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CHEMICAL COMPOSITION OF THE COMMERCE MINERAL WATERS VERSUS TAP WATER IN THE CITY OF KIELCE

PORÓWNANIE SKŁADU CHEMICZNEGO DOSTĘPNYCH W HANDLU WYBRANYCH WÓD MINERALNYCH ZE SKŁADEM WODY WODOCIĄGOWEJ MIASTA KIELCE

Abstract: Comparative analysis of the chemical composition of the commerce mineral and spring waters to tap water in the district city of Kielce has been presented in this paper. The research has been done using the latest analytical equipment which was stocked with ion chromatograph 883 Basic IC plus and spectrometer Optima 8000. The PHREEQC 2.17 program has been used in order to calculate the ion balances and *SI* index.

Keywords: mineral water, tap water, ion balance, *SI* index

Introduction

Recent observations show decrease in consumption of tap water and increase in consumption of the commerce mineral and spring water. Data obtained from the Nielsen agency show that over two billion litters of the mineral water (about 52 litters/person) worth over 2.2 billion PLN had been sold in Poland in 2008 [1].

So, in this paper we decided to answer the question: What do we drink?

In order to realise such a task ion compositions of the commerce mineral and spring water, described by the producers on the label of bottles, have been compared to these being the result of our investigation obtained using the latest analytical equipment. Additionally, the ion composition of tap water in the district city of Kielce has been determined.

The research has been done using the latest analytical equipment which among other things was stocked both with the ion chromatograph 883 Basic IC plus, produced by Metrohm company and the spectrometer Optima 8000, with excitation in plasma induced, produced by Perkin Elmer.

Ion composition of the analysed water

Three kinds of mineral water have been analysed in this paper. Low mineralized waters, such as: Kropla Beskidu, Zywiec Zdroj and Dobrowianka, with salts concentration ranged from 50 to 500 mg/dm^3; medium mineralized waters with salts concentration ranged from 500 to 1000 mg/dm^3, such as: Naleczowianka, Nestle Aquarel and Cisowianka and highly mineralized waters with salts concentration larger than 1500 mg/dm^3 such as: Staropolanka 2000, Muszynianka and Piwniczanka.

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The comparison of the results obtained in our investigation to the results declared by the producers of mineral waters is given in Table 1. The last row of Table 1 contains the results obtained for tap water in the city of Kielce.

Table 1

Comparison of the ion concentration values declared by the producers (P) to these obtained in our investigation (J)

Kind of mineral water	Ion concentration [mg/dm^3]									
	K		Na		Mg		Ca		Cl^-	
	P	J	P	J	P	J	P	J	P	J
Zywiec Zdroj	0	2.252	9.65	12.506	5.62	6.485	41.69	41.514	0	4.416
Kropla Beskidu	1	1.247	11.1	22.092	17.01	18.992	44.09	45.922	3.19	2.425
Dobrowianka	0	1.177	2	2.926	33.42	31.338	58.12	63.244	0	3.21
Naleczowianka	2.5	4.969	10	16.164	20	22.645	114.2	127.39	12.6	5.771
Nestle Aquarel	2.1	5.633	14	18.455	23.7	23.054	111.2	128.14	0	4.817
Cisowianka	2.5	4.242	11	14.798	21.9	25.362	130.3	141.04	2.5	1.5
Piwniczanka	13	9.971	133	116.6	87	82.79	180	213.6	0	11.28
Muszynianka	9	8.511	98	134.11	120	132.24	240	213.87	10	8.18
Staropolanka	52.3	46.249	128	145.66	59.8	55.6	309	335.7	2.9	7.844
Tap water	1.2	1.7387	10	15.883	8.53	9.241	90.19	86.275	27.9	21.943

The percent deviation of ion concentration values declared by the producers from these obtained in our investigation, larger than 20%, is specified in Table 2.

Table 2

Deviation of the ion concentration values declared by the producers larger than 20% from these obtained in our investigation

Sort of mineral water	Ion component				
	K^+	Na^+	Mg^{2+}	Ca^{2+}	Cl^-
Zywiec Zdroj	100.00	22.84	-	-	100.00
Kropla Beskidu	20.00	49.76	-	-	31.55
Dobrowianka	100.00	31.65	-	-	100.00
Tap water	30.98	37.04	-	-	27.15
Naleczowianka	49.69	38.13	-	-	118.33
Nestle Aquarel	62.72	24.14	-	-	100.00
Cisowianka	41.07	25.67	-	-	66.66
Piwniczanka	30.38	-	-	-	100.00
Muszynianka	-	26.93	-	-	22.25
Staropolanka	30.98	-	-	-	63.00

Ion balance errors

Ion balance errors have been determined for all mineral and spring waters taking into account in our investigation including additionally tap water in the city of Kielce.

The Excel and PHREEQC 2.17 programs have been used in calculation above. Considering the fact that such ions as: HCO_3^-, SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+} and Mg^{2+} constitute more than 90% and sometimes even 99% solubles in the underground waters only the ions mentioned above have been taken into account to obtain the ion balance [2, 4, 5].

