a high concentration of $HCO_3^-$ in such types of natural waters ensures the existence of $Ba^{2+}$ in solution as $Ba(HCO_3)_2$, which is a highly soluble salt. Taking into account the concentrations of barium determined in above-mentioned waters and the available toxicological data for this metal no long-term risk for human health could be expected (estimated Hazard Quotient indices ≤ 0.16).

**Key words:** *barium, human exposure, natural mineral and spring waters, legislative requirements, ICP-OES*

## STRESZCZENIE

**Wprowadzenie.** Sposób klasyfikacji naturalnych wód mineralnych i źródlanych oraz najwyższe dopuszczalne stężenia (NDS) metali występujących w tych wodach regulują dyrektywy: nr 2003/40/WE i 2009/54/WE oraz w kraju Rozporządzenie Ministra Zdrowia z dnia 30 marca 2011 roku w sprawie naturalnych wód mineralnych, wód źródlanych i wód stołowych. NDS baru w naturalnych wodach mineralnych i wodach źródlanych wynosi 1,0 mg/l, podczas gdy WHO określiła NDS tego metalu w wodzie przeznaczonej do spożycia przez ludzi na poziomie 0,7 mg/l.

**Cel badań.** Głównymi celami badań było oznaczanie baru w naturalnych wodach mineralnych i źródlanych (wody gazowane, niegazowane i średnio gazowane) produkowanych i butelkowanych na terenie Polski oraz oszacowanie narażenia ludzi na ten metal występujący w ww. rodzajach wód.

**Materiał i metoda.** Badania obejmujące oznaczenie baru w 23 rodzajach butelkowanych naturalnych wód mineralnych i w 15 rodzajach naturalnych wód źródlanych (zakupionych w dużych sieciach handlowych w Polsce) przeprowadzono

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w 2010 roku. Analizy wykonano za pomocą zwalidowanej metody oznaczania baru w wodzie techniką optycznej spektrometrii emisyjnej ze wzbudzeniem w plazmie indukcyjnie sprzężonej, przy zastosowaniu nowoczesnego schematu wewnętrznej kontroli jakości.

**Wyniki.** Oznaczone stężenia baru w naturalnych wodach mineralnych i źródlanych zawierały się odpowiednio w zakresach: od 0,0136 mg/l do 1,12 mg/l i od 0,0044 mg/l do 0,43 mg/l. Jedynie w pojedynczej próbce naturalnej wody mineralnej stwierdzono zawartość baru (1,12 mg/l), przewyższającą ww. wartość NDS obowiązującą w Polsce i w Unii Europejskiej - 1,0 mg/l. Wieloletni monitoring zawartości baru w innej naturalnej wodzie mineralnej (2006 - 2010), w której stwierdzono incydentalne przekroczenie NDS tego metalu w 2006 roku, pozwala stwierdzić, że stosowany w trakcie produkcji sposób mieszania wód pochodzących z sześciu ujęć jest prawidłowy i stężenia baru nie przekraczają 1,0 mg/l. Wyznaczone indeksy narażenia HQ zawarte były odpowiednio w zakresach: 0,0019 - 0,16 (naturalne wody mineralne) i 0,00063 - 0,061 (naturalne wody źródlane).

**Wnioski.** Naturalne wody mineralne zwykle charakteryzują się wyższymi stężeniami baru w stosunku do tych obserwowanych w przypadkach naturalnych wód źródlanych. Obecność wysokich stężeń $HCO_3^-$ w tego typu rodzajach wód naturalnych zapewnia występowanie jonu $Ba^{2+}$ w roztworze w postaci $Ba(HCO_3)_2$ - soli o dużej rozpuszczalności w wodzie. Biorąc pod uwagę stężenia baru stwierdzone w ww. badanych wodach i dostępne dane toksykologiczne dla tego metalu można przewidywać, że nawet wieloletnia konsumpcja tego typu wód nie stwarza zagrożenia dla zdrowia ludzi (wyznaczone indeksy narażenia HQ ≤ 0,16).

