CROATICA CHEMICA ACTA
CCACAA **80** (1) 91–100 (2007)

ISSN-0011-1643
CCA-3144
Original Scientific Paper

Determination of Arsenic and Other Trace Elements in Bottled Waters by High Resolution Inductively Coupled Plasma Mass Spectrometry

Željka Fiket,* Vibor Roje, Nevenka Mikac, and Goran Kniewald

Center for Marine and Environmental Research, Ruđer Bošković Institute, P.O. Box 180, HR-10002 Zagreb, Croatia

RECEIVED MAY 19, 2006; REVISED NOVEMBER 30, 2006; ACCEPTED JANUARY 19, 2007

Keywords
arsenic
bottled water
drinking water
HR ICP-MS
tap water
trace elements

Concentrations of arsenic and other trace elements in 18 different brands of bottled, mineral and spring, water in Croatia were investigated. For comparison, samples of tap water from Rijeka, Lourdes and Zagreb were also analyzed. The high resolution inductively coupled plasma mass spectrometry (HR ICP-MS) was used for the analysis. Results obtained were compared to Croatian maximum allowable levels for trace elements in drinking, mineral and tap water, as well as WHO and EPA drinking water standards. Concentration levels of all analyzed elements investigated in all examined water samples were below the maximum contaminant level prescribed by Croatian, WHO and EPA regulations.

INTRODUCTION

Water is an essential component for life and an important source of intake of trace elements in humans. Therefore, its quality is of great importance to human health. Trace elements can be categorized into those essential to human life, such as Co, Cr, Cu, Fe, Mn, Mo, Se and Zn, and those potentially toxic, like Ag, Al, As, Cd, Pb and Ni. The presence of non-essential and toxic elements does not necessarily indicate that water consumption poses a health risk. Also, certain essential trace elements (*e.g.*, Co, Cr, Fe, Mn, and Se) can be toxic when concentrations are raised above specific cut-off levels.

Recently, arsenic has become increasingly important in environmental geochemistry because of its significance for human health. It is widely distributed and human exposure is inevitable. Arsenic in drinking water is one of the most serious environmental health hazards faced by populations in many areas of the world, including the northeastern part of Croatia.[1] Arsenic is highly toxic and can lead to a wide range of health problems.[2,3] It is carcinogenic, mutagenic and teratogenic.[2-4] Among the various sources of As in the environment, drinking water probably poses the greatest threat to human health. Arsenic is naturally introduced into water by dissolution of minerals and ores, and by the percolation of groundwater through arsenic-enriched rocks. Anthropogenic sources of arsenic are wood preservatives, alloying agents and the combustion of fossil fuels. Inorganic arsenic occurs in the environment in several forms – in natural waters it is mostly found as the trivalent As^{III} arsenite species or the pentavalent arsenate As^{V}. Organic arsenic species, found in seafood, are easily eliminated by the human body and thus much less toxic than inorganic arsenic forms (ref. WHO factsheet 210, 2001). Following accumulation of the evidence for chronic toxicological effects of As in drinking water, recommended and regulatory

* Author to whom correspondence should be addressed. (E-mail: zeljka.fiket@irb.hr)

limits of many authorities are being lowered.[3,5] Croatia has set a new limit for As in mineral and spring water of 10 μg/L, starting from 1.1.2007.[6] The World Health Organization (WHO) guideline value for As in drinking water was provisionally lowered in 1993 from 50 to 10 μg/L.[7] The new recommended value is based largely on analytical capability. The United States Environmental Protection Agency (EPA) limit was also lowered from 50 to 10 μg/L in 2001.[8]

Trace metals may occur naturally in groundwater in very small amounts and may include arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver and zinc. In small amounts, these are harmless and in some cases even beneficial to health. Amounts over drinking water standards may have serious health effects. Essential or non-essential elements, when present at elevated levels can cause morphological abnormalities, reduced growth, increased mortality and mutagenic effects in humans.[9] To avoid potential health hazard caused by elevated concentrations of trace elements in drinking water, Croatia has passed regulations for maximum allowable levels of these elements in drinking and bottled, mineral and spring, water.[6,10-12] International standards have also been set by WHO[7] and EPA.[8]

Nowadays, bottled water is widely consumed due to its accessibility, relatively low cost, better taste and lower levels of impurities. Croatian bottled water is also an important export article to countries of the European Union and must therefore meet their standards for bottled waters. Apart from the use of bottled water as drinking water, it has found usage in food preparation, skin care and filling humidifiers.[13]

Determination of trace elements in drinking water requires a method where low levels of detection can be obtained. In the last decade, inductively coupled plasma mass spectrometry has become a method of choice in analysis of water samples of different origin.[14-17] Double focusing sector field ICP-MS enables direct determination of elements of interest with no preconcentration or isolation required.[17] Next to the ability for multielement analysis, double focusing ICP-MS also offers high sensitivity over a wide linear range and low limits of detection.[16-20]

This research was carried out to provide an insight into the levels of trace elements in bottled, mineral and spring, water currently present on the Croatian market.

Declarations on the chemical composition of bottled water (given by the producers) generally report only concentrations of major elements (Ca, Mg, Na, and K). In this study, bottled waters are classified as mineral and spring waters according to bottle declaration labels. The distinction between mineral and spring water is based on their specific characteristics, primarily their total dissolved solids content. According to the US Food and Drug Administration (FDA),[21] mineral water is distinguished from other types of bottled water by its constant level and relative proportions of mineral and trace elements at the point of emergence from the source, containing not less than 250 parts per million of total dissolved solids. Spring bottled water is the water derived from an underground source from which water flows naturally to the surface of the earth where it is collected only at the spring or through a borehole tapping the underground formation feeding the spring. Attention has been focused particularly on trace elements for most of which no data were available for mineral and spring waters of Croatia.

In this paper, the results of investigating the concentration of 23 trace elements (Ag, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, U, V and Zn) in 18 brands of bottled water are presented. For comparison, 5 samples of tap water, one from Rijeka and Lourdes and three from Zagreb were analyzed for the same elements. Aims of this study were (1) to quantify the levels of trace elements in bottled water in Croatia, and (2) to compare obtained values with the Croatian, WHO and EPA drinking water standards.

