General Chemistry of Bottled Waters on the Slovene Market

Splošne kemijske karakteristike ustekleničenih vod na slovenskem tržišču

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Abstract: Consumption of bottled waters and soft drinks similar to water is increasing every day. General overview of the market shows big differences among brands. During the consumption of these drinks several questions about their origin and chemical composition arose. In the article research results of 58 bottled waters and soft drinks similar to water bought on Slovene market in September 2004 are presented. Sampling was performed according to unbalanced hierarchical analysis of variance. Chemical analyses included determination of concentration of 67 elements by ICP-MS, anions by ion chromatography and isotopic composition of hydrogen, oxygen and dissolved inorganic carbon by mass spectrometry. Samples were classified into four groups (waters, soft drinks, carbonated and non-carbonated drinks). Nearly all elements are present in investigated samples, however their concentrations vary considerably. Results indicate different natural origin and geochemical processes as well as influence of industrial treatment and flavours on chemical composition of waters and drinks.

Izvleček: Potrošnja ustekleničenih voda in pijač, ki so podobne vodam narašča iz dneva v dan. Že bežen pregled tržišča pokaže, da se te pijače med seboj zelo razlikujejo. Pri potrošnji teh pijač se pogosto zastavljajo številna vprašanja o njihovem izvoru ter kemizmu. V članku so predstavljeni rezultati raziskav 58 ustekleničenih voda in pijač podobnih vodi, kupljenih na slovenskem tržišču septembra 2004. Vzorčenje je potekalo po shemi neuravnotežene analize variance. Analiza vzorcev je zajemala določitev koncentracije 67 elementov z ICP-MS, anionov z ionsko kromatografijo in izotopske sestave vodika, kisika in raztopljenega anorganskega ogljika z masno spektrometrijo. Vzorce smo razdelili na štiri skupine (vode in pijače ter gazirane in negazirane vode). V analiziranih vzorcih so prisotni skoraj vsi elementi, vendar v zelo različnih koncentracijah. Rezultati tudi nakazujejo različen naravni izvor in vpliv geokemijskih procesov kot tudi vpliv industrijske priprave in dodatkov na kemijsko sestavo vod in pijač.

Key words: bottled water, mineral water, spring water, soft drinks, water chemistry, stable isotopes.

Ključne besede: ustekleničene vode, mineralne vode, izvirske vode, pijače, kemija vode, stabilni izotopi.

Scientific paper

Introduction

The total world production of bottled waters is over $7x10^{10}$ L annually (Rowlands, 2001). The biggest consumers of bottled waters in the world are western countries. Each year, consumption in Germany, France, Switzerland, Italy and Belgium is over 100 L per capita. In new European countries the consumption of bottled waters is lower and big potential for market growing exist. This conclusion is in the agreement with Slovene bottled waters market status. In the year 1998 consumption of bottled waters in Slovenia was 34.4 L per capita (Hribar, 2000) and in year 2004 58 L per capita (Gider, 2005). From these data it is evident that Slovene bottled water market will become larger in future.

Bottled waters market in Slovenia is increasing each year and more and more brands of bottled waters and soft drinks similar to water appear in shopping centers. Bottles available on the market are labeled with many names, classifications and advertisements. Prices for bottled waters are very different and do not resemble the quality and legislative status of particular brand. In spite of relatively strict European and Slovene legislation we can find out disorder in the market. The consumers' behavior shows uncritical relation to waters available on the market and ignorance to present knowledge about water. A main criterion for purchasing bottled water is its price. The bottled waters market status and consumers' behavior shows that a lot of open questions, problems and controversies about drinking and bottled waters exist. This is the reason why more knowledge about bottled waters is needed.

In the present study the hydrochemical overview of most bottled waters available on the Slovene market is given. Therefore, it is not our intention to check the bottled water market status and to control whether the sampled bottles are in the agreement with legislation demands. All brands available on the market were treated on equal terms and no discrimination between domestic and foreign brands was made. Results are given as aggregate values without connection to their brand names.

