Environmental Engineering and Management Journal July 2018, Vol.17, No. 7, 1667-1677
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

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ANALYSIS OF COMMERCIALLY AVAILABLE BOTTLED WATER IN POLAND

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Abstract

Bottled water (commonly called mineral) makes an important source of minerals for humans. Its consumption has been systematically rising in the highly industrialized countries, even though not every water type has appropriate health properties. As a result, drinking bottled water ought to be supported with understanding its qualities and physicochemical content.
The following article presents the results of the research into pH levels, electrical conductivity, selected inorganic anions (F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}), cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}), metals and metalloids (Co, Ni, Cu, Zn, Cd, Pb, As, Cr, Mn, Ba, Rb, Sr, Ag, Tl, V, U, Bi, Mo, Sb) of determined for the 48 bottled waters commercially available in Polish supermarkets. The methodology optimization applied for the selected inorganic anions and cations as well as metals and metalloids helped to determine them on the ultra-trace levels ($<\mu g\ L^{-1}$). Inorganic ions were analyzed with the ion chromatography method. On the other hand, the ICP-MS method was applied to analyze metals and metalloids. The validation parameters (limits of detection and quantification, recovery, regression coefficients and coefficient of variation) were sufficient for the ultra-trace analysis. Due to the comparison of the obtained results with the data provided by producers, numerous significant differences were observed.

Key words: bottled water, ion chromatography, inorganic ions, metals, trace elements

Received: May, 2013; Revised final: September, 2014; Accepted: September, 2014; Published in final edited form: July 2018

1. Introduction

Water has vital importance for the human organism as it participates in the transportation of nutrients into cells and tissues. It also removes unwanted metabolic products. It is delivered not only by consuming various beverages, such as coffee or tea, or eating different dishes, but also by drinking bottled water, commonly called "mineral". There is a great number of the commercially available water types. To choose the one that is beneficial to human health, it is important to read the labels carefully. There are also many types of table water, which are often confused with mineral water. These are frequently distilled waters which producers supply with mineral salts. It is estimated that nearly 50% of the bottled water sold in the world is expensive tap water. The problem is that a liter of tap water is 250-600 times cheaper than a liter of bottled water, even though its quality is often as high as the one of the so-called mineral water. Bottled water makes an important source of minerals for the human organism. Its consumption has been systematically rising in the highly industrialized countries, even though not every water type has appropriate health properties. The World Bank estimates that the global mineral water market is worth $ 800 billion per year. In 2011, nearly $ 4.5 billion was spent on non-alcoholic beverages in Poland. Therefore, the quality of drinking bottled water has to be controlled systematically. Most tested mineral waters available in the Polish market are compliant with the required hygiene standards. The

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nomenclature concerning the so-called "mineral water" is equivocal (Diduch et al., 2011). The water is usually classified as lowly, medium and highly mineralized water. Curative, spring and table waters are incorrectly included within this category. It is also possible to classify water either as carbonated or non-carbonated.

Researchers believe that nearly 20 properly concentrated minerals should be present in the human body to ensure proper functions of the human organism and to maintain its homeostasis. Selected ions and metals/metalloids constitute these minerals (Birke, et al., 2010). Some of them can be found in drinking and mineral water. Mineral waters usually contain sodium, potassium, magnesium, calcium, chlorides, sulfates, and several trace metals and metalloids. If the mineral contents in the organism are not appropriate, several imbalances may occur. Some of them may lead to serious negative human effects (WHO, 2005). When water is saturated with CO_2, its taste becomes slightly tart, bacteria development is stopped and its expiry date is longer. CO_2 improves digestion and whets the appetite. As it enhances urine production and helps to detoxify the organism, it is advisable to drink after the physical effort. It should be drunk in small portions as it is easily absorbed. On the other hand, it is not recommended to people on a diet and or those who suffer from the peptic ulcer disease.

Non-carbonated water is appropriate for people suffering from heartburn, flatulence and cardiovascular disorders. Depending on its source, mineral water contains various amounts of macro and microelements (e.g. Mg, Na, K, Li, Ca, Sr, Zn, Mn, Fe, Se, Cu, chlorides, sulfates, fluorides, iodides, bromides, and nitrates) that have a significant impact on living organisms. Magnesium regulates heart work and participates in the thermoregulation and nerve conduction. Potassium helps to control the water-mineral balance, decreases blood pressure and regulates nerve and muscle activities. Calcium has impact on the muscle contractility, nerve impulse transmission, blood coagulation and it is contained in bones and teeth. Iron is essential for the transportation and storage of oxygen in the organism. Zinc, copper and manganese take part in the metabolic processes while chlorides regulate blood pH. On the other hand, people suffering from the elevated blood pressure and kidney problems should not drink sodium-rich water as this element increases blood pressure and contributes to water retention and edemas. The occurrence of those substances in water has usually a positive impact on human health. Unfortunately, consumers are not informed on the presence and concentrations of harmful substances that may also occur in water.

The maximum concentrations of the potentially harmful substances, i.e. those whose presence in water must be controlled in the Polish bottled waters, are listed in Annex 1 of the appropriate Directive (Regulation of the Minister of Health of 31 March 2011). The requirements concerning determination methods of the potentially toxic substances are given in Annex 2. Spring water undergoes the same standard analyses as the natural mineral water. Spring water at the intake and in bottles must meet specific microbiological, chemical, chemicophysical and organoleptic requirements defined for drinking water. Bottled table water must meet microbiological requirements.

It must also be compliant with the regulations on the permissible levels of chemical components, which are specifically defined for drinking water and whose excess could pose a threat for the public health. Mineral components that can be used in the table water production are: calcium chloride, magnesium chloride or sulfate, chlorides, sulfates, or potassium and sodium bicarbonates. Their chemical purity must comply with the regulations for foodstuff. Bottled water can be admitted for consumption only when the concentrations of its constituents do not exceed the standards specified in various legal regulations. Table 1 provides a list of such standards recommended both by the international and Polish institutions.