EXPERIMENTAL

Instrumentation

All measurements were carried out on a high resolution inductively coupled plasma mass spectrometer Element 2 (Thermo, Bremen, Germany). An autosampler (ASX 510, Cetac Technologies, USA) and sample introduction kit consisting of a conical nebulizer (Thermo, Bremen, Germany) and Scott-type glass spray chamber (Thermo, Bremen, Germany) were employed to transport the analytes into the plasma of the ICP-MS. Details of the ICP-MS operating conditions and the data acquisition parameters are summarized in Table I.

Before analysis, the HR ICP-MS measuring conditions were optimized using a solution containing Li, In, and U at a concentration of 1 μg/L.

Reagents and Standard Solutions

For preparation of standard and blank solution, high purity Milli-Q water obtained with a Millipore purification system (resistivity less than 18 MΩ/cm) was used.

Calibrating solutions (0.01, 0.05, 0.1, 0.5, 1, 10 μg/L) were prepared by appropriate dilution of 100 mg/L multielement stock standard solution (Analytika, Prague, Czech Republic) containing Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Se, Sr, Ti, Tl, V and Zn, into which single element standard solutions (1 g/L) of U (Aldrich, Milwaukee, WI, USA), Ag (Fluka, Steinheim, Switzerland) and Sb (Analytika, Prague, Czech Republic) were added. Working standards, as well as blank solutions were prepared with addition of 1 % high purity HNO_3 (Fluka, Steinheim, Switzerland) and 1 % high purity HCl acid (Merck, Darmstadt, Germany). For internal standardization, the solution of In at

TABLE I. Operating conditions of the HR ICP-MS and data acquisition parameters for the determination of selected trace elements in tap waters

Parameters	HR ICP-MS operating conditions
RF power	1200 W
Auxiliary Ar flow	1.02 L/min
Coolant Ar flow	15,50 L/min
Sample gas flow rate	1.004 L/min
Torch	Fassel type, 1.5 mm i.d.
Sample cone	Ni, 1.1 mm aperture i.d.
Skimmer cone	Ni, 0.8 mm aperture i.d.
Resolution	LR = 300 MR = 4000 HR = 10000
Sample uptake rate	1 mL/min
Ion sampling depth	adjusted daily
Ion lens setting	adjusted daily
Take up time	120 sec
Washing time between samples	60 sec
Isotopes measured	LR: ^{7}Li, ^{11}B, ^{95}Mo, ^{98}Mo, ^{107}Ag, ^{109}Ag, ^{111}Cd, ^{114}Cd, ^{121}Sb, ^{123}Sb, ^{138}Ba, ^{205}Tl, ^{208}Pb, ^{238}U; MR: ^{27}Al, ^{47}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{86}Sr; HR: ^{75}As, ^{77}Se
Acquisition mode	E-scan
Sample time	5 min
Samples per peak	50 (LR), 20 (MR, HR)

a concentration of 1 μg/L was used. Quantification of trace element concentration was performed by weighted regression of the calibration curves. All containers used were previously cleaned by soaking for several days in 10 % HNO_3 solution and rinsed with Milli-Q water before use.

Collection and Preparation of Samples

A total of 24 bottled water, 16 spring and 8 mineral, and 5 tap water samples were analyzed for total concentration of 23 trace elements (Ag, Al, As, Cd, B, Ba, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, U, V and Zn). Bottled water samples were obtained from two Croatian stores. All the brands were in plastic containers with plastic screw caps and capacity of 1.5 L, except one carbonated water brand in 1 L plastic container. Sparkling bottled waters were degassed by leaving overnight in a laminar flow clean air bench.

Tap water samples were collected in polyethylene containers from five different locations. Prior to sampling, the water was flushed for 2 minutes and the containers were rinsed three times with the water to be sampled. Samples were analyzed within two days from the time of collection.

Samples were acidified with 1 % HNO_3 and 1 % HCl and internal standard was added 24 hours before measurements were made. The mixture of HNO_3 and HCl was used as stabilizing agent for water samples since measurements of Sb require the addition of HCl for quantitative preservation. Also, better flushing of the system and lower retention of metals in the system is achieved with this mixture. No additional dilution of samples was performed. All samples were prepared in triplicate. Limits of detection were calculated as three times the standard deviation (3σ) of the blank values.

Quality Control

Riverine water reference material (SLRS-4, National Research Council Canada, Canada) with low elemental concentrations of elements of interest was used for the measurement quality control purposes. Good agreement between the analyzed and certified concentrations within their analytical uncertainties for all elements, except for Cd (Table II), was observed. A slight divergence of individual measurements was occasionally observed for Cd, resulting in about 20 % higher average values than the certified one, which can be a consequence of formation of some polyatomic interference in plasma (for example from Mo-oxides).

RESULTS AND DISCUSSION

The results of measurement of Ag, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, U,

TABLE II. Concentrations and standard deviations, expressed in μg/L, of trace elements in the certified water reference materials SLRS-4

Element	Found[(a)]	Certified
Al	49.9 ± 1.4	54 ± 4
As	0.74 ± 0.04	0.68 ± 0.06
B	11.2 ± 0.7	–
Ba	12.9 ± 0.7	12.2 ± 0.6
Cd	0.016 ± 0.002	0.012 ± 0.002
Cr	0.31 ± 0.02	0.33 ± 0.02
Co	0.038 ± 0.005	0.033 ± 0.008
Cu	1.89 ± 0.31	1.81 ± 0.08
Fe	96.3 ± 3.1	103 ± 5
Li	0.46 ± 0.04	–
Mn	3.31 ± 0.15	3.37 ± 0.18
Mo	0.23 ± 0.03	0.21 ± 0.02
Ni	0.59 ± 0.03	0.67 ± 0.08
Pb	0.091 ± 0.002	0.086 ± 0.007
Sb	0.259 ± 0.027	0.23 ± 0.04
Se	0.12 ± 0.02	–
Sr	25.4 ± 0.6	26.3 ± 3.2
Ti	1.14 ± 0.04	–
U	0.056 ± 0.005	0.050 ± 0.003
V	0.35 ± 0.01	0.32 ± 0.03
Zn	0.91 ± 0.04	0.93 ± 0.10

[(a)] $N = 3$.

