

SUGAR AND INORGANIC ANIONS CONTENT IN MINERAL AND SPRING WATER-BASED BEVERAGES

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ABSTRACT

Background. Carbonated and non-carbonated beverages manufactured based on mineral and spring waters have been present at the Polish market shortly, and their production and sales are regularly growing. The products have become commonly known as flavoured waters.

Objective. The aim of the work was to identify and assess the content of carbohydrates used for sweetening mineral and spring water-based beverages and to estimate a concentration of inorganic anions.

Material and methods. The study was undertaken for 15 mineral and spring water-based beverages subject to an analysis contents of fructose, glucose and sucrose with the high-performance liquid chromatography method with ELSD detection) and chlorides, nitrates and sulphates contents using the ion chromatography method.

Results. A chromatographic analysis has confirmed the total contents of sugar declared by the manufacturers. The carbohydrates identified included fructose, glucose and sucrose (added sugar). Chlorides and sulphates were found in the content of all the analysed beverages while nitrates were not determined in only one of the 15 examined beverages.

Conclusions. Mass consumption of mineral and spring water-based beverages should be considered as an important source of sugar and their excessive consumption may be disadvantageous for human health. A consumer should be informed by a manufacturer about a daily dose of sugar in a portion of a drink in per cents, and the easiest way to do it is to provide GDA marks on the label. Mineral and spring water-based beverages do not pose threats to consumer health in terms of their contents of inorganic ions: chlorides, nitrates and sulphates.

Key words: carbonated beverages, carbohydrates, anions, food labeling, nutritional requirements, nutritional value

STRESZCZENIE

Wprowadzenie. Gazowane i niegazowane napoje, produkowane na bazie wód mineralnych i źródłanych, obecne są na polskim rynku od niedawna, a ich produkcja i sprzedaż systematycznie wzrasta. Produkty te zyskały sobie potoczną nazwę „wód smakowych”.

Cel badań. Celem niniejszych badań była identyfikacja i ocena zawartości węglowodanów, użytych do słodzenia napojów na bazie wód mineralnych i źródłanych oraz oszacowanie stężenia anionów nieorganicznych.

Material i metody. Materiał do badań stanowiło 5 rodzajów napojów na bazie wód mineralnych i źródłanych, w których zbadano zawartość fruktozy, glukozy i sacharozy metodą wysokosprawnej chromatografii cieczowej (HPLC) z detekcją ELSD oraz zawartość chlorków, azotanów i siarczanów metodą chromatografii jonowej.

Wyniki. Analiza chromatograficzna badanych napojów potwierdziła sumaryczną zawartość węglowodanów deklarowaną przez producentów. Stwierdzono obecność fruktozy, glukozy i sacharozy (cukry dodane). We wszystkich 15 badanych napojach odnotowano zawartość chlorków i siarczanów, natomiast zawartości azotanów nie stwierdzono tylko w 1 napoju spośród 15 badanych.

Wnioski. Masowo konsumowane napoje na bazie wód mineralnych i źródłanych należy uznać za istotne źródło węglowodanów, a zbyt częste ich spożycie może być niekorzystne z punktu widzenia zdrowia człowieka. Konsument powinien być informowany przez producenta o procentowym stopniu realizacji zapotrzebowania na węglowodany w porcji napoju, poprzez umieszczenie na etykiecie oznaczeń GDA. Natomiast napoje na bazie wód mineralnych i źródłanych nie stwarzają zagrożenia zdrowia konsumentów pod względem zawartości anionów nieorganicznych: chlorków, azotanów i siarczanów.

Słowa kluczowe: napoje słodzone, węglowodany, aniony, znakowanie żywności, wymagania pokarmowe, wartość odżywcza

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INTRODUCTION

Carbonated and non-carbonated beverages manufactured based on mineral and spring waters have been present at the Polish market shortly, and their production and sales are regularly growing. The products have become commonly known as flavoured beverages. In the context of the EU food legislation, beverages manufactured based on mineral and spring water are not subject to regulations prescribing the quality of those waters [2, 13]. They are solely defined in a food category “Flavoured beverages”, and not as “Water, including natural mineral water (...) and spring water and all other bottled or packed waters” [14].

The reputation of popular brands of mineral waters and health resorts producing them is playing a significant role in the growing popularity of such commodities. Such factor is also determining a consumer’s approach to this category of beverages, which are regarded as healthy and safe as mineral and spring waters. Their attractive price is also not without significance (as compared to brand soft drinks) and a more favourable taste than the source water. All this is driving the sales of the products higher as opposed to juices, nectars, energy drinks and isotonic sport drinks, and even source mineral and spring waters [3, 7, 10].