Table 1. Regulations and standards for bottled water intended for human consumption

Parameter	***European Economic Community (2003)***	***International Bottled Water Association (2009)***	***U.S. Food and Drug Administration (2010)***	***Polish legalization Dz. U. Nr 85, poz.466 (May 7th, 2011)***
Physical parameters				
Color	-	5	15	5
pH	-	6.5-8.5	6.5-8.5	6.5-8.5
Total dissolved substances	-	500	500	-
Turbidity	-	0.5	5	-
Disinfection by-products [μg/L]				
Bromate	-	10	10	3
Chlorine	-	100	4000	-
Chlorite	-	1,000	1000	-
Haloacetic acids	-	60	60	-
Trihalomethanes (total)	-	10	80	-
Inorganic chemicals [mg/L]				
Aluminum	-	0.2	0.2	-

Ammonium	-	-	-	-
Antimony	0.005	0.006	0.006	0.005
Arsenic	0.01	0.01	0.01	0.01
Barium	-	1	2	1
Beryllium	-	0.004	0.004	-
Boron	1	-	-	5
Cadmium	0.003	0.005	0.005	0.003
Chloride	-	250	250	-
Chromium	0.05	0.05	0.1	0.05
Copper	1	1	1	1
Cyanide	0.07	0.1	0.1	0.07
Fluoride	5	-	-	5
Iron	-	0.3	0.3	-
Lead	0.01	0.005	0.005	0.01
Manganese	0.5	0.05	0.05	0.5
Mercury	0.001	0.001	0.002	0.001
Molybdenum	-	-	-	-
Nickel	0.02	0.1	0.1	0.2
Nitrate	50	50	50	50
Nitrite	0.1	1	1	0.1
Selenium	0.01	0.01	0.05	0.01
Silver	-	0.025	0.1	-
Sodium	-	-	-	-
Sulfate	-	250	250	-
Thallium	-	0.002	0.002	-
Uranium	-	0.03	0.03	-
Zinc	-	5	5	-
Organic chemicals [μg/L]				
Acrylamide	-	-	-	-
Benzene	-	0.001	0.001	-
Pesticides (the sum of)	-	-	-	-
Phenols	-	0.001	0.001	-

The analytical chemists must develop reliable and conclusive methods for determinations a wide range of substances present in bottled waters in the qualitative and quantitative ways. Determining contents of inorganic and organic compounds is difficult, due to: low levels of individual compounds present in samples; complex compositions (high mineralization degree); interactions between the constituents present in samples; and possible changes in the composition during transport and storage resulting from reactions and potential desorption of constituents from the packaging materials (Birke at al., 2010; Muntean and Mihaiescu, 2016). Therefore, it is necessary to use appropriate, sensitive and selective methods, such as gas and liquid chromatography coupled with the mass spectrometry detectors (Jin et al., 2010). The aim of the study was to test 48 mineral waters available in the Polish market to determine the contents of selected inorganic anions and cations, several dozens of trace elements, and the pH and electrical conductivity values. Additionally, the data obtained from water producers and the research results was compared whenever it was possible.

2. Experimental

2.1. Research subject and range

A number of 48 types of bottled water (mineral, table, spring and curative ones) were bought in a few Polish supermarkets. The samples were determined in terms of the electrical conductivity, pH and contents of the main inorganic anions (F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}), cations (Li^+, Na^+, NH_4^+, Mg^{2+} and Ca^{2+}), selected metals and metalloids (Co, Ni, Cu, Zn, Cd, Pb, As, Cr, Mn, Ba, Rb, Sr, Ag, Tl, V, U, Bi, Mo, Sb).

2.2. Research methods

Electrical conductivity and pH were measured with the multifunction CX-401 meter (Elmetron, Poland) with the ERH 111 electrode (Hydromet, Poland) and CD-2 conductivity detector (Hydromet, Poland). Inorganic ions were determined with an ion chromatograph (Metrohm, Switzerland) equipped with: IC 818 pump, IC 837 eluent degasser, IC 830 interface, IC 820 separation center, Valco injection valve, Metrodata 2.3 software, IC 838 automatic sample feeder and IC 819 conductivity detector. The Institute of Environmental Engineering of the Polish Academy of Sciences in Zabrze, where analyses were carried out, has the laboratory that possesses the ISO 17025 ISO (ISO standard, 2005) accreditation of the Polish Accreditation Centre (PCA), number 950.

The analytical conditions for the determination of inorganic ions were:

– Anions (F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-});
– Column-Metrohm Metrosep A Supp 3;
– Eluent-1.7 mM Na_2CO_3 + 1.6 mM $NaHCO_3$;

- Eluent flow rate-0.85 mL/min;
- Injection volume-20 µL;
- Detection-suppressed conductivity;
- Cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+});
- Column-Metrohm Metrosep C3;
- Eluent-5 mM HNO_3;
- Eluent flow rate-1.0 mL/min;
- Injection volume-100 µL;
- Detection-non-suppressed conductivity.

The contents of selected metals and metalloids were determined with the ICP-MS technique (ICP-MS Elan 6100 DRC-e Perkin Elmer spectrometer). The ICP-MS spectrometer analytical parameters are given in Table 2.

Table 2. ICP-MS spectrometer parameters

Parameter	***Settings***
RF generator power [W]	1,125
Argon - plasma gas flow [L/min]	15
Argon - nebulizer gas flow [L/min]	0.76-0.82
Argon - auxiliary gas flow [L/min]	1.15-1.16
Nebulizer	cross-flow
Torch	quartz
Scanning mode	peak hopping
Dwell time [ms]	250
Sweeps/Reading	1
Number of replicates	830

2.3. Reagents

$NaHCO_3$ and Na_2CO_3 of analytical purity were used to prepare the eluent for the inorganic anion determinations. Ultrapure HNO_3 (POCh, Gliwice, Poland) was employed to prepare the cation determination eluent. The properly composed and concentrated eluents were prepared by weighing an appropriate sample mass (or collecting appropriate volume) of a given substance. It was then solved in a 2-L laboratory flask. Standard solutions of specific anions (F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) and cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were made with the Fluka reference materials (Steinheim, Switzerland). Their concentrations amounted to 1000 ± 2 mg/L. Water used for standards and eluents preparation came from the Millipore deionizer (Merck, Germany). Its electrical conductivity was < 0.05 µS/cm. Calibration solutions were made by diluting appropriate standard solutions right before their application. All solutions were kept in glass or high-density polyethylene (HDPE) containers at room temperature.