According to the authors' knowledge all bottled waters and water for soft drinks that are similar to water available on the Slovene market have their source in the groundwater. As a consequence the present analysis gives also opportunity to check what type of groundwater is filled in the bottles. The available data set gives also possibility to develop general procedures for controlling water brands agreement with legislation demands.

Sampling and Methodology

Sampling of bottled waters and soft drinks similar to water was made in several steps:

a) Overview of bottled waters on the market,
b) Sampling plan,
c) Purchasing of bottled waters on the market,
d) Samples preparation,
e) Transport to laboratories.

During first step of sampling survey of mainly all big shopping centers in Ljubljana and its vicinity was performed. Based on this survey the list of all available brands of bottled waters and soft drinks similar to water was made. We believe that with this procedure nearly all brands available in the Slovene market on September 2004 were included. Altogether 58 different brands were found, among them 34 are waters and the other 24 are soft drinks similar to water. The later are mixtures of water and some flavours such are aromatic flavours, organic acids or flavours based on sugars. Among all brands 16 are carbonated and other 42 are non-carbonated. None of the soft drinks was carbonated. Most bought brands were stored in plastic bottles and only 3 were in glass bottles.

During the second step it was decided to sample waters from the list according to unbalanced hierarchical analysis of variance. According to this analysis 9 brands and 7 bottles among all are repeated.

During the third step purchasing of brands was performed. By chance one of the big shopping centers was chosen. All available brands in the shop were bought according to the sampling plan prepared before. But not all waters were available in this shop. This was the reason for new shopping in the second shop. The procedure was repeated also in the third shop where the list was completed. The bottles from the shop shelves or package on the floor of the shop were taken incidentally without any prejudice.

After the shopping was complete all bottles were taken to the laboratory where the preparation of samples began. All plastic flasks and seals, except for anions, were washed with diluted HNO_3 and after that washed off with distilled water. After washing they were air-dried. Before filling with the sample plastic flasks were washed off also with the same brand, as it was latter filled into the flask. When sampling begin first all plastic flasks were filled with samples. After that pH and electrical conductivity was measured. Conductivity was referred to the 20 °C. Samples for anion determination were filed into 1 L plastic flasks, samples for $\delta^{18}O$ and $\delta^{2}H$ into 100 ml plastic flasks, for $\delta^{13}C$ determination in dissolved inorganic carbon (DIC) into 12 mL glass exeteiners and for multielement analyses into 100 mL plastic flasks. Samples for multielemental analysis were acidified with Suprapur® HNO_3 produced by Merck. To control accuracy of the analytical procedures 5 samples of standard fresh water NIST 1643e were added to the whole set of samples and also four samples of very pure MilliQ® water were added as a blank.

The final step of sampling is represented by transport. Samples for multielement analyses were send by the carrier overseas. Other samples were carried by car into the laboratories. Before transport all samples were stored in the refrigerator at 4 °C.

Multielement analysis was performed by ICP-MS at ActivatedLab in Canada. The accuracy and precision of multielemental analysis were determined as reasonable. The concentration of NH_4^+ was determined by SIST ISO 7150-1 method, concentration of NO_2^- by SM 4500-NO_2B method, NO_3^-, SO_4^{2-} by SIST EN ISO 10304-1 method, F^- by method SIST EN ISO 10304-2, PO_4^{3-} by SM 4500P-C method, HCO_3^- was determined by titration, and Cl^- was determined by gas chromatography. All anions, except Cl^- were determined at chemical laboratory of Ljubljana waterworks.

Table 1. Averages and number of samples (N) with values greater than detection limit of different waters and soft drinks classifications – multielemental and anion analyses.
Tabela 1. Povprečja in število vzorcev z vrednostmi višjimi od detekcijske meje glede na različne skupine vod in pijač podobnim vodam - multielementne in anionske analize.