According to the standard PN 89/C-04638/02 the permissible error of the ion balance is 5-10% if the sum of ions concentration in water ranges from 3 to 5 mval/dm^3. When such a sum ranges from 5 to 15 mval/dm^3 the acceptable error of the ion balance is 2-5% and

finally for the ions sum larger than 15 mval/dm^3 the error of this balance should be less than 2% [3]. The above standard is very restricted and therefore in the paper [4, 6] it has been proposed that the determination of the ion composition in water is correct if the error of the ion balance is not larger than 10%.

Values of the ion balance errors obtained from the data given by the producers are presented in Figure 1. The ion balance errors received from the data obtained for the corresponding waters in our investigation are shown in Figure 2.

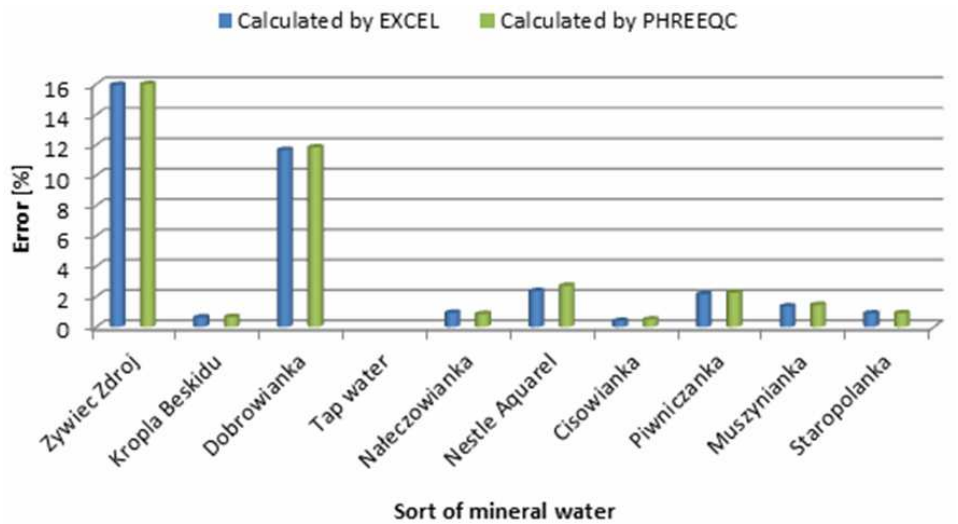

Fig. 1. Values of the ion balance errors obtained from the data given by the producers

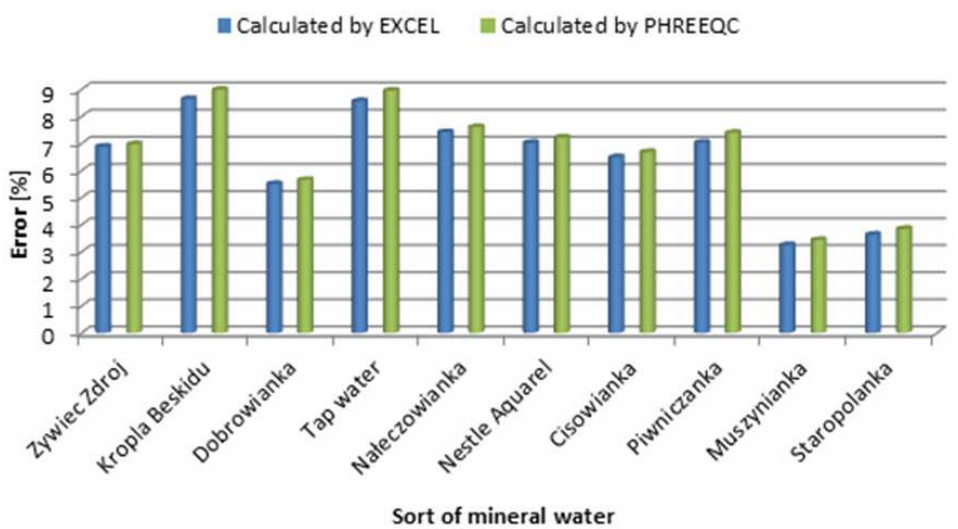

Fig. 2. Values of the ion balance errors received from the our data

Figure 1 shows that the values of the ion balance errors, obtained from the data placed on the labels of bottles, are less than 2% except of two waters: Zywiec Zdroj and Dobrowianka for these the ion balance error is larger than 10%. Such a high value of these errors is caused by the absence on the labels of the bottles concentrations of potassium, chlorine and sulfate ions.

The ion balance errors calculated from the data obtained in our investigation differ much more from these presented in Figure 1. The errors above 8% were obtained for tap water in the city of Kielce and for the mineral water Kropla Beskidu. The lowest results, a little below 3%, were received for the mineral waters like Muszynianka and Staropolanka 2000. The balance errors obtained for the other waters ranged from 5 to 7%.