TABLE III. Concentrations of elements, expressed in μg/L, in bottled water from Croatia (arithmetic mean ± standard deviation of 3 replicate measurements)

	Ag	Al	As	B	Ba	Cd	Co	Cr	Cu	Fe	Li	Mn
LOD	0.001	0.020	0.005	0.020	0.020	0.001	0.001	0.010	0.050	0.100	0.010	0.005
Spring water												
Bistra	0.006	0.635±0.05	1.845±0.04	7.398±0.02	55.35±0.28	0.004±0.001	0.007±0.001	0.534±0.01	0.078±0.001	<0.100	3.300±0.01	0.048±0.01
Bistra[(a)]	0.003±0.001	0.518±0.06	2.013±0.07	20.18	61.93±1.12	0.002±0.000	0.009±0.002	0.527±0.01	<0.050	0.273±0.004	5.113±1.07	0.067±0.01
Bistrica[(a)]	<0.001	0.533±0.07	0.222±0.02	6.823	7.483±0.23	0.003±0.001	0.006±0.001	0.182±0.01	0.070±0.01	0.297±0.08	0.564	0.080±0.01
Clever	0.003±0.000	3.009±0.19	0.107±0.01	2.290±0.12	4.674±0.23	0.006±0.001	0.025±0.001	0.175±0.002	0.199±0.01	1.225±0.11	0.181±0.03	0.025±0.004
Cetina	0.002±0.000	2.216±0.27	0.083±0.01	2.702±0.08	5.436±0.07	0.003±0.000	0.013±0.002	0.159±0.002	0.254±0.03	<0.100	0.163±0.03	0.015±0.001
Cetina[(b)]	0.007±0.001	1.157±0.09	0.086±0.01	3.496±0.20	6.54±0.33	0.003±0.000	0.009±0.001	0.280±0.004	7.714±0.03	<0.100	0.245±0.03	0.076±0.003
Čista	<0.001	0.069±0.004	0.007±0.001	12.41±0.06	1.118±0.12	0.010±0.002	<0.001	0.061±0.01	<0.050	<0.100	0.285±0.03	0.033±0.01
Jana	0.010±0.004	0.406±0.01	0.224±0.01	6.445±0.08	11.53±0.09	<0.001	0.006±0.001	0.252±0.01	<0.050	<0.100	3.011±0.03	0.009±0.002
Mercator	0.005±0.001	0.171±0.03	0.412±0.01	10.07±2.14	21.87±0.46	0.034±0.001	0.039±0.002	0.048±0.003	0.203±0.05	0.470±0.07	1.812±0.01	0.079±0.003
Radenska	0.003±0.001	0.242±0.02	0.232±0.04	11.38	41.44±0.75	<0.001	0.011±0.002	0.167±0.01	<0.050	0.188±0.03	28.17±0.98	139.3±2.2
Sveti Rok	0.003±0.001	10.294±0.62	0.032±0.006	2.614±0.01	14.63±0.09	0.005±0.000	0.012±0.001	0.247±0.01	0.306±0.004	3.247±0.24	0.112±0.01	0.223±0.003
Sveti Rok[(a)]	0.004±0.000	5.106±0.46	0.036±0.006	3.259±0.44	19.51±0.19	0.008±0.002	0.011±0.001	0.243±0.003	0.373±0.04	3.793±0.72	0.183±0.03	0.324±0.01
Studena	0.006±0.001	0.108±0.01	0.343±0.02	10.99±0.48	47.63±0.49	0.005±0.002	0.035±0.005	0.236±0.003	<0.050	0.404±0.07	9.337±0.09	0.077±0.01
Tiha	0.002±0.001	1.642±0.04	0.159±0.02	2.578±0.05	8.199±0.19	0.011±0.001	0.010±0.000	0.116±0.002	0.459±0.01	0.355	0.499±0.01	0.019±0.004
UN1QUE	1.310±0.012	0.229±0.06	0.357±0.01	6.956±0.15	35.75±0.22	<0.001	0.038±0.005	0.658±0.01	2.969±0.01	0.250±0.01	1.299±0.02	0.892±0.01
Zala	0.003±0.001	0.339±0.05	0.192±0.01	20.09±0.31	19.65±0.21	0.005	0.066±0.002	0.422±0.01	0.065±0.01	<0.100	0.881±0.001	<0.005
Mineral water												
Clever[(a)]	0.005±0.001	5.509±0.15	0.255±0.02	969.6±3.1	240.6±2.1	<0.001	0.035±0.001	0.048±0.003	<0.050	0.655±0.14	92.47±0.85	20.32±0.13
Donat Mg[(a)]	0.005±0.001	0.289±0.07	2.924±0.07	3781±349	3.245±0.87	0.003±0.001	8.642±0.17	1.597±0.05	<0.050	0.754±0.05	2893±305	4.162±0.28
Jamnica	0.004±0.001	0.668±0.08	0.673±0.03	444.4±8.5	43.31±0.71	0.004±0.001	0.616±0.01	0.026±0.001	<0.050	0.846±0.06	111.9±2.3	213.1±2.1
Jamnica[(a)]	<0.001	0.642±0.02	0.186±0.04	3680±46	54.71±3.51	0.003±0.001	1.110±0.07	0.065±0.002	<0.050	2.496±0.23	1155±13	196.6±26.2
Kapljice[(a)]	0.007±0.002	0.629±0.06	1.087±0.03	776.1±18.8	69.52±1.99	0.003±0.000	0.064±0.002	0.426±0.02	1.812±0.06	2.814±0.21	649.9±16.3	91.22±3.78
Radenska[(a)]	0.009±0.001	0.227±0.03	0.306±0.02	2101±61	104.9±2.2	0.003	0.287±0.01	<0.010	<0.050	3.534±0.47	810.6±24.2	98.98±7.83
Studenac[(a)]	0.010±0.001	1.413±0.06	1.112±0.03	343.7±1.9	45.46±0.14	0.005	0.019±0.001	0.016±0.002	<0.050	0.581±0.03	143.3±1.1	1.726±0.02
Studenac light[(a)]	0.006±0.001	1.280±0.04	1.085±0.02	265.8±2.8	45.58±0.59	0.007±0.002	0.009±0.002	0.035±0.003	<0.050	0.438±0.09	172.3±1.2	2.644±0.06

(cont.)