Parameter	DL1	DL2	All samples		Waters		Soft drinks		Non-carbonated		Carbonated	
			Average	N	Average	N	Average	N	Average	N	Average	N
Al	20	2	38	19	8	10	72	9	44	15	16	4
As	0.3	0.03	0.59	49	0.58	28	0.61	21	0.47	38	1.03	11
Au	0.02	0.002	0.016	6	0.004	3	0.027	3	0.021	4	0.004	2
Ba	1	0.1	65.7	59	99.7	33	22.6	26	28.9	45	183.8	14
Br	30	3	222	29	257	24	52	5	25	19	597	10
Ca	7000	700	71806	60	66396	35	79378	25	71632	44	72284	16
Cd	0.1	0.01	0.09	23	0.09	19	0.11	4	0.01	19	0.07	4
Ce	0.01	0.001	0.135	38	0.010	20	0.275	18	0.161	31	0.023	7
Co	0.05	0.005	0.38	19	0.68	8	0.16	11	0.15	12	0.77	7
Cr	5	0.5	5.8	10	1.4	2	6.9	8	5.8	10		
Cs	0.01	0.001	2.87	29	3.76	22	0.08	7	0.22	17	6.62	12
Cu	2	0.2	2.7	26	2.7	21	2.8	5	1.3	18	5.9	8
Dy	0.01	0.001	0.074	11	0.024	2	0.085	9	0.085	9	0.024	2
Er	0.01	0.001	0.041	13	0.005	6	0.071	7	0.046	11	0.014	2
Eu	0.01	0.001	0.023	20	0.017	14	0.038	6	0.019	13	0.032	7
Fe	100	10	100	23	62	18	240	5	95	17	118	6
Ga	0.1	0.01	0.08	3	0.08	3			0.04	1	0.10	2
Gd	0.01	0.001	0.051	23	0.018	6	0.064	17	0.061	18	0.019	5
Ge	0.1	0.01	0.98	13	0.98	13			0.22	5	1.45	8
Hf	0.01	0.001	0.023	19	0.023	8	0.024	11	0.020	13	0.030	6
Ho	0.01	0.001	0.025	6	0.002	1	0.030	5	0.030	5	0.002	1
I	10	1	58	52	82	31	23	21	16	38	172	14
K	300	30	19801	60	13963	35	27975	25	16583	44	28652	16
La	0.01	0.001	0.14	35	0.004	18	0.29	17	0.17	30	0.009	5
Li	10	1	360	21	460	16	37	5	35	10	654	11
Lu	0.01	0.001	0.011	4	0.001	1	0.015	3	0.015	3	0.001	1
Mg	2	0.2	73052	63	102903	35	35739	28	31133	47	196190	16
Mn	1	0.1	104.4	34	161.9	15	59.0	19	76.0	23	163.9	11
Mo	1	0.1	1.3	16	1.0	12	2.0	4	1.3	13	1.1	3
Na	50	5	130601	63	194151	35	51165	28	34701	47	412309	16
Nb	0.05	0.005	0.05	4	0.02	1	0.06	3	0.06	3	0.02	1
Nd	0.01	0.001	0.137	42	0.015	20	0.248	22	0.155	36	0.028	6