**Słowa kluczowe:** *bar, narażenie ludzi, naturalne wody mineralne i źródlane, wymagania legislacyjne, ICP-OES*

## INTRODUCTION

The significant growth of natural mineral and spring waters consumption is observed in the last decades. A method of the classification of natural mineral and spring waters and maximum admissible concentrations of metals present in such types of waters are regulated by Commission Directive 2003/40/EC of 16 May 2003 [3], Directive 2009/54/EC of the European Parliament and of the Council of 18 June 2009 [4] and Ordinance of Minister of Health of 30 March 2011 on the natural mineral waters, spring waters and potable waters [11]. Therefore the quality of natural mineral and spring waters has to be continuously monitored in the member states of the European Union.

The composition of natural mineral and spring waters depends mainly on the nature of the geologic background the groundwater passed through. Barium is one of the constituents which is naturally present in mineral and spring waters. This element is mainly derived in above-mentioned natural waters from the dissolution of a carbonate mineral (dolomite and limestone) which also includes meaningful amounts of minerals containing barium like witherite (barium carbonate) and barite (barium sulfate). More than 98% of the total concentration of barium occurs in natural mineral waters as free ions ($Ba^{2+}$), while other species: $BaB(OH)_4^+$, $BaCl^+$, $BaCO_3$, $BaNO_3^+$, and $BaOH^+$, occur in lesser percentages [14].

It was found that exposure for short periods of time to a barium concentration exceeding 2 mg/l led to muscular weakness and gastrointestinal disturbances [1, 12], while long-term exposure caused high blood pressure [2, 10]. Food is the main barium source of intake for the non-occupationally exposed population (300 - 1770 μg Ba/day [15]). Nevertheless, when barium concentration levels in water are high, for example in the cases of natural mineral or spring waters, these types of waters may contribute significantly to total intake. Therefore, maximum admissible concentration of barium in natural mineral waters and natural spring waters was set at 1.0 mg/l [3, 11], while the World Health Organization determined the guidelines value for this metal in water intended for human consumption at the level of 0.7 mg/l [9]. If the barium concentration exceeds above-mentioned limit, the water producer is obliged to reduce their amount in natural mineral or spring water.

In this work comprehensive investigations of barium concentrations in bottled natural mineral and spring waters (produced on the base of Polish groundwater intakes) were performed. On the basis of available toxicological data for this metal long-term risk for human health was assessed after taking into account calculated Hazard Quotient indices.

## MATERIAL AND METHODS

An inductively coupled plasma optical emission spectrometer - Iris Advantage ER/S Duo (Thermo Jarrell Ash, USA) with the application of radial observation system was used for the determination of barium in natural mineral and spring waters. The concentration of barium was determined using spectral line 455,403 nm (raw 74). The sample introduction system, the operating conditions and validation parameters of the analytical method for barium determination in water by ICP-OES, were described previously in detail [6]. Validation parameters of the applied method of barium determination in water [6] - limit of detection (0.0023 mg/l), precision (as repeatability: 1.1% ÷ 1.7%) and trueness (-2.5% ÷ -3.6%) meet the requirements listed in the Appendix No. 2 of Minister of Health Ordinance on the natural mineral waters, spring waters and potable waters [11]: LOD≤0.25 mg/l; precision ≤25%; trueness within the range of ±25%.

The internal quality control scheme described previously for other elements [7] was applied for the determination of barium in water using ICP-OES. It consists of: maintenance of optimal performance of ICP-OES spectrometer, calibration of ICP-OES spectrometer, performing fixed sequence of analytical batch for obligatory measurements and determination of barium in certified reference material (CRM).

Calibration solutions (containing barium in the concentration range of 0.1 - 1.0 mg/l) were prepared with the use of: deionized water obtained from Simplicity 185 UV system (Millipore SAS, France), UltraPUR concentrated nitric acid (60%; GR; Merck, Germany) and stock solution 'Barium ICP Standard 1000 mg/l Ba CertiPUR' (Merck, Germany). 'Check standard' solution containing barium at the concentration level of 0.2 mg/l was prepared by appropriate dilutions of stock solution 'ICP Multi-Element Standard Solution IV CertiPUR' of 1000 mg/l Ba (Merck, Germany). Calibration of ICP-OES spectrometer was performed at the beginning of each measurement day and correlation coefficients better than 0.9999 were achieved in all cases of Ba calibration graphs (type: weighted linear regression). Each sequence of analytical batch (run) consisted of 14 sample measurements (or lower measurements for shorter series with lower number of analytical samples) with obligatory measurements of: procedural (reagent) blank, analytical samples (samples No. 1 - 10), replicate sample (this sample is achieved by dividing one of analytical samples No. 1 - 10 into two sub-samples), 'check standard' and CRM. Almost all the natural mineral and spring waters were analyzed directly, without preliminary dilution. In the single case when the barium concentration exceeded the linear range, 10-fold dilution was made.