TABLE III *(continued)*.

	Mo	Ni	Pb	Sb	Se	Sr	Ti	Tl	U	V	Zn
LOD	0.010	0.050	0.010	0.001	0.010	0.020	0.005	0.002	0.001	0.002	0.100
Spring water											
Bistra	1.012±0.02	0.286±0.01	0.012	0.422±0.06	0.505±0.04	168.9±0.9	<0.005	0.050±0.001	0.838±0.01	0.397±0.01	0.489±0.07
Bistra[(a)]	1.053±0.01	0.287±0.01	<0.010	0.265±0.01	0.529±0.08	193.2±2.9	<0.005	0.053±0.001	0.992±0.01	0.388±0.01	0.128±0.02
Bistrica[(a)]	0.302±0.01	<0.050	0.077±0.004	0.277±0.01	0.131±0.002	30.93±0.4	<0.005	0.016±0.001	0.581±0.02	0.228±0.01	1.934±0.03
Clever	0.342±0.01	<0.050	0.014±0.002	0.150±0.01	–	103.8±1.3	0.223±0.05	0.011±0.001	0.500±0.01	0.460±0.01	0.552±0.08
Cetina	0.469±0.01	<0.050	<0.010	0.188±0.03	0.074±0.001	138.4±0.8	0.024±0.002	0.003±0.001	0.536±0.003	0.514±0.01	1.473±0.15
Cetina[(b)]	0.365±0.01	0.094±0.02	0.398±0.004	0.131±0.02	0.693	104.9±1.2	0.005±0.001	<0.002	0.486±0.01	0.365±0.001	6.242±0.26
Čista	0. 032±0.002	<0.050	<0.010	0.028±0.01	0.021±0.003	28.79±2.87	<0.005	<0.002	<0.001	<0.002	<0.100
Jana	0.336±0.002	<0.050	0.015±0.001	0.258±0.02	0.093±0.01	123.8±0.5	<0.005	0.014±0.001	0.976±0.003	1.056±0.01	<0.100
Mercator	2.805±0.04	0.219±0.01	0.036±0.01	0.323±0.02	0.161±0.02	123.9±3.3	<0.005	0.082±0.004	1.263±0.01	0.098±0.003	6.433±0.48
Radenska	0.209±0.01	<0.050	<0.010	0.289±0.02	<0.010	268.9±2.3	<0.005	<0.002	0.121±0.003	<0.002	<0.100
Studena	0.450±0.02	0.097±0.002	0.007	0.260±0.01	–	201.2±1.4	<0.005	0.010±0.003	1.248±0.01	0.042±0.004	0.825±0.06
Sveti Rok	0.056±0.001	0.057±0.003	0.015±0.002	0.111±0.01	–	27.85±0.05	0.316±0.03	0.003±0.00	0.215±0.002	0.187±0.01	0.492±0.06
Sveti Rok[(a)]	0.076±0.01	0.691±0.01	0.024±0.002	0.307±0.01	–	28.92±0.32	0.098±0.01	0.009±0.001	0.271±0.004	0.167±0.003	0.737±0.10
Tiha	0.031±0.003	0.192±0.01	<0.010	0.219±0.01	0.101±0.01	29.66±0.23	<0.005	0.01±0.001	0.156±0.003	0.194±0.01	0.997±0.03
UN1QUE	0.700±0.002	0.115±0.01	<0.010	0.225±0.03	0.306±0.05	230.6±3.9	<0.005	<0.002	1.093±0.01	0.207±0.003	1.032±0.21
Zala	0.078±0.002	0.086±0.02	<0.010	0.423±0.04	0.087±0.001	130.8±1.5	<0.005	<0.002	0.743±0.003	0.275±0.004	<0.100
Mineral water											
Clever[(a)]	0.449±0.011	1.754±0.03	<0.010	0.409±0.001	–	405.9±3.8	0.119±0.001	<0.002	0.256±0.002	0.150±0.004	0.212±0.02
Donat Mg[(a)]	0.283±0.005	9.137±0.28	<0.010	0.265±0.05	0.066±0.01	2020±349	0.026±0.004	0.028±0.002	1.465±0.06	0.095±0.003	2.025±0.50
Jamnica	0.467±0.067	1.821±0.02	0.038±0.004	0.179±0.01	0.044±0.01	173.5±1.1	0.015±0.002	0.008±0.001	0.137±0.01	0.034±0.002	0.408±0.09
Jamnica[(a)]	0.312±0.001	4.199±0.05	0.061±0.01	0.413±0.003	0.106±0.03	720.4±30.6	0.025±0.004	0.012±0.001	0.207±0.003	0.072±0.001	0.356±0.02
Kapljice[(a)]	0.705±0.027	0.399±0.01	<0.010	0.214±0.01	0.239±0.01	267.5±7.3	0.068±0.006	<0.002	0.780±0.02	0.325±0.01	1.132±0.07
Radenska[(a)]	0.016	2.319±0.06	<0.010	0.821±0.04	–	1519±30	0.010±0.002	0.317±0.01	0.070±0.003	0.111±0.01	<0.100
Studenac[(a)]	0.385±0.017	<0.050	<0.010	0.498±0.01	–	263.9±1.2	0.010±0.002	0.030±0.001	0.990±0.01	0.047±0.001	2.119±0.08
Studenac light[(a)]	0.385±0.017	0.068±0.002	<0.010	0.396±0.05	–	311.1±3.9	0.012±0.001	0.022±0.004	1.124±0.01	0.051±0.003	2.142±0.12

[(a)] Sparkling water.
[(b)] Sample taken from water-cooler.