The ICP-MS spectrometer was optimized daily with a 10-µg/L solution (Mg, Cu, Rh, Cd, In, Ba, Ce, Pb, U) in 1% HNO_3 Elan 6100 Setup/Stab./Masscal. Solution (Perkin-Elmer). An application enabling measurements of 53Cr, 55Mn, 59Co, 60Ni, 65Cu, 66Zn, 69Ga, 75As, 85Rb, 88Sr, 98Sr, 107Ag, 114Cd, 121Sb, 130Te, 138Ba, 205Tl, 208Pb, 209Bi, 238U isotopes was prepared. To determine Pb in a quantitative way, a correction equation (Pb208=Pb208+Pb206+Pb207) was employed. The analyses were carried out with the internal standard method, which was constituted by 10 µg/L Rh solution introduced on-line with a peristaltic pump. All solutions and standards were made with the high-quality deionized Milli-Q-Gradient Millipore water (Merck, Germany). 1 g/L single-element standard solutions of Cd, Pb, Zn, Sb (Merck, Germany) and a certified multi-element standard solution were used for calibration. It was obtained by diluting 10 mg/L of the VI calibration solution (Merck, Germany). Calibration was verified with another certified multi-element standard, i.e. XXI (Merck, Germany). All standards were prepared daily with weight dilution. The method validation was performed on the basis of the certified reference material - NIST 1643e Trace Elements In Water.

2.4. Sample preparation

The carbonated water samples were degassed in a sonic bath before the analysis. The examined water samples were filtered through a 0.2-µm nitrocellulose filter. Subsequently, they underwent chromatographic and ICP-MS analyses. Water samples were acidified with the ultra-pure concentrated nitric acid (Merck, Germany) before the quantitative analysis with ICP-MS spectrometer.

2.5. Validation of the applied analytical methods

Taking into consideration the inorganic ion determination methodologies, the calibration was performed in compliance with the ISO 8466-1 (ISO Standard, 1990). 7 standard solutions which contained various concentrations of given ions were prepared to define validation parameters for the methodology of the inorganic anion determination. Each solution went through the chromatographic analysis three times. The obtained peak areas of the specific ions served to calculate: standard deviation, variation coefficient, limits of detection and quantification, and correlation coefficient. The results are given in Table 3.

Table 3. Validation parameters for the ion chromatographic method (inorganic ions)

Parameter	***Anions***					***Cations***				
	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Concentration range [mg/L]	0.2-2.0	1-100	0.2-20	0.2-20	1-100	1-100	0.2-2.0	0.5-50	1-100	1-100
Standard deviation [mg/L]	0.019	0.232	0.079	0.029	0.132	0.098	0.159	0.102	0.081	0.115
Coefficient of variation [%]	2.68	4.57	2.76	4.82	3.17	3.82	4.94	1.84	3.67	3.43
Limit of detection [mg/L]	0.012	0.064	0.048	0.019	0.131	0.091	0.027	0.095	0.17	0.211
Limit of quantification [mg/L]	0.036	0.192	0.144	0.057	0.353	0.273	0.081	0.285	0.51	0.633
Regression coefficient (r^2)	0.999	0.999	0.999	0.999	0.999	0.999	0.998	0.999	0.999	0.998

The ICP-MS method validation was performed on the basis of the certified reference material - NIST 1643e Trace Elements in Water. The validation parameters are given in Table 4.

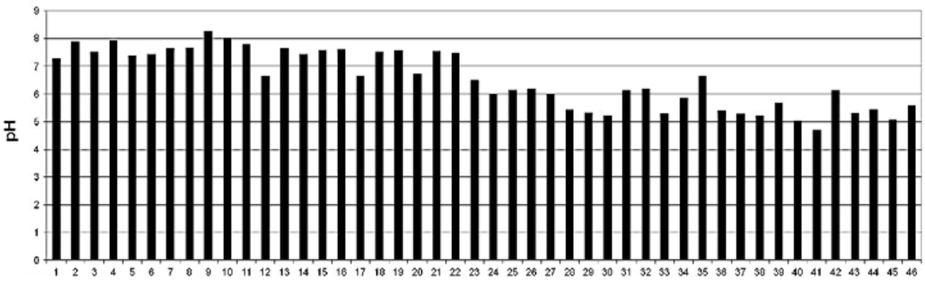
2. Results and discussion

25 non-carbonated, 12 lightly carbonated and 11 carbonated waters constituted the analyzed group of the 48 water brands. The bottle volume was usually 0.5 L or 1.5 L, however there were also 0.33-L and 2.5-L bottles. As it is apparent from the data in Table 1, the requirements of various organizations for the quality of bottled waters are highly diverse.

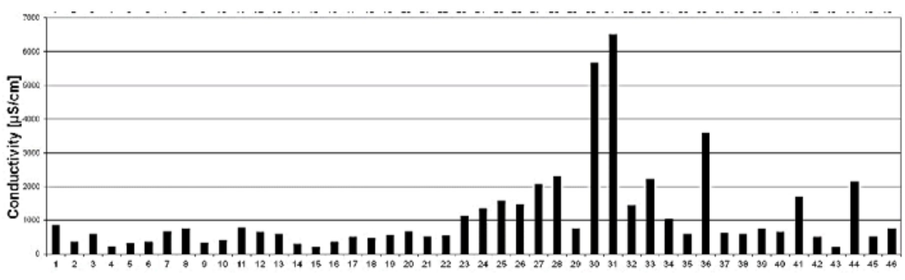
The qualitative and quantitative ranges of substances regulated by the International Bottled Water Association (IBWA) and U.S. Food and Drug Administration (U.S. FDA) are much greater than the ranges defined by the European Economic Community and Polish regulations. Fig. 1 presents conductivity and pH values for the analyzed water samples. The results of the selected inorganic anion (F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) and cation (Li^+, Na^+, NH_4^+, Mg^{2+} and Ca^{2+}) determinations are shown in Figs. 2 and 3, respectively. The water producer values given in Figs. 2 and 3 are marked in red, and the black color concerns the analysis data.