Appropriate control charts were prepared for blank level monitoring. No statistically essential change of the detection limit for barium previously established during validation process [6] was observed. Trueness of determination of barium was monitored using CRM -TMDA-51.3 'A high level fortified standard for trace elements' (Environment Canada, Canada) and additionally 'check standard' measurements were performed for control the stability of calibration. All results of barium determinations in CRM were achieved with trueness better than ±10%. All estimated precisions of Ba determinations in replicate sample and in correlated original analytical sample (divided before measurements) expressed as relative standard deviations were better than 5%.

Natural mineral and spring waters were sampled directly after opening original bottles, filtered (when it was necessary) with the use of PTFE membrane syringe filters 0.45 µm (Millipore, USA) and acidified with concentrated nitric acid (0.5 ml of 60% UltraPUR nitric acid per 100 ml of sample).

## RESULTS

Bottled natural mineral waters M1 - M23 (23 producers) and bottled natural spring waters S1 - S15 (15 producers) were bought in Polish retail outlets. It should be underlined that within single type of natural water, carbonated, noncarbonated and medium-carbonated versions of waters (when available) were analyzed. Location of groundwater intakes of natural mineral and spring waters (analyzed within the presented work) on the area of Poland is presented in Figure 1.

The average results of barium determinations in natural mineral waters and in natural spring waters, the estimated appropriate daily intakes and Hazard Quotient indices are given in Table 1 and Table 2, respectively. The average Ba concentration was estimated as the arithmetic mean of results of determination of this metal in water samples collected from two independent bottles of single type of natural water (the same lot number). Additionally, total dissolved solids (TDS) and concentrations of $HCO_3^-$ described on the labels of individual natural waters were presented in Table 1 and 2.

Concentrations of barium determined in natural mineral waters were in the range from 0.0136 mg/l to 1.12 mg/l, while natural spring waters characterized

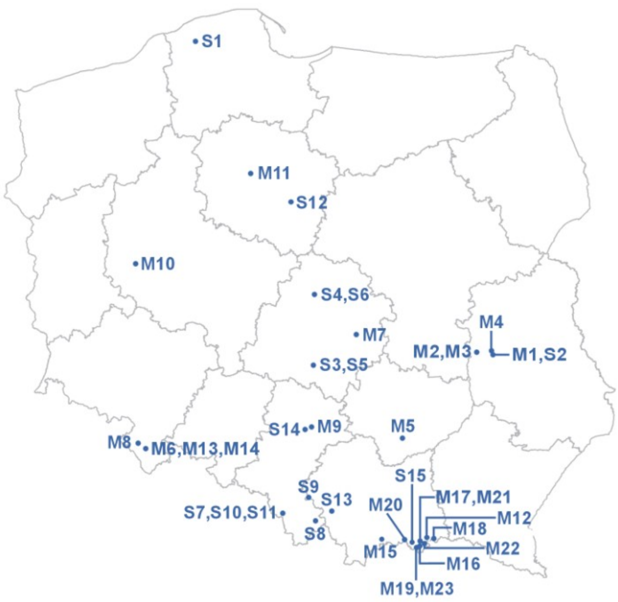


Figure 1. Location of groundwater intakes of natural mineral waters (M1 - M23) and natural spring waters (S1 - S15) on the area of Poland

Table 1. The average results of barium determinations in natural mineral waters, the estimated appropriate daily intakes and Hazard Quotient indices, total dissolved solids (TDS) and hydrogen carbonate ion concentrations