TABLE IV. Concentrations of elements, expressed in μg/L, in tap water from Croatia (arithmetic mean ± standard deviation of 3 replicate measurements)

	Ag	Al	As	B	Ba	Cd	Co	Cr	Cu	Fe	Li	Mn
Tap water												
Rijeka	0.005±0.002	4.634±0.06	0.05±0.01	3.478±0.85	3.688±0.14	0.012±0.001	0.008±0.001	0.350±0.002	1.666±0.03	2.774±0.14	0.112±0.03	0.058±0.01
Lourdes	0.003±0.001	2.578±0.16	0.22±0.02	5.787±0.06	6.807±0.06	<0.001	0.014±0.001	0.377±0.01	0.622±0.01	1.360±0.12	1.569±0.02	0.244±0.01
$Zagreb_1$	0.006±0.001	4.778±0.32	0.26±0.01	57.51±0.17	38.69±0.22	0.039±0.001	0.073±0.003	0.149±0.004	10.52±0.15	20.42±2.45	5.583±0.04	26.955±0.62
$Zagreb_2$	0.013±0.04	1.072±0.04	0.15±0.01	169.3±3.1	90.58±1.09	0.119±0.01	0.096±0.02	0.464±0.01	16.609±0.49	7.829±1.01	1.059±0.01	0.520±0.03
$Zagreb_3$	0.003±0.001	0.476±0.07	0.098±0.02	69.90±7.10	47.01±1.43	0.027±0.001	0.066±0.01	0.216±0.003	4.987±0.03	10.44±0.06	2.907±0.94	0.698±0.02

	Mo	Ni	Pb	Sb	Se	Sr	Ti	Tl	U	V	Zn
Tap water											
Rijeka	0.032±0.003	<0.050	17.18±0.22	0.061±0.01	0.008±0.002	34.27±0.11	0.149±0.01	0.003±0.001	0.220±0.002	0.489±0.01	13.00±0.98
Lourdes	0.210±0.004	0.060±0.01	–	0.136±0.01	0.200±0.03	167.1±0.5	0.153±0.01	0.003±0.000	0.529±0.01	0.197±0.001	–
$Zagreb_1$	0.146±0.01	1.055±0.04	0.174±0.01	0.161±0.05	0.139±0.02	157.2±1.4	0.258±0.06	0.010±0.01	0.364±0.003	0.66±0.01	52.03±0.19
$Zagreb_2$	0.210±0.02	0.659±0.08	4.877±1.894	0.345±0.15	0.844±0.08	316.6±2.4	0.031±0.001	0.018±0.001	1.410±0.014	0.198±0.003	169.7±8.2
$Zagreb_3$	0.27±0.01	0.263±0.01	0.283±0.002	0.061±0.004	0.528±0.11	230.9±6.7	0.012±0.001	<0.002	1.544±0.015	0.138±0.004	208.2±3.4

V and Zn in bottled and tap water are shown in Tables III and IV, respectively. The majority of elements were found at part per billion (ppb) level, so all values are reported as μg/L. Ranges of concentrations for each individual element in spring, mineral and tap water are summarized in Table V. Measured concentrations of elements of interest were compared with the maximum contaminant level (MCL) regulated by Croatian, WHO and EPA directives for ground, drinking and tap water (Table VI).

Due to its high toxicity and chronic toxicological effects, the recommended and regulatory limits for ARSENIC in drinking water were recently lowered by many authorities.[3,5] Structurally very similar to phosphate (PO_4^{3-}), arsenic in the +5 oxidation state as oxyanion arsenate (AsO_4^{3-}) interferes with the biological function of phosphate, which is the basis of its toxicity.[22] However, the most serious risk of human intoxication with arsenic by drinking arsenic contaminated water comes from As^{III}, which is ~60 times more toxic than As^{V} [23,24] and is the prevalent form of arsenic in anoxic groundwater.[3,25] In the analyzed samples, As level was higher in bottled water than in tap water.

TABLE V. Ranges of concentrations for each individual element in spring, mineral and tap water, expressed in μg/L

Element	Tap water	Spring water	Mineral water
Ag	0.001–0.017	<0.001–1.322	<0.001–0.015
Al	0.40–5.10	0.07–10.91	0.20–5.66
As	0.044–0.269	0.006–2.083	0.143–2.994
B	2.63–172.29	2.17–20.40	262.97–4131.72
Ba	3.5–91.7	1.00–55.63	3.55–242.61
Cd	<0.001–0.314	<0.001–0.035	<0.001–0.008
Co	0.007–0.115	<0.001–0.625	0.005–8.813
Cr	0.145–0.470	0.025–0.672	<0.010–1.650
Cu	0.61–22.18	<0.050–7.740	<0.050–1.871
Fe	1.24–22.86	<0.100–4.571	<0.100–3.999
Li	0.08–5.63	0.11–29.15	2.98–3199.20
Mn	0.05–27.57	<0.005–141.56	1.71–222.79
Mo	0.029–0.284	<0.050–2.843	0.073–0.732
Ni	<0.050–1.09	<0.050–0.701	<0.050–9.417
Pb	0.169–17.402	<0.010–0.402	<0.010–0.042
Sb	0.056–0.496	0.022–0.485	0.203–0.506
Se	0.006–0.921	<0.010–0.608	0.034–0.250
Sr	34.1–319.0	25.9–271.2	172.4–2371.2
Ti	0.030–0.316	<0.005–0.341	0.008–0.074
Tl	<0.002–0.019	<0.002–0.086	<0.002–0.322
U	0.218–1.559	<0.001–1.273	0.067–1.526
V	0.134–0.675	<0.002–1.069	0.032–0.335
Zn	12.02–211.56	<0.100–6.912	0.197–2.263

TABLE VI. Maximum contaminant level for trace elements, given in μg/L, allowed by Croatian, WHO and EPA regulations

Element	Croatia		WHO	EPA
	Drinking water[11]	Mineral and spring water[5,9,10]	Drinking water[6]	Ground and drinking water[7]
Ag	10	–	–	10
Al	150	–	200	50–2000
As	10	50 (10)[(a)]	10	10
B	1000	–	500	–
Ba	700	2000 (1000)[(a)]	700	2000
Cd	5	5 (3)[(a)]	3	5
Cr	50	50	50	100
Cu	2000	1000	2000	1000
Fe	200	–	300	300
Mn	50	2000 (500)[(a)]	400	50
Mo	–	–	70	–
Ni	20	–	20	–
Pb	100 (10)[(b)]	50 (10)[(a)]	10	15
Sb	5	(50)[(a)]	20	6
Se	10	10	10	50
Tl	–	–	–	2
U	–	–	15	30
V	5	–	–	–
Zn	3000	5000	–	5000

(a) 1.1.2007.
(b) 2013.