Table 4. Validation parameters for metals and metalloids determined with ICP-MS

Element	*Limit of detection [μg/L]*	*Limit of quantification [μg/L]*	*Relative standard deviation of reproducibility [%]*	*Relative standard deviation of repeatability [%]*	*Recovery [%]*
Co	0.002	0.007	6.4	3.3	116.43
Ni	0.024	0.072	3.8	3.2	82.09
Cu	0.064	0.191	10.4	6.3	96.07
Zn	0.181	0.543	4.6	4.6	80.27
Cd	0.04	0.12	4.6	3.9	87.99
Pb	0.036	0.107	5.8	3.5	108.08
As	0.096	0.289	11.4	7.6	106.95
Cr	0.013	0.039	5	4.8	109.63
Se	0.041	0.123	3.1	3.9	96.81
Mn	0.033	0.098	5.1	5.9	107.31
Ba	0.01	0.03	6.9	3.2	111.14
Rb	0.003	0.008	5.3	13.9	104.62
Sr	0.008	0.025	8.2	6.5	95.39
Ag	0.002	0.007	7.1	3.9	107.02
Tl	0.002	0.006	13.9	11.3	105.67
V	0.09	0.27	5.5	5.9	103.25
U	0.011	0.033	4.7	3.7	-
Te	0.008	0.024	6.3	5.1	101.44
Bi	0.018	0.054	5.8	5.5	98.36
Ga	0.042	0.126	5.2	4	-
Mo	0.027	0.081	9.7	8.1	99.87



(a)



(b)

Fig. 1. Conductivity and pH values of the analyzed samples: (a) pH, (b) conductivity

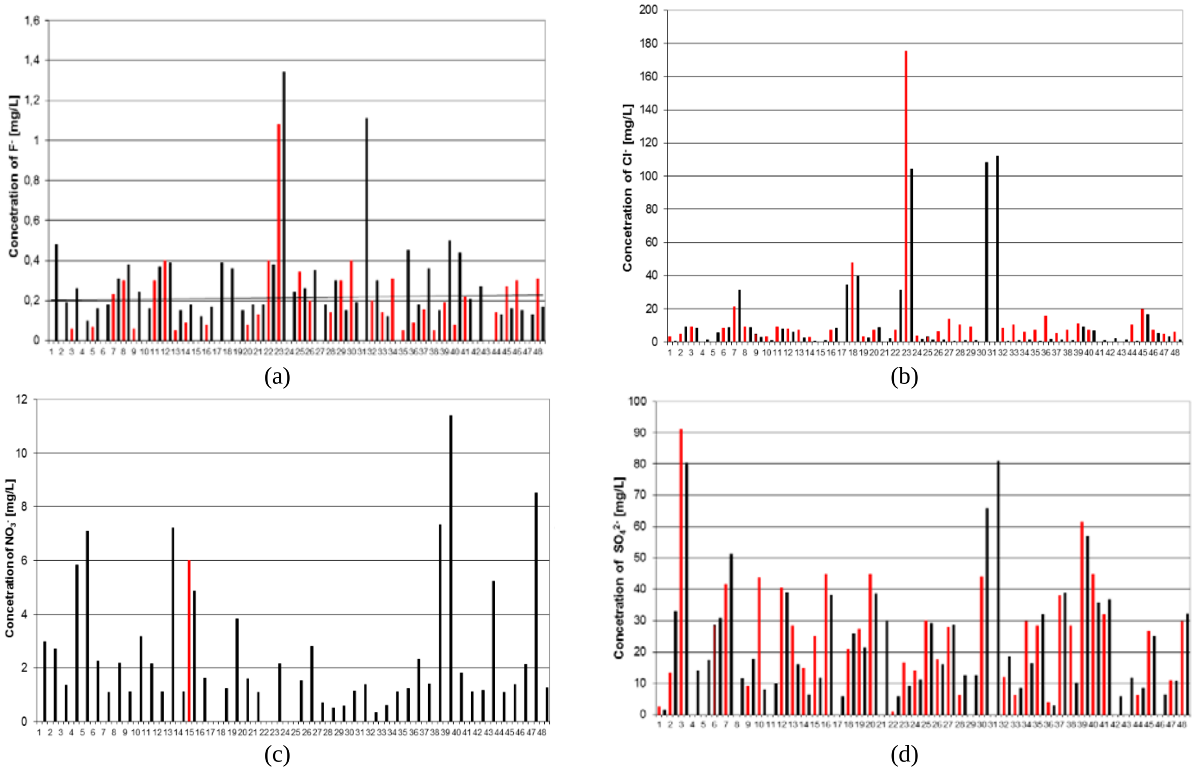


Fig. 2. Concentrations of common inorganic anions in the analyzed samples: (a) F^-, (b) Cl^-, (c) NO_3^- (d) SO_4^{2-}