A few dozens of such products produced by the majority of mineral and spring water manufacturers are currently available at the Polish market. The manufacturers of such products frequently refer to their health-related properties by highlighting positive characteristics as compared to classical soft drinks [11]. Information can be found on their labels claiming “crystal clear mountain water”, “flavour of tasty fruit”, “refreshing composition of fruit flavours”, etc. Instead, artificial or natural fruit aromas are found in the content of such beverages, sweeteners (Aspartame, Acesulfame Potassium, Sucralose, Sodium Cyclamate, Sodium Saccharin, Steviol Glycosides), antioxidants (ascorbic acid), acidity regulators (citric acid), preservatives (sodium benzoate), and more rarely – fruit juices obtained from concentrated fruit juices.

“Carbohydrates” or “sugar” are often declared on labels as sweeteners, however without specifying, what chemical compounds are involved. It is also note worthy that the labels of mineral and spring water-based beverages do not have the information required for classical mineral and spring waters, in particular what inorganic anions form their part [2, 13].

The aim of this work was to determine what carbohydrates have been used for sweetening mineral and spring water-based beverages and to determine the profile of three inorganic anions (chlorides, nitrates and sulphates) in the investigated samples.

MATERIAL AND METHODS

15 samples of mineral and spring water-based beverages were taken to analysis. The products were bought in shops at the area of Rzeszow.

The Dionex ICS 1000 ion chromatography system, controlled with Chromeleon version 6.8 software, was used for analysing the content of anions in the tested samples. A reference solution, containing seven anions, was sourced from Thermo Scientific company. A mobile phase was prepared by diluting hundred times the initial solution of 0,8M Na_2CO_3 /0,1M (from Thermo Scientific), dedicated to the AS 14A analytical column. Isocratic flow with a flow rate of 1 ml per min. was used. Chromatographic separation was carried out by means of the IonPack AS 14A analytical column together with the AS 14G guard column by Thermo Scientific. The column was thermostated at the temperature of 30°C. Conductometric detection was used and the measuring cell temperature was 35°C. The ASRS-4 mm suppressor was used for suppressing the phase conductivity. A data collection rate was set at 5.0 Hz. Data processing was carried out with Chromeleon 6.8 software.

The basic validation parameters of the IC analytical method applied were estimated. The specificity of the method was confirmed through the injection of the set of standards of seven inorganic anions. The linearity of detector response to the set concentrations of standard solutions within the range of 1.0 to 25 $\text{mg}\cdot\text{L}^{-1}$ was also determined for the three mentioned inorganic anions: chlorides, nitrates and sulphates. The precision of the analytical method described was confirmed by repeating three times the injection of the set of standards and each of the samples. The stability of the chromatographic system was controlled at intervals lasting five hours by injecting the set of standards in which the concentrations of anions corresponded to the results obtained most often for the prepared samples. In addition, each sample was controlled through fortification with the standard of seven anions in order to confirm the identification of the individual anions. The calibration curves were obtained by plotting concentration (in $\text{mg}\cdot\text{L}^{-1}$) against peak area. Responses obtained in the examined range were expressed by the linear equation $y = ax + b$.

The samples were degassed for 60 minutes prior to a chromatographic analysis. The undiluted samples, before injection onto the chromatographic system, were filtered through the MCE 0.45 μm syringe filters supplied by Alchem.

High-performance liquid chromatography (HPLC) system controlled with Varian Workstation software version 6.9.1, consisting of two high pressure Varian LC 212 pumps, an autosampler Varian ProStar 410, an evaporative light scattering detector Varian ELSD 385

LC and an integrating module Varian Star 800, was used for analysing the content of sugar in mineral and spring water-based beverages. The Cosmosil Sugar-D, 4.6 x 250 mm chromatographic column was used for chromatographic separation. A data collection rate was set at 5.0 Hz. Data processing was carried out with Varian Workstation software, version 6.9.1.

Optimum parameters of the chromatographic analysis were determined. Isocratic flow; mobile phase composition: acetonitrile: water (80:20 v/v); mobile phase flow rate: 1 ml per min.; injection volume: 25 µl; temperature inside the column thermostat: 35°C; the autosampler tray temperature: 4°C. The following ELSD detector parameters were used: the flow rate of gas of 1.2 L per min., the nebulizer temperature of 80°C and the evaporator temperature of 80°C. Acetonitrile was supplied by the Polish chemical company POCh.

The basic validation parameters of the analytical method applied were estimated. The specificity of the method was confirmed with injections of single standards of the three examined carbohydrates: fructose, glucose and sucrose and their mixture. The linearity of detector response to the set concentrations of standard

solutions within the range of 0.5 to 30 mg·ml⁻¹ was also determined for the three mentioned carbohydrates. The repeatability of the detector's responses to known concentrations of the studied carbohydrates was controlled by periodic injections of the kit of standards: fructose, glucose and sucrose. The calibration curves were obtained by plotting concentration (in mg·ml⁻¹) against peak area. Responses obtained in the examined range were expressed by the linear equation $y = ax + b$. The standards of carbohydrates were supplied by Sigma Aldrich.