Maximum concentrations (2–3 μg/L) were obtained from two brands of bottled water, Bistra and Donat Mg. However, all samples examined contain lower concentrations than the current WHO and EPA guideline values of 10 μg/L. This is a clear indication that all of the analyzed mineral and spring waters are derived from sources that do not seem to be influenced by underground aquifers with elevated As levels in northeastern Croatia.[1]

ALUMINUM and TITANIUM display a similar pattern of concentration distribution in samples. Concentrations range from 0.07 to 10.9 μg/L and from below limits of detection to 0.34 μg/L for Al and Ti, respectively. Higher values of Al correspond to higher values of Ti in samples. Maximum concentrations of 10.9 and 0.34 μg/L for Al and Ti, respectively, were recorded in Sveti Rok spring water. The level of Al in all samples was much lower than the Croatian, WHO and EPA water standards (50 μg/L), while there are no proposed guideline values for Ti.

Bottled waters contain slightly higher levels of ANTIMONY than tap waters. With concentrations ranging from 0.022 to 0.506 μg/L all samples were below the proposed EPA safe limits of 6 μg/L. Measured values are, however, much higher than the average concentrations for Sb of a few μg/L in fresh water systems.[26] It was recently reported that a continual release of Sb from PET containers is observed and that the Sb concentrations in bottled waters mainly reflect the duration of their storage.[27]

For BORON, a wide range of concentrations, 2 to 4100 μg/L, is observed. Much higher values (up to 4 mg/L) of B were obtained for mineral than for spring and tap waters All tap waters were below the WHO guideline value of 500 μg/L. However, B in mineral waters was up to 4 times higher than the maximum allowable concentration in drinking waters pursuant to Croatian regulations (Table VI). For mineral waters, however, no upper limit for B has been set to date (it should be defined in 2006 according to Ref. 12, NN mineral waters 2004), probably just because some natural mineral waters may contain very high concentrations of this element and special guidelines for B in particular types of mineral water should be fixed.

Concentrations of BARIUM display a great diversity among samples, ranging from 1 to 250 μg. Nevertheless, all samples examined were below the proposed WHO drinking water standards of 700 μg/L.

The CADMIUM level was significantly higher in tap water than in bottled water. Contamination of tap water with Cd probably originates from the pipe system. In all samples, the level of Cd was far below the proposed WHO guideline value of 3 μg/L.

Low CHROMIUM concentration (up to 1.6 μg/L) was found in all analyzed samples. EPA has recommended 100 μg/L of Cr as the safe limit whereas the Croatian maximum allowable level and the WHO guideline for Cr are set at 50 μg/L. Its toxicity is related to the reduction of chromate to Cr^{III} and radicals produced by the reaction.

In all samples, COBALT was present at very low levels, partly below detection limits. Where measurable, Co concentration did not exceed 1 μg/L, except for Donat Mg mineral water containing 9 μg/L. No proposed guideline for Co is available.

By comparing bottled and tap waters, much higher values of COPPER were obtained in tap water (0.6 to 22 μg/L), probably due to properties of pipe systems. The only bottled water containing higher concentrations of Cu (~8 μg/L) was Cetina, taken from a water cooler. The cooling/heating system containing a brass-coil heater can be the source of elevated concentration of Cu in this sample. Safe limits set by the Croatian and WHO regulations and EPA standards are 2000 and 1000 μg/L, respectively.

IRON was found at relatively higher concentrations in tap than in bottled water. The highest values (10 to 20 μg/L) were recorded for Zagreb tap waters. All samples examined contain concentrations that are lower than the current Croatian and EPA safe limits (300 μg/L).

The widest range of concentrations, from 0.2-3200 μg/L was obtained for LITHIUM. Mineral bottled waters contain up to 200 times more Li than non-mineral and tap waters. No upper limit has been set for this metal in drinking water.

LEAD was found at a very low level in all bottled and two tap water samples with values below 0.4 μg/L.

Much higher concentrations were found in two tap waters, from Zagreb and Rijeka. Lead is present in tap water to some extent as a result of its dissolution from natural sources but primarily from household plumbing systems in which the pipe solder, fittings, or service connections to homes contain lead.[28,29] The amount of lead dissolved from the plumbing system depends on several factors, including the presence of chloride, dissolved oxygen, pH, temperature, water hardness and the standing time of water.[30,31]

A wide range of concentrations was obtained for MANGANESE, from below limits of detection to 222 μg/L. Three brands, Jamnica, Kapljice and Radenska, contain significantly higher concentrations of Mn (90-215 μg/L) compared to other bottled and tap waters (up to 30 μg/L). Nevertheless, all values obtained were below the proposed safe limits for bottled water in Croatia (2000 μg/L). Mn is widely distributed in the environment and naturally present in many surface water and groundwater sources.[7] Therefore, Mn levels in mineral water samples reflect the naturally occurring Mn in water.

MOLYBDENUM concentration in all samples was less than 1 μg/L, except for the Mercator (2.8 μg/L) sample and was slightly lower in tap waters. A health-based guideline value of 70 μg/L was proposed in 1993 by WHO on the basis of a 2-year study of humans exposed to molybdenum in their drinking water.[32]

In all the samples, NICKEL was found below the proposed WHO safe drinking standard of 70 μg/L. Generally higher values were observed in mineral water, with concentrations up to 9.4 μg/L while in tap and spring waters Ni concentration did not exceed 1.1 μg/L. The highest concentration (9.2 μg/L) was found in the Donat Mg mineral water.

SILVER was found at a very low concentration (typically less than 10 μg/L) in all except one sample. The only value found at μg/L level (1.3 μg/L) was observed in the spring bottled water UN1QUE. However, even this much higher value was about 10 times lower than the current Croatian and EPA safe limits for Ag of 10 μg/L.

Concentrations of SELENIUM were found to be similar in bottled and tap water and far below the proposed Croatian, WHO and EPA safe limits of 10 and 50 μg/L, respectively.

All samples contain substantial amounts of STRONTIUM, up to 2 mg/L. Highest values were obtained for Donat Mg and Radenska mineral water also containing the highest levels of Ca. No health-based guideline values are proposed for Sr.