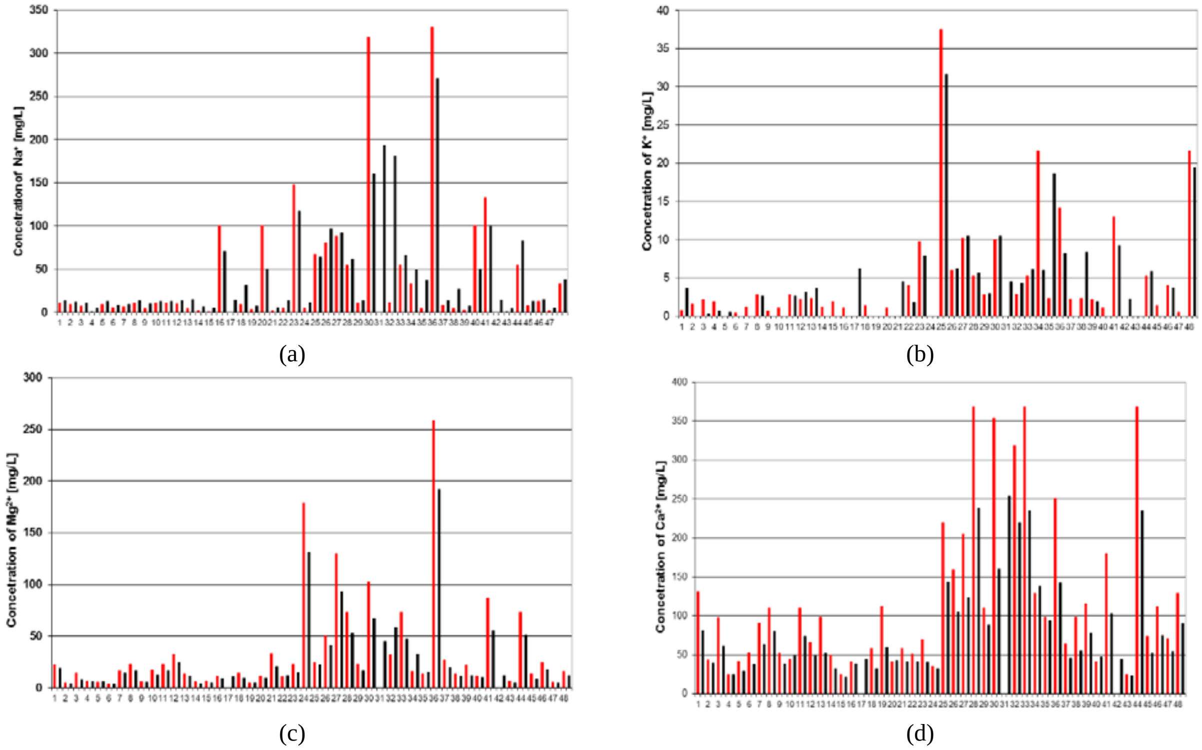


Fig. 3. Concentrations of common inorganic cations in the analyzed samples: (a) Na^+, (b) K^+, (c) Mg^{2+}, (d) Ca^{2+}

Figs. 4-8 present the determination results for the selected metal and metalloid concentrations. Before deliberating over the trace elements, some major elements should be discussed as they are usually reported on the label. Manufacturers do not give the information on the metal and metalloid concentrations, which was the subject of this research. Usually, only the content of the main inorganic anions and cations is given. The graphical comparison of the study results for inorganic ions with the values reported by producers on the bottled water labels is shown in Fig. 9.

In some cases, the same water type was analyzed but either the bottles in which it was sold differed (samples 11 and 29, 28 and 33, 30 and 31) or the water was saturated with carbon dioxide to a different extent (samples 4 and 15, 16 and 40, 34 and 48). Most of the examined water types came from Poland but some were produced in the Czech Republic (sample 24) or Lithuania (samples 17, 22, 30 and 31). Multinational corporations, such as PepsiCo (samples 4, 15 and 43), Coca-Cola (samples 10 and 26) and Nestle (samples 8, 11, 29 and 46), produce several popular water types in Poland. The obtained pH values ranged between 4.69 (sample 43) and 8.28 (sample 9). Higher pH values were determined for non-carbonated water, while lower ones were observed for carbonated water (Fig. 1). A classic example is sample 4. The non-carbonated water version had pH of 7.91, but when saturated with carbon dioxide (sample 43), it was only 4.69. There were slighter differences in the case of the lightly carbonated sample 34 (pH= 5.29) and carbonated sample 48 (pH=5.59). The average value of electrical conductivity for non-carbonated water was < 1,500 µS/cm. What seems interesting is the fact that this value was the same for a few carbonated water types (Fig. 1). Samples 30 and 31 had definitely higher values, which were > 5,000 µS/cm.

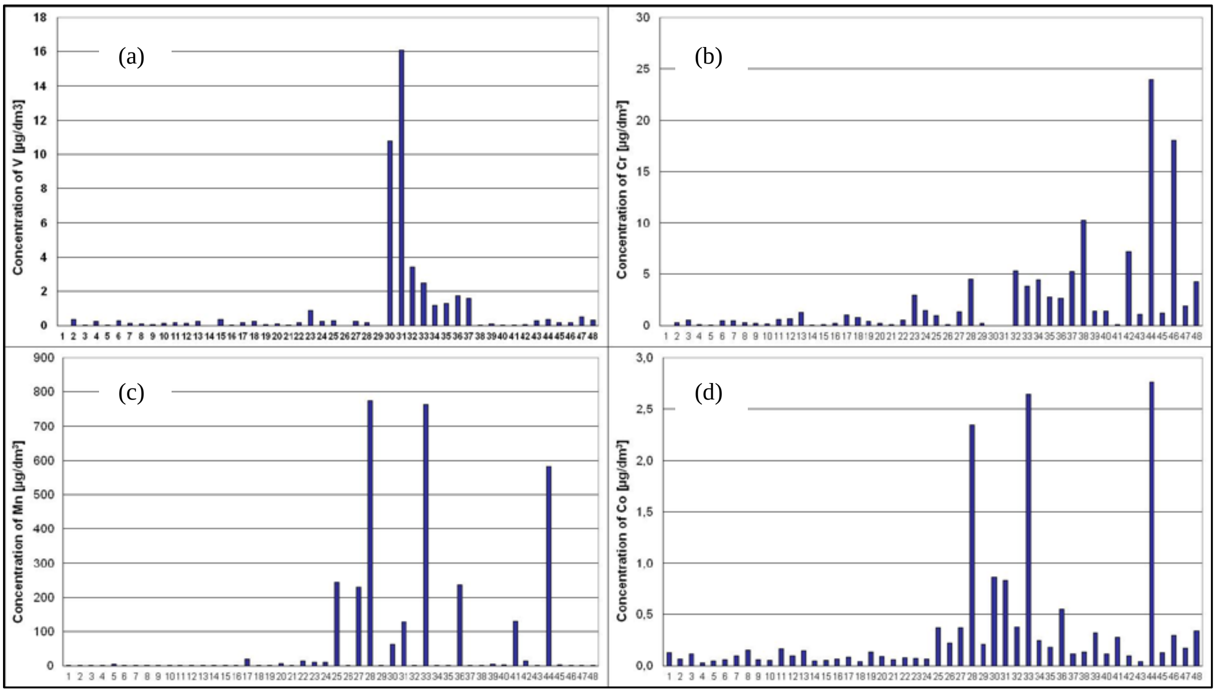


Fig. 4. Concentrations of V, Cr, Mn and Co in the analyzed samples: (a) V, (b) Cr, (c) Mn, (d) Co