The samples were degassed for an hour prior to a chromatographic analysis and filtered through MCE syringe filters with the pore diameter of 0.45 µm supplied by Alchem.

RESULTS

A note about total carbohydrates and sugar contained was provided on the labels of eleven out of the twelve examined beverages prepared based on mineral water and spring water. The labels informed about the

Table 1. Declared and determined content of carbohydrates in the tested beverages

Name of beverages	Content declared (in 100 ml of beverages)	Content determined			Total sugar [g/100 ml]
		Fructose [mg·ml ⁻¹] ± SD (n=3)	Glucose [mg·ml ⁻¹] ± SD (n=3)	Sucrose [mg·ml ⁻¹] ± SD (n=3)	
<i>Raspberry-flavoured Żywiec Zdrój</i>	Sugar; total carbohydrates of 4.5 g	18.93 ±0.082	19.22 ±0.190	7.24 ±0.052	4.53
<i>Orange-flavoured Żywiec Zdrój</i>	Sugar; carbohydrates 4.9 g incl. sugar 4.9 g	19.47 ±0.255	19.87 ±0.164	12.11 ±0.098	5.14
<i>Apple-flavoured Żywiec Zdrój</i>	Sugar, apple juice of concentrated juice; carbohydrates 4.8 g including sugar 4.8 g	17.67 ±0	17.9 ±0.069	11.88 ±0.081	4.74
<i>Strawberry-flavoured Żywiec Zdrój</i>	Sugar, raspberry juice of concentrated juice; total carbohydrates of 6.0 g incl. sugar 6.0 g	23.61 ±0.015	23.83 ±0.054	11.21 ±0.094	5.86
<i>Lemon-flavoured Żywiec Zdrój</i>	Sugar; total carbohydrates of 5.6 g incl. sugar 5.6 g	21.88 ±0.097	22.15 ±0.171	9.91 ±0.031	5.39
<i>Wysowianka Lemon</i>	Sugar, sodium cyclamate, sodium saccharin; sugar content undeclared	16.47 ±0.043	16.67 ±0.071	7.31 ±0.042	4.04
<i>Strawberry-flavoured Waterr</i>	Cane sugar, raspberry juice of concentrated raspberry juice, lemon juice of concentrated lemon juice; carbohydrates 5.9 g	19.49 ±0.016	19.29 ±0.056	21.2 ±0.125	5.99
<i>Lemon-flavoured Waterr</i>	Cane sugar, lemon juice of concentrated lemon juice; carbohydrates 4.4 g	6.6 ±0.032	6.6 ±0.056	31.73 ±0.401	4.49
<i>Raspberry-flavoured Arctic Plus</i>	Sugar, aspartame, acesulfame potassium, carbohydrates 2.8 g incl. sugar 2.8 g	5.03 ±0.09	4.98 ±0.067	17.02 ±0.08	2.7
<i>Lemon-flavoured Arctic Plus</i>	Sugar, aspartame, acesulfame potassium, carbohydrates 2.8 g incl. sugar 2.8 g	6.79 ±0.09	6.72 ±0.026	12.97 ±0.125	2.64
<i>Non-carbonated raspberry-flavoured Nałęczowianka</i>	Glucose-fructose syrup and sugar, acesulfame potassium, sucralose; carbohydrates 3.0 g incl. sugar 3.0 g	10.61 ±0.155	12.52 ±0.071	8.04 ±0.038	3.11

Table 2. Declared and determined inorganic anions content in the tested beverages

Name of beverages	Declared anions content	Concentration determined		
		Chlorides [mg·L ⁻¹] ± SD (n=3)	Nitrates [mg·L ⁻¹] ± SD (n=3)	Sulphates [mg·L ⁻¹] ± SD, (n=3)
<i>Non-carbonated lemon-flavoured Nałęczowianka</i>	None	5.00 ± 0.045	1.31 ± 0.011	3.33 ± 0.005
<i>Non-carbonated strawberry-flavoured Aquarel Nestle</i>	None	5.46 ± 0.051	1.37 ± 0.094	4.73 ± 0.043
<i>Non-carbonated strawberry-flavoured Żywiec Zdrój</i>	None	7.47 ± 0.03	4.84 ± 0.059	19.06 ± 0.022
<i>Non-carbonated peach-flavoured Aquarel Nestle</i>	None	5.01 ± 0.012	1.42 ± 0.015	3.53 ± 0.009
<i>Non-carbonated orange-flavoured Żywiec Zdrój</i>	None	4.87 ± 0.019	2.2 ± 0.056	23.09 ± 0.017
<i>Non-carbonated strawberry-flavoured Nałęczowianka</i>	None	5.07 ± 0.024	1.34 ± 0.098	3.26 ± 0.057
<i>Non-carbonated lemon-flavoured Żywiec Zdrój</i>	None	5.38 ± 0.024	5.1 ± 0.009	18.31 ± 0.045
<i>Non-carbonated raspberry-flavoured Żywiec Zdrój</i>	None	4.79 ± 0.019	4.34 ± 0.094	16.11 ± 0.028
<i>Non-carbonated strawberry-flavoured Aqua</i>	None	3.33 ± 0.083	-	16.25 ± 0.084