Parameter	DL1	DL2	All samples		Waters		Soft drinks		Non-carbonated		Carbonated	
			Average	N	Average	N	Average	N	Average	N	Average	N
Ni	3	0.3	7.4	19	7.9	14	5.8	5	2.9	11	13.5	8
Pb	1	0.1	0.18	24	0.15	20	0.38	4	0.15	18	0.29	6
Pd	0.1	0.01	0.2	5	0.2	2	0.2	3	0.2	3	0.2	2
Pr	0.01	0.001	0.075	12	0.001	1	0.082	11	0.082	11	0.001	1
Rb	0.05	0.005	30.0	63	48.2	35	7.3	28	6.0	47	100.5	16
Re	0.01	0.001	0.006	19	0.004	13	0.010	6	0.006	18	0.002	1
Sb	0.1	0.01	0.27	54	0.31	32	0.21	22	0.23	41	0.38	13
Sc	10	1	9	10	9	10			2	3	12	7
Se	2	0.2	1.3	9	0.7	7	3.4	2	1.4	6	1.0	3
Si	2000	200	12391	60	13621	33	10888	27	8975	45	22639	15
Sm	0.01	0.001	0.063	14	0.007	5	0.095	9	0.086	10	0.007	4
Sn	1	0.1	27	2		0	27	2	27	2		
Sr	0.4	0.04	486	63	750	35	155	28	243	47	1199	16
Ta	0.01	0.001	0.043	30	0.004	3	0.048	27	0.046	28	0.006	2
Tb	0.01	0.001	0.026	5		0	0.026	5	0.026	5		
Th	0.01	0.001	0.07	13	0.05	2	0.079	11	0.079	11	0.047	2
Ti	1	0.1	4.1	44	4.1	26	4.1	18	2.9	32	7.4	12
Tl	0.01	0.001	0.06	27	0.055	19	0.077	8	0.046	18	0.092	9
Tm	0.01	0.001	0.011	5	0.001	2	0.018	3	0.018	3	0.001	2
U	0.02	0.001	0.479	62	0.470	34	0.490	28	0.486	47	0.457	15
V	1	0.1	0.6	19	0.6	17	0.8	2	0.6	15	0.8	4
W	0.2	0.02	0.03	3	0.04	2	0.02	1	0.03	3		
Y	0.03	0.003	0.31	29	0.04	17	0.69	12	0.36	23	0.11	6
Yb	0.01	0.001	0.034	13	0.007	5	0.051	8	0.037	11	0.018	2
Zn	5	0.5	13.9	38	13.9	25	13.8	13	9.6	29	27.7	9
Zr	0.1	0.01	1.1	32	1.3	19	0.8	13	0.5	21	2.2	11
Cl^-	0.2		35.2	63	35.0	35	35.0	28	23.6	47	69.1	16
F	0.03/0.05		186	37	187	33	185	4	124	22	279	15
HCO_3^-	/		609000	63	1087000	35	12000	28	125000	47	2030000	16
NH_4^+	0.02		180	4	180	4			180	4		
NO_2^-	0.5		46	5	1	4	228	1	47	5		
NO_3^-	0.001		1	15	1	11	1	4	1	15		
PO_4^{3-}	0.05		890	27	240	10	1270	17	1020	22	330	5
SO_4^{2-}	2		126000	49	181000	31	32000	18	23000	36	412000	13

All units are in µg/l. DL1 – detection limit for the solution with TDS >500 mg/l, DL2 – detection limit for the solution with TDS <500 mg/l. Nitrogen species are given as nitrogen concentrations.

The concentration of Cl^- was determined at Joanneum Research, Institute of Water Resources Management, Graz, Austria. According to purpose of the study the accuracy and precision of anion analyses were determined as reasonable.

Isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) was determined on CO_2 collected after reaction of sample with 100 % H_3PO_4 on a continuous flow Europa 20-20 ANCA-TG stable isotope mass spectrometer at Jožef Stefan Institute. Results are expressed in relative (δ) notations as deviations in per mil (‰) from the V-PDB standard. Measurement reproducibility of duplicates was generally better than ±0.3 ‰.

Isotopic composition of oxygen ($\delta^{18}O$) was determined by equilibration of CO_2 with water samples on a dual inlet Finningan DELTA^{plus} stable isotope mass spectrometer, and isotopic composition of hydrogen (δ^2H) was measured on H_2 generated by reduction of water over hot chromium on a continuous flow Finnigan DELTA^{plus} XP stable isotope mass spectrometer at the Joanneum Research, Institute of Water Resources Management, Graz, Austria. Results are reported as per mil deviations from the V-SMOW standard. Measurement reproducibility of duplicates was better than ±0.05 ‰ for $\delta^{18}O$ and ±1 ‰ for δ^2H.

RESULTS

A large data set was obtained according to sampling and performed analyses. In this paper are presented only results as averages according to the type of water and soft drinks that are similar to water. Averages for different groups of waters are given in Table 1, together with detection limits that are reported in two groups. Average values were calculated for brands and their bottle replicates, therefore total number of all statistical units is 63. Sample replicates are not included in this number; sample and control sample were joined as two sample value before the average value calculations.

The first group of detection limits DL1 is valid for samples with total dissolved solids larger than 500 mg/l and the second group DL2 for samples with total dissolved solids smaller than 500 mg/l. Only one detection limit is given for anions, except for fluoride.