| Marking | Location of groundwater intake/-s applied for production of mineral water | Type[a] | Volume of bottle [l] | TDS [mg/l] | Concentration of $HCO_3^-$ [mg/l] | Average Ba concentration ±SD[b] [μg/l] | Daily intake (DI) [μg/(kg·day)] | Hazard Quotient |
|---|---|---|---|---|---|---|---|---|
| M1 | Nałęczów | NC | 0.5 | 650 | 454 | 14.0 ±0.14 | 0.400 | 0.0020 |
| | | C | 0.5 | | | 13.6 ±0.071 | 0.389 | 0.0019 |
| M2 | Kazimierz Dolny | C | 1.5 | 589 | 388 | 18 ±1.7 | 0.514 | 0.0026 |
| M3 | Kazimierz Dolny | NC | 1.5 | 619 | 362 | 20.0 ±0.50 | 0.571 | 0.0029 |
| M4 | Drzewce (n. Nałęczów) | NC | 0.7 | 714 | 519 | 20.7 ±0.14 | 0.591 | 0.0030 |
| | | C | 0.7 | | | 18.9 ±1.1 | 0.540 | 0.0027 |
| M5 | Busko Zdrój | NC | 0.33 | 786 | 378 | 28.3 ±0.92 | 0.809 | 0.0040 |
| M6 | Gorzanów (n. Polanica Zdrój) | C | 1.5 | 947 | 616 | 29.3 ±1.8 | 0.837 | 0.0042 |
| M7 | Tomaszów Mazowiecki | NC | 0.3 | 1168 | 320 | 33.7 ±2.8 | 0.963 | 0.0048 |
| | | C | 0.3 | | | 34 ±1.7 | 0.971 | 0.0049 |
| M8 | Polanica Zdrój | NC | 0.5 | 895 | 628 | 53.2 ±0.14 | 1.52 | 0.0076 |
| | | C | 0.5 | 891 | 622 | 46.7 ±0.14 | 1.33 | 0.0067 |
| M9 | Postęp | C | 1.5 | 500 | 330 | 59 ±1.2 | 1.69 | 0.0084 |
| | | NC | 1.5 | 500 | 329 | 57.5 ±0.85 | 1.64 | 0.0082 |
| M10 | Grodzisk Wielkopolski | NC | 1.5 | 413 | 260 | 64.3 ±0.71 | 1.84 | 0.0092 |
| M11 | Ostromecko | C | 0.3 | 600 | 259 | 70.4 ±0.21 | 2.01 | 0.010 |
| M12 | Tylicz | C | 1.5 | 383 | 241 | 76 ±6.2 | 2.17 | 0.011 |
| | | NC | 1.5 | | | 80.8 ±0.35 | 2.31 | 0.012 |
| M13 | Gorzanów (n. Polanica Zdrój) | NC | 1.5 | 947 | 616 | 91.5 ±4.5 | 2.61 | 0.013 |
| M14 | Gorzanów (n. Polanica Zdrój) | C | 1.5 | 945 | 613 | 96 ±2.1 | 2.74 | 0.014 |
| M15 | Krościenko | NC | 0.7 | 513 | 336 | 130 ±0 | 3.71 | 0.019 |
| M16 | Powroźnik | MC | 1.5 | 2507 | 1849 | 137 ±3.5 | 3.91 | 0.020 |
| M17 | Krynica Zdrój | NC | 2 | 1755 | 1294 | 202 ±12 | 5.77 | 0.029 |
| M18 | Wysowa-Zdrój | MC | 0.33 | 1973 | 1172 | 416 ±0.71 | 11.9 | 0.059 |
| M19 | Muszyna | C | 1.5 | 1834 | 1398 | 468 ±13 | 13.4 | 0.067 |
| | | MC | 1.5 | 1500 | 1398 | 506 ±20 | 14.5 | 0.072 |
| M20 | Piwniczna Zdrój | NC | 0.5 | 1729 | 1260 | 724 ±2.1 | 20.7 | 0.10 |
| | | C | 1.5 | 1756 | 1255 | 707 ±38 | 20.2 | 0.10 |
| | | MC | 1.5 | 1729 | 1260 | 930 ±12 | 26.6 | 0.13 |
| | | MC | 0.5 | 1729 | 1260 | 688 ±33 | 19.7 | 0.10 |
| M21 | Krynica Zdrój | MC | 1.5 | 2459 | 1818 | 890 ±4.2 | 25.4 | 0.13 |
| | | C | 1.5 | | | 780 ±59 | 22.3 | 0.11 |
| M22 | Szczawnicze Potoki (n. Krynica Zdrój) | NC | 0.5 | 1495 | 1098 | 943 ±4.2 | 26.9 | 0.13 |
| | | C | 0.5 | | | 955 ±12 | 27.3 | 0.14 |
| M23 | Muszyna | MC | 1.5 | 1548 | 1154 | 1120 ±28 | 32.0 | 0.16 |
| | | C | 1.5 | | | 859 ±17 | 24.5 | 0.12 |

[a] Type of natural mineral water: NC - noncarbonated; C - carbonated; MC - medium-carbonated.
[b] Standard deviation for two results of Ba determinations in natural mineral water sampled from two independent bottles (the same lot number).

by lower concentrations of this metal in the range of 0.0044 - 0.43 mg/l.