In all samples, except one, THALLIUM was found at very low concentrations (up to 0.1 μg/L). The highest concentration (0.32 μg/L) was detected in bottled Radenska mineral water, still being far below the EPA drinking water standard of 2 μg/L.

No significant difference in URANIUM concentrations between bottled and tap water was detected. Values of U in analyzed samples range from below limits of detection to maximal 1.6 μg/L being below the WHO proposed guideline of 15 μg/L. This is designated as provisional because of outstanding uncertainties regarding the toxicology and epidemiology of uranium. EPA has recommended 30 μg/L of U in water as the safe limit for drinking purposes.

All samples analyzed contain much lower levels of VANADIUM than the maximum permissible limits of 5 μg/L suggested by Croatian regulations. The highest value was observed in bottled Jana non-mineral water containing 1 μg/L.

None of the analyzed samples exceeded the levels of ZINC set by the Croatian water quality standards (5000 μg/L), although wide discrepancy is observed between bottled and tap waters. Bottled waters, mineral and spring, contain up to 7 μg/L of Zn while in tap water significantly higher values (12-211 μg/L) were found. The natural concentration of zinc in water depends on a multitude of factors such as the nature and age of geological formations through which the water flows, along with biological, physical and chemical conditions.[33] However, much higher concentrations of Zn observed in tap water are probably a result of the pipe system technical conditions.

Table V summarizes data for different types of water, spring, mineral and tap water. We can see from the presented ranges that some trace elements are of the same order of magnitude in all types of analyzed water (Al, Cr, Mo, Sb, Se, Ti, Tl, U and V), some of them are significantly higher in bottled water, especially in mineral water (As, Ag, B, Ba, Co, Li, Mn, Ni, Sr) and some are significantly higher in tap water (Cd, Cu, Fe, Pb, Zn). Figure 1 shows the distribution of average concentrations of toxic elements in drinking water (Ag, Al, As, Cd, Ni and Pb) between different types of water, mineral, spring and tap, analyzed in this study. In order to explain these differences, we were looking for correlation between various elements in bottled and tap water and also for correlation between trace elements in bottled water with the concentration of macroelements (Na, Ca, K and Mg) that were declared on the bottles. In bottled water, the concentration of Li was highly correlated ($r > 0.9$) with Na, Ca, K and Mg, so Li is a trace element that is a good indicator of the overall mineral content of water. Therefore, for elements that are highly correlated with Li ($r > 0.8$) as are As, B, Co, Cr, Ni and Sr, we can suppose to be of natural origin. A good correlation of these elements with Li was found both in bottled and tap water, indicating that these elements are of natural origin in all types of analyzed water. Higher concentrations of Ag, B, Ba, Co, Li, Mn, Ni, Sr obtained in mineral waters are thus a consequence of high contents of minerals in these waters. The other group of elements showing good correlation

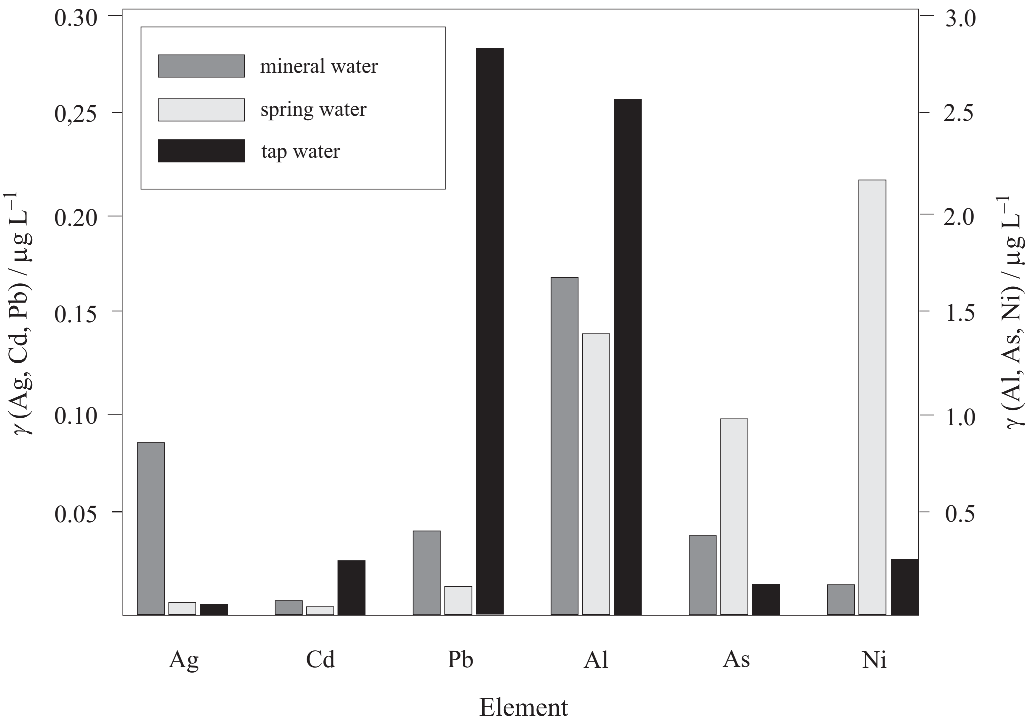

Figure 1. Distribution of average concentrations of toxic elements in drinking water (Ag, Al, As, Cd, Ni and Pb) in different types of water, mineral, spring and tap water.

with each other, but not with Li, were Cd, Cu, Zn and to a lesser extent Fe and Pb. This correlation suggests a common origin of these metals, and their higher concentrations in tap water suggest that the origin of these metals is anthropogenic. The origin of these metals in tap water is obviously corrosion of traditional metal pipe systems, which are still largely used in Croatia. According to the most recent Croatian regulation (NN 182/2004), these systems should within the next 10 years be gradually replaced with non-metal transportation systems in order to reduce concentrations of metals, especially Pb, in tap waters.

CONCLUSIONS

This study showed that all elements analyzed in all selected bottled and tap waters were below the Croatian maximum allowable levels and EPA and WHO drinking water standards.