According to different measurement procedures and different physical meaning average values of conductivity, pH and isotopic composition of hydrogen, oxygen and DIC for different groups of waters are reported separately (Table 2).

Table 2. Averages and number of samples of different waters and soft drinks classifications – conductivity (20°C), pH and stable isotopes.

Tabela 2. Povprečja in število vzorcev glede na različne skupine vod in pijač podobnim vodam - elektroprevodnost (20°C), pH in stabilni izotopi.

Parameter		All samples		Waters		Soft drinks		Non-carbonated		Carbonated	
		Average	N	Average	N	Average	N	Average	N	Average	N
Conduct.	μSi/cm	1283	63	1646	35	831	28	687	47	3038	16
pH		5.4	63	6.6	35	3.8	28	5.3	47	5.7	16
δ^2H	‰	-66	63	-66	35	-66	28	-65	47	-70	16
$\delta^{18}O$	‰	-9.6	63	-9.7	35	-9.6	28	-9.4	47	-10.2	16
$\delta^{13}C_{DIC}$	‰	-11.9	63	-12.6	35	-11.1	28	-10.8	47	-15.3	16

Table 3. Classification of elements and anions according to the share of samples under the detection limit [%].
Tabela 3. Klasifikacija elementov in anionov glede na delež vzorcev pod detekcijsko mejo [%].

Share of samples under the detection limit [%]	Element	Number of elements
90 – 100	Au, Ga, Ho, Lu, Nb, Pd, Sn Tb, Tm, W,	10
80 – 90	Cr, Dy, Er, Pr, Sc, Se, Sm, Yb , NH_4^+, NO_2^-	8
70 – 80	Al, Co, Eu, Ge, Gd, Hf, Mo, Ni, Re, V, Th, NO_3^-	11
60 – 70	Cd, Fe, Li, Ti, PO_4^{3-}	4
50 – 60	Br, Cu, Cs, Pb, Ta, Zr, Y	7
40 – 50	Ce, La, Mn, F^-	3
30 – 40	Nd, Zn	2
20 – 30	As, Ti,	2
10 – 20	I, Sb, SO_4^{2-}	2
0 – 10	Ba, Ca, K, Si, U	4
0	Na, Mg, Rb, Sr, Cl^-, HCO_3^-	4

The statistics for water and soft drinks similar to water are divided into five main groups (Table 1 and 2). The first group represents results from all analyzed bottles; the second only of waters and the third are the results of all soft drinks similar to water. The last two groups represent samples divided according to the presence of gaseous CO_2. Samples with gaseous CO_2 are defined as carbonated and without as non-carbonated. The two classifications of soft drinks and non-carbonated waters are partially covered over. All soft drinks are non-carbonated. This is the reason why they are included into the group of non-carbonated samples.

The average values were calculated only for values above detection limit; censured values below detection limit were simply omitted from the calculations. Concentrations of elements Ag, Be, Bi, Hg, In, Os, Pt, Ru, Te were in all samples under the detection limit. The classification of elements and anions according to the share of samples under the detection limit for other elements and anions are given in Table 3.

The averages calculated with this procedure are biased to the right of the determined element or ion empirical distribution. This bias is larger for determinations with greater share of values below detection limit than for the determinations with lower share. In the geochemical literature the approach of Miesch (1976) is usually adopted where only variables with more than 70 % of determinations are included in data reduction. In the present study this approach was used only in graphical presentation of the results (see Discussion).

Discussion

Results show that mainly all elements that are possible to detect with ICP-MS are present in analyzed drinks. But only few elements and ions are present in all samples. This fact leads us to the conclusions that such chemical composition is the consequence of various sources and geochemical processes. Different chemical composition of waters and soft drinks similar to water is also a consequence of various filling and pumping procedures, while in soft drinks it depends also on composition and combinations of flavours.

Table 4. Comparison of different groups of waters and soft drinks similar to water according to the overall average.
Tabela 4. Primerjava različnih skupin vod in pijač podobnih vodam glede na celotno povprečje analiziranih vzorcev.