contents of “sugar”, “glucose-fructose syrup” or “cane sugar”. The only manufacturer that did not provide contents of sugar on the label was the manufacturer of a carbonated orange-lime-flavoured drink “Wysowianka Lemon” produced based on water from the Wysowa-Zdrój spring; the contents for fructose was, respectively: 1.64 g/100 ml, for glucose: 1.66 g/100 ml, for sucrose: 0.73 g/100 ml. The tests conducted confirmed that the declared amounts of carbohydrates corresponded to the amount determined. The highest disparity recorded (orange-flavoured Żywiec Zdrój drink) did not exceed 250 milligrams for the declared amount of 4.9 g/100 ml and for the determined amount of 5.14 g/100 ml. The presence of three carbohydrates in various quantitative proportions was confirmed in all the tested beverages, i.e.: fructose, glucose and sucrose. The rate of glucose to fructose concentrations was close to 1:1 for all the beverages (Table 1).

The content of chlorides, nitrates and sulphates was determined in the tested beverages. The amount of chlorides varied between 3.33 to 7.47 mg·L⁻¹, nitrates between 1.31 to 5.1 mg·L⁻¹ and for sulphates between 3.26 to 23.09 mg·L⁻¹ (Table 2).

DISCUSSION

The sugar content in food products, including beverages, has become discussed more and more intensively. Efforts have been taken not only to impose restrictions but also to prohibit the sale of sweetened beverages [7]. The basis of a heated debate is the commonly known impact of sugar on the development of civilisation diseases

such as obesity, diabetes, atherosclerosis, hypertension, tumorous diseases, tooth decay [1, 5, 6, 9, 16].

The Nutritional Guidelines for the Polish Population of 2012 provide that the guideline daily amount of sugar should be 130 grams, and the amount of energy coming from the consumed, added sugar should not be higher than 10% of total energy demand [4, 15]. The following three manufacturers: Żywiec Zdrój S.A., Hoop Polska Sp z o.o. and Nestlé Waters Polska S.A. provide on its products GDA (*Guideline Daily Amount*) information indicating a recommended daily amount. A single, quarter-litre portion of a spring or mineral water-based beverages of Żywiec Zdrój S.A. may cover between 4 to 6% of the daily amount for total sugar, between 12 to 17% of the demand for added sugar, i.e. carbohydrates added to food in food production (these include fructose, glucose and sucrose for the product category discussed) and between 2 to 3% of energy demand [15]. Such amounts are, on average, two times lower as compared to classical soft drinks, as, e.g. a quarter-litre portion of a cola drink containing 26.5 g of total added sugar may satisfy as much as 29% of the guideline daily amount of sugar and cover 5% of the energy demand.

The labels of the tested mineral and spring water-based beverages are lacking information about the content of inorganic anions, which is legally required for manufacturers of classical mineral and spring waters [2, 13]. The identified concentrations of inorganic anions did not exceed the permitted standards which, for nitrates, are at the level of 10 mg·L⁻¹ (for natural mineral water extracted at the territory of the Republic of Poland) and of 50 mg·L⁻¹ (for water intended for human consumption) and at the level of 250 mg·L⁻¹ for sulphates and chlorides [12, 13].

CONCLUSIONS

1. Mineral and spring water-based beverages should be considered as an important source of sugar in diet. A high consumption of such products at a rate of one litre per day may easily supply excessive amounts of such nutrients to an organism, hence causing unfavourable effects likely to lead to civilisation diseases.
2. Tested beverages contained fewer added sugar than classical soft drinks (such as cola, tonics, orange beverages do not pose threats to consumer health in terms of their contents of inorganic ions: chlorides, nitrates and sulphates).
3. Care should be taken that consumers can easily differentiate the labels of mineral and spring water-based beverages from classical mineral and spring waters.
4. The best way to attract attention to high contents of sugar in mineral and spring water-based beverages is to provide GDA information on labels indicating the demand for, notably, sugar and energy in per cents when consuming one portion of a given product.

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