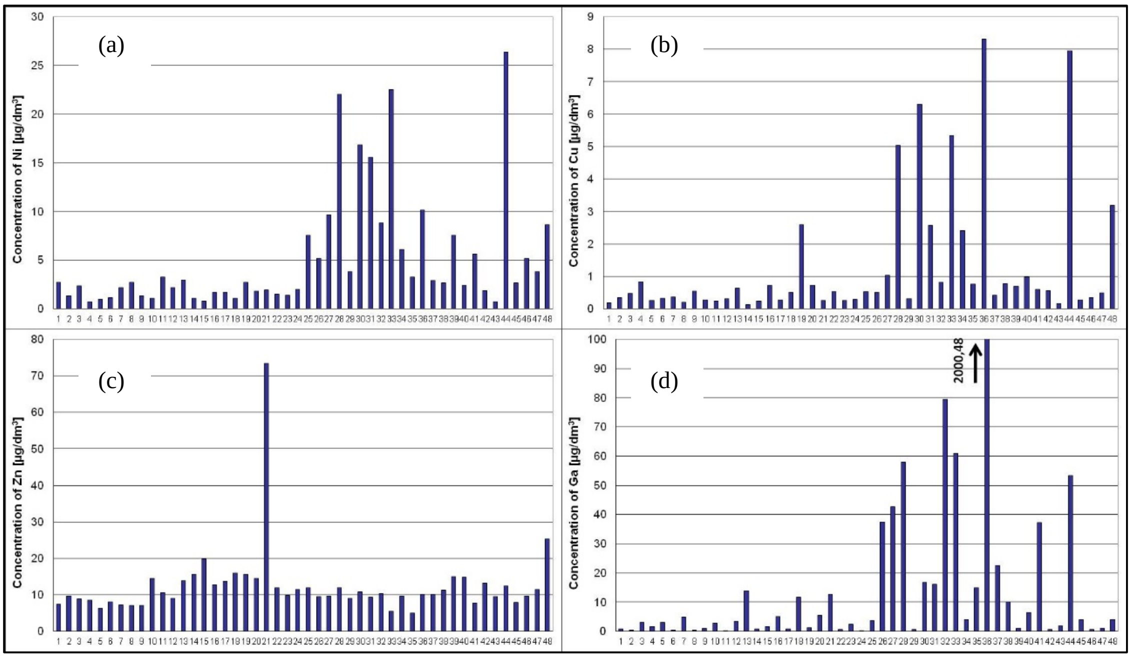


Fig. 5. Concentrations of Ni, Cu, Zn and Ga in the analyzed samples: (a) Ni, (b) Cu, (c) Zn, (d) Ga

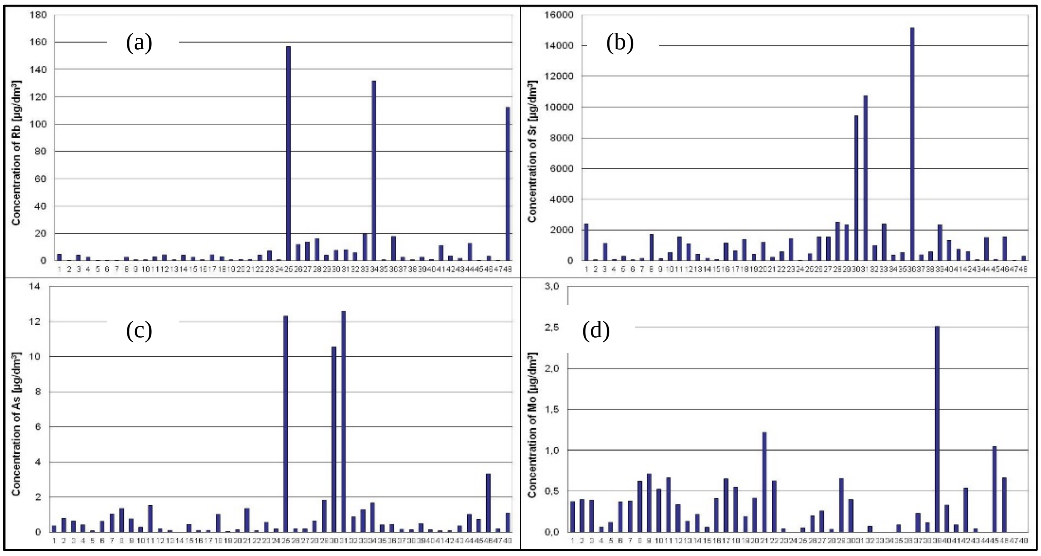


Fig. 6. Concentrations of Rb, Sr, As and Mo in the analyzed samples: (a) Ru, (b) Sr, (c) As, (d) Mo