Parameter	Waters	Soft drinks	Non - carbonated	Carbonated
As	-	+	-	+
Ba	+	-	-	+
Ca	-	+	-	+
I	+	-	-	+
K	-	+	-	+
Mg	+	-	-	+
Na	+	-	-	+
Rb	+	-	-	+
Sb	+	-	-	+
Si	+	-	-	+
Ti	0	0	-	+
U	-	+	+	-
Cl^-	+	-	-	+
HCO_3^-	+	-	-	+
SO_4^{2-}	+	-	-	+

+ average of the group is larger than overall average, - average of the group is smaller than overall average, 0 average of the group is the same as overall average

Calculated averages show big differences between various groups of waters. This can be seen from the general characteristics such as pH and electrical conductivity (Table 2). Soft drinks have relatively low average pH, much lower than other groups. This fact is the consequence of added organic acids, mainly citron acid that should act as refresher. Carbonated waters have much higher electrical conductivity than other waters.

To define the differences among groups of waters and soft drinks comparison between average value for all samples and averages for particular group was made. The comparison was made numerically without statistical testing and the results are presented in Table 4 and Figure 1. When the group average in the Table 4 is higher than overall average (+) is given, otherwise (–) is presented. It can be clearly seen that in all cases the average value of element or anion is higher for carbonated waters then for non-carbonated waters. Only in the case of uranium the average is higher for non-carbonated waters. Nevertheless the differences for all elements and anions are small and the average values are very similar.

The comparison between soft drinks and waters is not so straightforward as it is in the case of gaseous CO_2, however it shows that waters have in general higher averages than soft drinks. Sampled soft drinks are waters without gaseous CO_2. Therefore, we can expect that the pattern in Table 4 should be similar as is in the case of the comparison between carbonated and non-carbonated samples. But higher concentrations of some elements in soft drinks direct to the interpretation that some flavours change original chemistry of water that represent the base for soft drinks and therefore they have higher average concentrations.

Differentiation between carbonated and non-carbonated samples is mainly a consequence of the presence of highly mineralized waters in samples that have their source from deep groundwater in east and northeast Slovenia. These waters are carbonated and have high mineral content. Those samples with high total dissolved solids are usually without flavours and they contribute to higher averages of waters.

It is not intention of the present study to deeply analyze the isotopic content of the sampled waters and soft drinks. Better interpretation of the results is possible with the data reduction based on particular samples. However, according to the isotopic composition different groups of waters and soft drinks are very similar (Table 2). Differences in calculated averages are characteristic between particular groups for $\delta^{13}C_{DIC}$, while for $\delta^{18}O$ only carbonated waters differ considerably. Carbonated waters have slightly lower $\delta^{13}C_{DIC}$. This result is not in agreement with belief that CO_2 in these waters is geogenic.

Conclusions

The present study shows that chemical composition of waters and soft drinks similar to water available on the Slovene market is very wide. Nearly all elements that are possible to detect with ICP-MS are present but only few elements and anions are detected in all samples. The general