## DISCUSSION

Only in the single case of natural mineral water (M23 - medium-carbonated), the concentration of barium - 1.12 mg/l, exceeded established MAC for this metal, which is obligatory in Poland and in the European Union. The long-term monitoring of barium concentration (2006 - 2010) in another natural mineral water - M20, in which incidental exceeding MAC was observed in 2006 (carbonated: $c_{Ba}$ = 1.54 mg/l; noncarbonated and medium-carbonated: $c_{Ba}$ = 1.50 - 1.61 mg/l), was conducted. All measured barium concentrations in this water were lower than 1.0 mg/l (including data achieved in 2010). Therefore it is possible to state that the proper method of mixing waters taken from six independent groundwater intakes (P-2, P-5, P-6, P-8, P-9 and P-11) applied during production is actually used.

The barium concentrations in Polish natural waters were generally higher than those determined in imported bottled natural mineral and spring waters (bought in Polish retail outlets) which were included in the ranges of 0.0023 - 0.578 mg/l and 0.0037 mg/l - 0.0889 mg/l,

Table 2 The average results of barium determinations in natural spring waters, the estimated appropriate daily intakes and Hazard Quotient indices, total dissolved solids (TDS) and hydrogen carbonate ion concentrations

| Marking | Location of groundwater intake/-s applied for production of spring water | Type[a] | Volume of bottle [l] | TDS [mg/l] | Concentration of $HCO_3^-$ [mg/l] | Average Ba concentration ±SD[b] [μg/l] | Daily intake (DI) [μg/(kg·day)] | Hazard Quotient |
|---|---|---|---|---|---|---|---|---|
| S1 | Damnica (n. Słupsk) | NC | 0.5 | 266 | 161 | 8.05 ±0.071 | 0.230 | 0.0012 |
| S2 | Nałęczów | C | 1.5 | 679 | 482 | 13 ±1.3 | 0.371 | 0.0019 |
| | | NC | 1.5 | | | 4.4 ±0.85 | 0.126 | 0.00063 |
| S3 | Kleszczów | NC | 1.5 | 289 | 170 | 17.8 ±0.25 | 0.509 | 0.0025 |
| S4 | Aleksandria (n. Ozorków) | C | 1.5 | 275 | 181 | 18 ±1.2 | 0.514 | 0.0026 |
| S5 | Kleszczów | NC | 2 | - | 170 | 18.5 ±1.7 | 0.529 | 0.0026 |
| S6 | Aleksandria (n. Ozorków) | C | 1.5 | 263 | 173 | 21.3 ±0.071 | 0.609 | 0.0030 |
| | | NC | 1.5 | 248 | 165 | 20.8 ±0.071 | 0.594 | 0.0030 |
| S7 | Ustroń | C | 0.33 | - | - | 29.5 ±0.53 | 0.843 | 0.0042 |
| | | NC | 0.33 | | | 29.5 ±0.61 | 0.843 | 0.0042 |
| S8 | Jeleśna | NC | 1.5 | 232 | 136 | 76.5 ±0.71 | 2.19 | 0.011 |
| | | C | 1.5 | 312 | 202 | 18.5 ±0.14 | 0.53 | 0.0026 |
| | | MC | 1.5 | | | 18 ±1.6 | 0.51 | 0.0026 |
| S9 | Kęty | NC | 1.5 | 230 | b.d. | 78.9 ±0.21 | 2.25 | 0.011 |
| S10 | Ustroń | NC | 1.5 | 507 | 337 | 118 ±9.2 | 3.37 | 0.017 |
| S11 | Ustroń | C | 0.5 | 442 | 275 | 122 ±0 | 3.49 | 0.017 |
| S12 | Nieszawa | C | 1.5 | 700 | 451 | 125 ±4.2 | 3.57 | 0.018 |
| | | NC | 1.5 | | | 140 ±0 | 4.00 | 0.020 |
| S13 | Sucha Beskidzka | NC | 1.5 | 600 | 384 | 134 ±0.71 | 3.83 | 0.019 |
| S14 | Rzeniszów | NC | 1.5 | 405 | 284 | 271 ±0 | 7.74 | 0.039 |
| | | MC | 1.5 | 402 | 287 | 269 ±20 | 7.69 | 0.038 |
| S15 | Zubrzyk | MC | 0.5 | 1792 | 1352 | 419 ±9.9 | 12.0 | 0.060 |
| | | C | 0.5 | | | 430 ±30 | 12.3 | 0.061 |