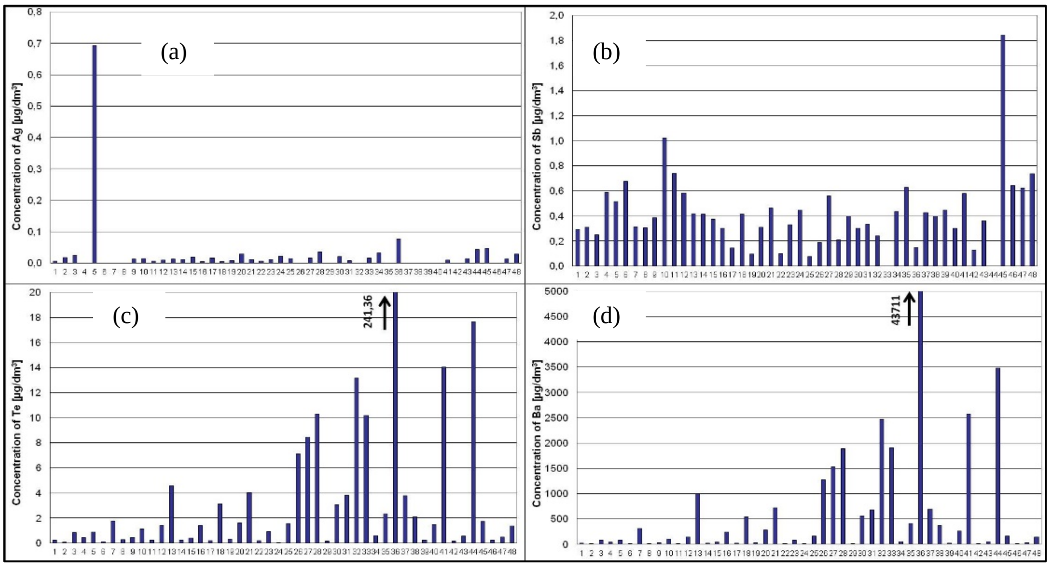


Fig. 7. Concentrations of Ag, Sb, Te and Ba in the analyzed samples: (a) Ag, (b) Sb, (c) Te, (d) Ba

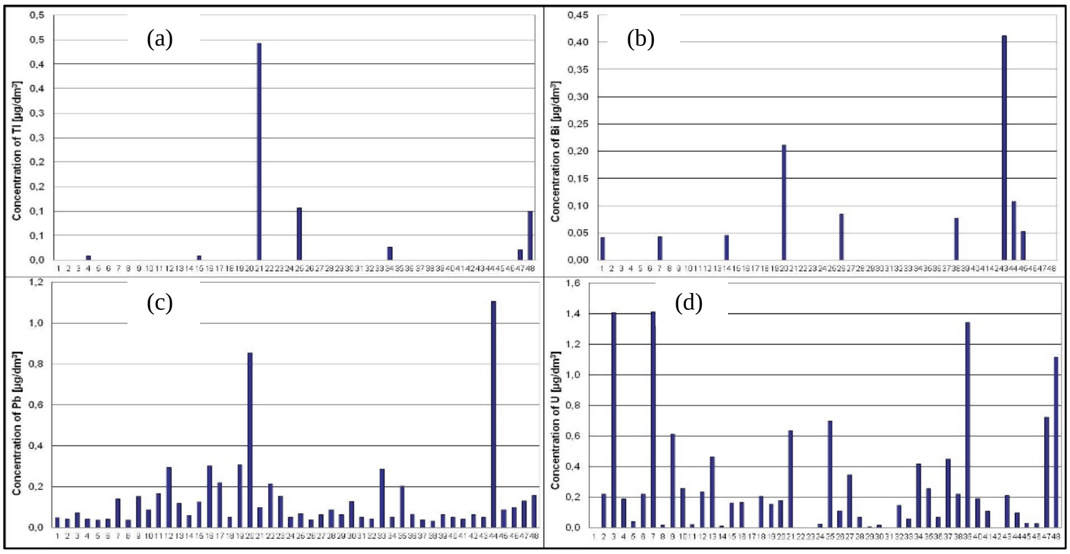


Fig. 8. Concentrations of Tl, Bi, Pb and U in the analyzed samples: (a) Tl, (b) Bi, (c) Pb, (d) U

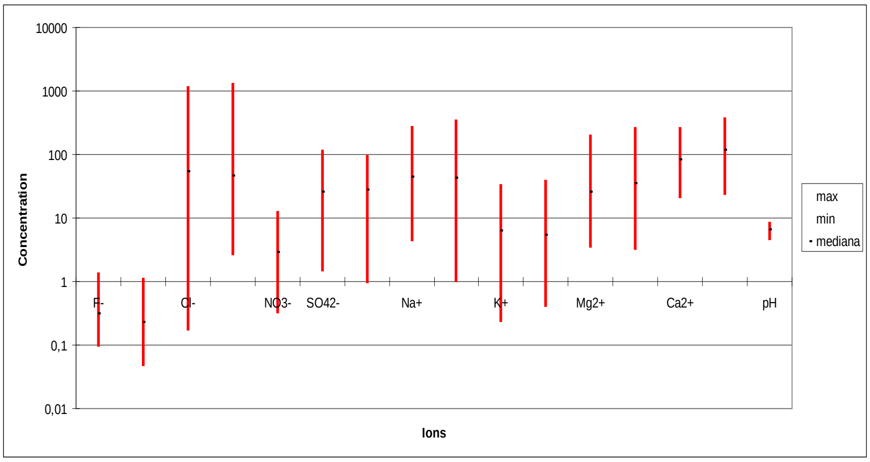


Fig. 9. Graphical comparison of the study results with the values reported on the bottled water labels. The first line applies to the results obtained in the laboratory; the second (parallel) line concerns the value declared by the manufacturer for a given parameter, if it was stated on the bottle label

The average contents of F^- ions for most water types did not exceed 0.5 mg/L (Fig. 2). Higher values, close to the limit, were detected for samples 23 and 31. When comparing the obtained results with the data provided by producers, numerous significant differences were observed. In many cases, the information given by producers (if specified in the label) indicated lower values than those determined in the research process. There may be multiple explanations of this fact. Nevertheless, the most important one seems to be the fact that producers present information (analyses are performed only when necessary) which is very convenient as they possibly assume that the consumers are not be able to verify the actual data. The water composition at intakes may change. It happens not only in emergency situations. Moreover, the cost of such analyses is high. The Directive allows for deviations from the declared characteristic component contents that are not higher than 20%. The average content of chloride ions did not exceed 20 mg/L (Fig. 2). However, an unusually high value (over 1.0 g/L) was observed for samples 30 and 31. The analyzed water types did not contain NO_2^- ions, whereas the NO_3^- content ranged between 0.51 mg/L (sample 28) and 11.41 mg/L (sample 39). Unfortunately, only one manufacturer presented the declared nitrate ion content in the produced water (Fig. 2). The PO_4^{3-} content was not indicated in any label. Their contents varied between 1.28 and 1.56 mg/L and only three examined water types had PO_4^{3-} levels below the detection limit.