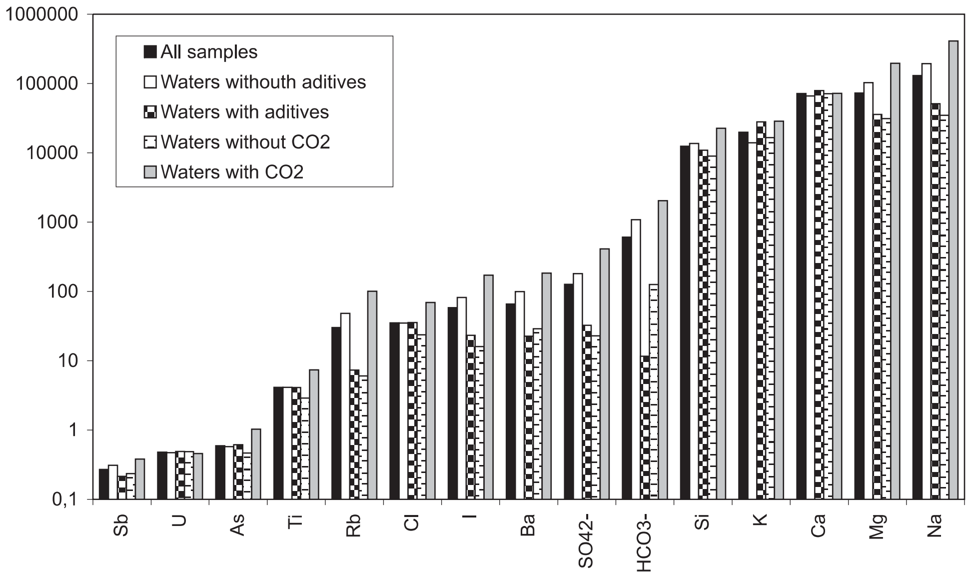

Figure 1. Comparison of different groups averages of waters and soft drinks similar to water.
Slika 1. Primerjava povprečij različnih skupin vod in pijač podobnih vodam.

characteristics such as pH and conductivity show that the composition of samples differs according to the type of water and soft drinks. In general we can differentiate within samples with gaseous CO_2 or without it and between water with or flavours additives. The CO_2 differentiation is mainly a consequence of the presence of highly mineralized waters originating from east and northeast Slovenia. They are carbonated and those with high total dissolved solids are usually without flavours.

Average isotopic composition of hydrogen, oxygen and DIC for different groups of waters and soft drinks is very similar. From the calculated averages difference are seen mainly in $\delta^{13}C_{DIC}$ and in waters with CO_2 in $\delta^{18}O$. However, more detailed analyses of obtained isotopic results will show big differentiation among various types of waters and soft drinks.

The aim of the present study was to give a geochemical overview of bottled waters and soft drinks similar to water available on the market in Slovenia. Adopted approach was used to establish the procedure for sampling and analyses, to expose open questions related to bottled waters and present exploration of groundwater for bottling of water. However, further work is needed on the statistical analyses and more rigorous statistical testing should be applied. Several multivariate statistics could be performed; among them analysis of variance, multivariate regression analysis, discriminant analysis, cluster analysis and factor analysis of R and Q type. Waters must be classified according to the hydrogeochemical classifications and more interpretation is needed in connection with the origin of waters. Further research will be directed also in more differentiate classification of samples based on cross-tabulation.

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Povzetek

Splošne kemijske karakteristike ustekleničenih vod na slovenskem tržišču

Potrošnja ustekleničenih vod in pijač, ki so podobne vodam, narašča iz dneva v dan. Že bežen pregled tržišča pokaže, da se te pijače med seboj zelo razlikujejo. Na tržišču bomo našli vode, ki so opredeljene kot mineralne vode, kot izvirske vode ali pa kot vode z dodatki. Takšne razmere na tržišču so posledica dejanskega slabšanja nekaterih vodnih virov, naraščujoče zavesti potrošnikov, še bolj kot to pa zakonitosti tržišča in proizvajalcev, ki skušajo čimbolj povečevati prodajo. Pri potrošnji teh pijač se pogosto zastavljajo številna vprašanja o kvaliteti, njihovem izvoru in kemizmu.

V članku so predstavljeni rezultati raziskav 58 ustekleničenih voda in pijač podobnih vodi, kupljenih na slovenskem tržišču septembra 2004. Vzorčenje je potekalo po shemi neuravnotežene analize variance.

Analiza vzorcev je zajemala določitev koncentracije 67 elementov z ICP-MS, anionov z ionsko kromatografijo in izotopske sestave vodika, kisika in raztopljenega anorganskega ogljika z masno spektrometrijo. Vzorce smo razdelili v štiri skupine (vode in pijače ter gazirane in negazirane vode).

Rezultati analiz kažejo, da so v analiziranih pijačah prisotni skoraj vsi elementi, ki jih lahko določimo z metodo ICP-MS (tabela 1). Toda le nekateri elementi so prisotni v vseh analiziranih vzorcih (tabela 3). Takšne razlike nas privedejo do sklepa, da je kemijska sestava analiziranih vzorcev posledica različnega izvora in geokemičnih procesov. Razlike v kemijski sestavi so tudi posledica različnih postopkov polnjenja in črpanja podzemne vode, ki predstavlja osnovo za izdelavo teh pijač. Pri pijačah, ki so podobne vodam, pa na kemizem vplivajo tudi različni dodatki.