[a] Type of natural spring water: NC - noncarbonated; C - carbonated; MC - medium-carbonated.
[b] Standard deviation for two results of Ba determinations in natural spring water sampled from two independent bottles (the same lot number).

respectively [13]. On the other hand, in the cases of natural mineral waters (based on groundwater intakes) applied for therapeutic and balneoclimatic purposes, the concentrations of barium can achieve up to 24.0 – 25.18 mg/l (Poland [5, 6] and 3.5 mg/l (Romania [14]).

The total dissolved solids (TDS) were presented in natural mineral and spring waters in the ranges of: 383 - 2507 mg/l and 230 - 1792 mg/l, respectively. The TDS was determined to have positive correlation with barium concentration (mineral waters: r = 0.704, and spring waters: r = 0.798). $HCO_3^-$ is the predominant constituent of all natural mineral and spring waters examined in this study (concentration ranges in mineral and spring waters: 241 - 1849 mg/l and 136 - 1352 mg/l, respectively). It was found to be correlated with the barium concentrations present in these type of waters (mineral waters: r = 0.742, and spring waters: r = 0.794). The presence of a high concentration of hydrogen carbonate ions in the natural mineral and spring waters under investigation ensures the existence of $Ba^{2+}$ in solution as $Ba(HCO_3)_2$, which is a highly soluble salt [14].

Barium enters into human body through several pathways including food chain, dermal contact and inhalation but in comparison to oral intake all others are negligible. The daily intake (*DI*) based on ingestion of natural mineral or spring water can be calculated according to the previously described equation for another metal [8]:

$$DI = C_{Ba} \times IR_W / BW$$

where, $C_{Ba}$, $IR_W$ and $BW$ represent: the concentration of barium in natural mineral or spring water (mg/l), ingestion rate of water (2 l/day) and body weight (70 kg), respectively.

A reference dose (*RfD*) of 0.2 mg·kg$^{-1}$·day$^{-1}$ for chronic exposure to non-cancerogenic element was estimated for barium [15]. Thus, the Hazard Quotient (HQ) indices (connected with the consumption of natural water) can be calculated directly by comparing the estimated daily intake (*DI*) with *RfD* of barium [8].

The estimated Hazard Quotient indices are in the ranges of 0.0019 - 0.16 (natural mineral waters M1 - M23) and 0.00063 - 0.061 (natural spring waters S1 - S15). It should be noted that all estimated HQ indices are significantly less than 1 (HQ<<1). Therefore it is possible to state that there is no appreciable risk that adverse health effects will occur.

## CONCLUSIONS

1. Concentrations of Ba determined in bottled natural mineral waters produced in Poland (0.0136 - 1.12 mg/l) were generally higher than these observed in natural spring waters (0.0044 - 0.43 mg/l).
2. Only in the single case of natural mineral water (M23), the concentration of Ba (1.12 mg/l) exceeded established MAC. Therefore this water can be used for drinking purposes only after the reduction of Ba content.
3. The long-term monitoring of Ba concentration in natural mineral water M20 has shown that all measured Ba concentrations were lower than 1.0 mg/l and therefore, it is possible to state that the proper method of mixing waters taken from six independent groundwater intakes applied during production is actually used.
4. The presence of a high concentration of $HCO_3^-$ in such types of natural waters ensures the existence of $Ba^{2+}$ in solution as $Ba(HCO_3)_2$, which is a highly soluble salt.
5. On the basis of available toxicological data for barium, observed concentrations of this metal in natural mineral and spring waters did not imply long-term risk for human health, as estimated HQ indices were significantly lower than 1 (HQs ≤ 0.16).

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