The determined sulfate ion values did not differ as much as the Cl^- ion contents and ranged between 1.51 mg/L (sample 1) and 80.85 mg/L (sample 31). In most cases, the declared values of sulfate ions were consistent with the calculated ones. Fig. 3 shows results of the selected cation determinations. Lithium and ammonium ions (over the detection limit) were not present in any sample. The medium concentration of Na^+ ions was lower than 20 mg/L for non-carbonated water. In the remaining cases, it varied between 50 and 270 mg/L (sample 36).

The highest content of K^+ ions (31.68 mg/L) was observed for sample 25, even though the producer had declared the value of 37.5 mg/L. In most cases, the K content did not exceed 10 mg/L and was usually the same as the one given in the label (Fig. 2). Calcium and magnesium make important constituents of the so-called mineral water. Most producers indicated their contents but they were often higher than the determined ones (Fig. 3). The highest Mg value (131.14 mg/L) was determined in sample 24 but it was still much lower than the declared one (179 mg/L). A similar situation was observed for Ca^{2+} ions. The contents did not exceed 100 mg/L in most water types. Interestingly, these values were usually lower than the declared ones. The highest Ca^{2+} level was found in samples 33 (238.13 mg/L; producer data - 369 mg/L) and 34 (138.57 mg/L; producer data-129 mg/L).

Sample 5 is interesting in terms of the Ag content. Its value reached 0.7 µg/L. The average value for the remaining 45 samples was < 0.1 µg/L (Fig. 7). Similar deviations were observed for Te (sample 36, Fig. 7), Ba (sample 36, Fig. 7), Tl (sample 21, Fig. 8) and Ga (sample 36, Fig. 5). The Pb content did not exceed 0.2 µg/L in most cases. However, it was higher for samples 20 and 44 (Fig. 8). Bismuth was detected in 9 water types (Fig. 8). The highest Mo content was determined in sample 39, while the median value was < 0.5 µg/L (Fig. 6). Interestingly, U was detected in almost all water types (Fig. 8). The highest U value (approx. 1.2 µg/L) was observed for samples 3, 7 and 39. It did not exceed 0.2 µg/L in most remaining samples.

Most water types contained Cr (< 1 µg/L). However, its content for samples 44 and 46 was approx. 20 µg/L (Fig. 4). A slighter diversification was noticed for Sb. Its average concentrations ranged between 0.3 and 0.8 µg/L (Fig. 7). Its highest value was observed for sample 45. Taking into account the quality requirements for bottled water, Table 5 summarizes the number of times when the limit values for all the analyzed waters was exceeded.

Table 5. Number of times when water standards were exceeded

Parameter	*European Economic Community (2003)*	*International Bottled Water Association (2009)*	*U.S. Food and Drug Administration (2010)*	*Polish legalization Dz. U. Nr 85, poz.466 (May 7th, 2011)*
Antimony	13	8	8	13
Arsenic	3	3	3	3
Barium	-	8	4	8
Chloride	-	2	2	-
Chromium	0	0	0	0
Copper	0	0	0	0
Fluoride	0	0	0	0
Lead	0	0	0	0
Manganese	3	9	9	3
Nickel	3	0	0	0
Nitrate	1	1	1	1
Silver	-	0	0	-
Sulfate	-	0	0	-
Thallium	-	0	0	-
Uranium	-	0	0	-
Zinc	-	0	0	-

In the literature, there are various examples of modern analytical techniques (including ion chromatography) applied to examine mineral water compositions. The studies concerned Slovenia (Gros and Gorenc, 1994), South Korea (Jong-Hun, 1997), Turkey (Guler, 2007; Guler and Alpaslan, 2009), Sri Lanka (Herath et al., 2012), Italy (Dinelli et al., 2012), the USA (Saleh, 2008), or Arabic countries (Shomar, 2012). The Polish mineral water was also investigated (Astel et al., 2014; Ciężkowski et al., 2007; Michalski, 2003), but the research range was different from that described in the following paper. In conclusion, there is a steady tendency related to the bottled water consumption. Hopefully, the decision whether to drink it and which one to drink could be facilitated by the findings provided in this article.

4. Conclusions

In the following study, 48 various carbonated, lightly carbonated and non-carbonated mineral waters available in the Polish market were examined. The researchers determined the pH and electrical conductivity values, and the concentrations of the main inorganic ions, metals and metalloids.

Most of the measured parameter values were below the permissible limits defined by the WHO, EU and Polish institutions. For the metal and metalloid contents, some values were exceeded in a few cases (antimony – 13 waters; barium – 8 waters; manganese – 3 waters; and arsenic – 3 waters). No value exceeded the permissible limits for the inorganic anions and cations. Nonetheless, it must be stated that the qualitative research range embraced a much larger number of analytes than that to which the regulations on mineral waters apply.

The comparison of the analysis results with the water label data showed a significant discrepancy between the declared and measured values (for ions, metals and metalloids). Importantly, it should be noticed that the mineral water composition may change due to the long-term storage, which could be investigated in the further research.

Abbreviations

FDA-United States Food and Drug Administration
IBA-International Bottled Water Association
IC-Ion Chromatography
ICP-MS-Inductively Coupled Plasma Mass Spectrometry
ISO-International Standardization Organization
NIST-National Institute of Standards and Technology
PCA-Polish Accreditation Centre
WHO-World Health Organization

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