A discerning analysis of the data placed on the label of the bottles by the producers shows the tendency to keep the ion balance errors below 2%. Of course, it might be caused by a very high accuracy of measurement of the ions concentration ordered by the producers but more probable it may be the attempt of such modelling of the ions composition of the mineral waters to fulfil the standard PN 89/C-04638/02.

Stability index (*SI*) of minerals in mineral water

Basing on the results of our investigation and using the program PHREEQC 2.17 one have determined the *SI* index for all waters being under consideration. From the theoretical point of view if for a given mineral its index $SI < 0$ then this mineral will dissolve in water, for $SI > 0$ the mineral will precipitate from water and finally if the $SI = 0$ the state of equilibrium between water and mineral is achieved. In practice however, due to the analytical errors, the state of equilibrium mineral-water is determined by the system of inequalities $-0.5 \leq SI \leq 0.5$, so solubility and precipitation of the minerals in/from water are described by the following inequalities:

$$SI < -0.5 \text{ and } SI > 0, \text{ respectively}$$

Values of the index *SI*, obtained for the low mineralized waters and for tap water in the city of Kielce are presented in Table 3.

Table 3

Values of the index *SI* for the low mineralized waters

Mineral	Kind of low mineralized water			
	Kropla Beskidu	Dobrowianka	Zywiec Zdroj	Tap water
Anhydrite	–2.73	–2.56	–2.67	–2.13
Aragonite	–0.44	0.10	–0.28	–0.03
Calcite	–0.29	0.25	–0.13	0.12
Dolomite	–0.70	0.00	–0.18	–0.45
Gypsum	–2.50	–2.32	–2.44	–1.90
Halite	–7.50	–7.58	–7.60	–8.02

The data given in Table 3 show that all low mineralized water and tap water in the city of Kielce are stable with respect to aragonite and calcite. All these waters show a slight tendency to dissolve anhydrite and gypsum and a high ability to dissolve halite.

Values of the index *SI* obtained for the medium mineralized waters are given in Table 4.

Table 4

Values of the index *SI* for the medium mineralized water

Mineral	Kind of medium mineralized water		
	Naleczowianka	**Nestle Aquarel**	**Cisowianka**
Anhydrite	–2.86	–3.03	–3.58
Aragonite	0.08	0.50	0.26
Calcite	0.23	0.64	0.40
Dolomite	0.00	0.83	0.35
Gypsum	–2.68	–2.80	–3.34
Halite	–8.61	–8.63	–9.24

The data given in Table 4 show that all medium mineralized waters are stable with respect to aragonite. The high tendency to dissolve halite and slightly lower to dissolve gypsum and anhydrite characterise all these waters. Stability with respect to calcite and dolomite shows Cisowianka but Nestle Aquarel shows a little tendency to precipitates these minerals from water. Values of the index *SI* obtained for the highly mineralized waters are shown in Table 5.

Table 5

Values of the index *SI* for the highly mineralized waters

Mineral	Kind of highly mineralized waters		
	Piwniczanka	**Staropolanka**	**Muszynianka**
Anhydrite	–2.73	–2.56	–2.67
Aragonite	–0.44	0.10	–0.28
Calcite	–0.29	0.25	–0.13
Dolomite	–0.70	0.00	–0.18
Gypsum	–2.50	–2.32	–2.44
Halite	–7.50	–7.58	–7.60

The data given in Table 5 show that all highly mineralized waters are stable with respect to aragonite and calcite. A tendency to dissolve anhydrite, gypsum and halite show all these waters. The mineral water Muszynianka is stable with respect to dolomite.

Conclusions

Tap water in the city of Kielce characterises with a shortage of magnesium, calcium and acid carbonates ions. So, it cannot be used as a supplier of these elements to the water consumers. However such mineral waters like Muszynianka, Piwniczanka and Staropolanka 2000 may be used in this purpose. The mineral water Staropolanka 2000 characterises with the largest concentration of acid carbonates and calcium ions among the highly mineralized waters being considered in our investigation and may be treated as a supplier of these ions.

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Abstrakt: W pracy porównano skład chemiczny dostępnych w handlu wybranych wód mineralnych z wodą wodociągową miasta Kielce. Badaniami objęto wody mineralne niskomineralizowane: Kroplę Beskidu, Żywiec Zdrój i Dobrowiankę; średniomineralizowane: Nałęczowiankę, Nestle Aquarel i Cisowiankę oraz wysokomineralizowane: Staropolankę 2000, Muszynianke i Piwniczankę. Oznaczenia wykonano, posługując się najnowocześniejszym sprzętem analitycznym, tj. chromatografem jonowym 883 Basic IC plus firmy Metrohm oraz spektrometrem emisyjnym ze wzbudzeniem, w indukowanej plaźmie, Optima 8000 firmy Perkin Elmer. Bilanse jonowe oraz wartość indeksów stabilności uzyskano, wykorzystując programy Exel oraz PHREEQC 2.17.

Słowa kluczowe: woda mineralna, woda wodociągowa, bilans jonowy, indeks stabilności *SI*