Izračunana povprečja kažejo na zelo velike razlike med pijačami (tabeli 1 in 2). Te razlike zlahka opazimo že, če med seboj primerjamo splošne karakteristike skupin, kot sta pH in elektroprevodnost (tabela 2). Vode z dodatki imajo relativno nizek pH, mnogo nižji kot ostale skupine. To je posledica različnih dodatkov, predvsem organskih kislin in še posebaj citronske kisline, ki naj bi delovala kot osvežilo. Vode s prostim plinskim CO_2 pa imajo dosti višjo električno prevodnost kot pijače iz ostalih skupin.

Primerjava med povprečji posameznih skupin je bila izvedena le numerično, brez statističnih testiranj. Rezultati primerjave so predstavljeni v tabeli 4 in na sliki 1. Če je povprečje skupine višje kot povprečje celotnega niza vzorcev je ta razlika predstavljena s +, če je nižja pa z -. Iz primerjave v tabela 4 sledi, da je pri gaziranih pijačah v vseh primerih koncentracija elementov in anionov višja od koncentracije v negaziranih vodah. Le v primeru koncentracije urana je povprečna koncentracija višja pri negaziranih kot pri gaziranih pijačah. Razlika med gaziranimi in negaziranimi pijačami je posledica prisotnosti visoko mineraliziranih vod, ki imajo svoj izvor v globoki podzemni vodi severovzhodne in vzhodne Slovenije. Kljub temu pa so razlike majhne in izračunana povprečja zelo podobna.

Primerjava med skupinama vod in vod z dodatki pa ni tako premočrtna, kot je to v primeru gaziranih in negaziranih vod. Kljub temu primerjava pokaže, da imajo vode brez dodatkov pravilom višje koncentracije kot vode z dodatki. Analizirane vode z dodatki so negazirane, kar bi lahko pojasnilo razliko, saj imajo gazirane vode višjo mineralizacijo. Na podlagi tega bi lahko pričakovali, da bo primerjava med vodami in vodami z dodatki v tabeli 4 podobna primerjavi med gaziranimi in negaziranimi pijačami. Toda višje koncentracije nekaterih elementov v vodah z dodatki nas napeljujejo na interpretacijo, da nekateri dodatki spremenijo kemizem vode, ki predstavlja osnovo za izdelavo pijače.

Rezultati izotopskih analiz kažejo, da so si analizirane skupine med seboj dokaj podobne (tabela 2). Razlike v izračunanih povprečjih so med skupinami opazne predvsem pri $\delta^{13}C_{DIC}$, medtem ko pri $\delta^{18}O$ znatno odstopajo le gazirane vode. Gazirane vode imajo nekoliko nižjo vrednost $\delta^{13}C_{DIC}$, kar nakazuje, da izvor CO_2 v nekaterih vodah ni geogenega izvora.

Namen članka je predstaviti osnovne geokemijske značilnosti ustekleničenih voda in vod z dodatki, ki jih je mogoče kupiti na slovenskem tržišču. V okviru opravljene raziskave smo poizkušali vzpostaviti postopek za vzorčenje in odpreti nekatera vprašanja, ki se navezujejo na polnjenje ustekleničenih voda ter na izkoriščanje podzemne vode za potrebe ustekleničenja. Predstavljeni rezultati so le prvi korak k iskanju odgovorov na ta vprašanja. V nadaljnjih koraki bo potrebno izvesti podrobnejšo statistično analizo z rigoroznejšimi statističnimi testi. Statistične analize bodo usmerjene v multivariatne statistike kot so multipla analiza variance, multivariatna regresijska analiza, diskriminantna naliza, clusterska analiza ter faktorska analiza tipa Q in R. Pri nadaljnji analizi bo potrebno izvesti tudi nekatere fizikalno kemijske izračune in hidrogeokemijske klasifikacije ter jih navezati na hidrogeološki izvor vode. Nadaljnje raziskave bodo usmerjene tudi v podrobnejšo klasifikacijo vzorcev.

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