Concentrations of As were the lowest in tap water (< 1 µg/L), and all analyzed water samples had As levels less than 3 µg/L, which is below the Croatian and European limit of 10 µg/L for drinking water. Tap water contains higher levels of Cd, Cu, Pb, Zn and Fe than bottled water. Partial solubilization of the materials involved in the treatment and especially classical metal supply systems, tanks, pipes, valves and pumps that are used in Croatia could be the origin of these metals. Therefore, higher concentrations of Cd, Cu, Fe, Pb and Zn in tap water can be attributed to the corrosive nature of water in the distribution pipes and water tanks.[28-31] Bottled water contains higher levels of Ag, As, B, Co, Li, Mn, Ni and Sr than tap water. Concentrations of B, Co, Li, Mn, Ni and Sr are significantly higher in mineral than in spring water. For Al, Ba, Cr, Mo, Sb, Se, Ti, Tl, U and V, no significant difference between bottled and tap water was observed. Water quality based on the chemical constituents analyzed appears to be satisfactory for tap water as well as for bottled water.

Acknowledgements. – This work was supported by the Ministry of Science, Education and Sports of the Republic of Croatia, under Grant No. 0098132. The authors are grateful to the editor and two anonymous reviewers for their helpful comments.

REFERENCES

1. S. Ćavar, T. Klapec, R. Jurišić Grubešić, and M. Valik, *Sci. Total Environ.* **339** (2005) 227–282.
2. J. A. Plant, *Arsenic and Selenium*, in: H. D. Holland and K. K. Turekian (Eds.) *Environmental Geochemistry*, Treaties in Geochemistry, Vol. 9, Elsevier, 2003.
3. P. L. Smedley and D. G Kinniburgh, *Appl. Geochem.* **17** (2002) 517–568.
4. National Research Council. *Arsenic in Drinking Water.* National Academy Press, Washington DC, 1999.
5. P. L. Smedley and D. G. Kinniburgh, *Source and behavior of arsenic in natural waters*, in: *Arsenic in drinking water,* World Health Organization, 2003.

6. Regulations on mineral, spring and table water (in Croat.), *Narodne Novine*, No. 2, 2005.
7. WHO, *Guidelines for drinking water quality*, 3rd ed., World Health Organization, Geneva, 2004.
8. EPA, *Drinking water standards*, Office of Drinking Water, US Environmental Protection Agency, Washington DC, 2003.
9. S. M. Pier and K. Bang Moon, *Environment and health,* in: N. M. Trieff (Ed.) Ann. Arbor Science, The Butterworth Group, 1980, p. 127.
10. Regulations on primary standards for mineral, spring and table water (in Croat.), *Narodne Novine*, No. 58, 1998.
11. Amendment to the regulations on primary standards for mineral, spring and table water (in Croat.), *Narodne Novine,* No. 17, 1999.
12. Regulations on health safety of drinking water (in Croat.), *Narodne Novine*, No. 182, 2004.
13. D. W. Warburton, *Can. J. Microbiol*. **39** (1993) 158–168.
14. F. Vanhaecke, J. Goossens, R. Dams, and C. Vandecasteele, *Talanta* **40** (1993) 975–979.
15. L. Moens, H. Vanhoe, F. Vanhaecke, J. Goossens, M. Campbell, and R. Dams, *J. Anal. At. Spectrom.* **3** (1994) 187–191.
16. I. Rodushkin and T. Ruth, *J. Anal. At. Spectrom.* **10** (1997) 1181–1185.
17. J. Riondato, F. Vanhaecke, L. Moens, and R. Dams, *J. Anal. At. Spectrom.* **12** (1997) 933–937.
18. U. Giessmann and U. Greb, *Fresenius J. Anal. Chem.* **350** (1994) 186–193.
19. J. Riondato, F. Vanhaecke, L. Moens, and R. Dams, *J. Anal. At. Spectrom.* **15** (2000) 341–345.
20. L. Moens, F. Vanhaecke, J. Riondato, and R. Dams, *J. Anal. At. Spectrom.* **10** (1995) 569–574.
21. L. M. Posnick and H. Kim, *Food Safety Magazine*, Aug./Sep. 2002.
22. D. H. Nies, *Appl. Microbiol. Biotech.* **51** (1999) 730–750.
23. J. F. Ferguson and J. Davis, *Water Res.* **6** (1972) 1259–1274.
24. J. Ryu, S. Guo, R. Dahlgren, and R. A. Zierenberg, *Geochim. Cosmochim. Acta* **66** (2002) 2981–2994.
25. M. Stoeppler, *Arsenic*, in: E. Merian, M. Anke, M. Inhat, and M. Stoeppler (Ed.), *Elements and their Compounds in the Environment, Metals and their compounds,* Vol. 2, 2nd ed., Wiley-VCH, Weinheim, 2003, pp. 1321–1364.
26. M. A. Rish, *Antimony*, in: E. Merian, M. Anke, M. Inhat, M. Stoeppler (Ed.), *Elements and their Compounds in the Environment, Metals and their compounds,* Vol. 2, 2nd ed. Wiley-VCH, Weinheim, 2003, pp. 659–667.
27. W. Shotyk, M. Krachler, and B. Chen. *J. Environ. Monit.* **8** (2006) 288–292.
28. M. A. Saleh, E. Ewane, J. Jones, and B. L. Wilson, *J. Food Compos. Anal.* **14** (2001) 127–152.
29. I. Al-Saleh and I. Al-Doush, *Sci. Total Environ.* **216** (1998) 181–192.
30. M. R. Schock, *J. Am. Water Works Assoc.* **81** (1989) 88.
31. M. R. Schock, *J. Am. Water Works Assoc.* **82** (1990) 59.
32. M. K. Anke, *Molybdenum*, in: E. Merian, M. Anke, M. Inhat, and M. Stoeppler, (Ed.), *Elements and their Compounds in the Environment, Metals and their compounds,* Vol. 2, 2nd ed., Wiley-VCH, Weinheim, 2003., pp. 1007–1037.
33. S. Peganova and K. Eder, *Zinc*, in: E. Merian, M. Anke, M. Inhat, and M. Stoeppler, (Eds.), *Elements and their Compounds in the Environment, Metals and their compounds,* Vol. 2, 2nd ed., Wiley-VCH, Weinheim, 2003, pp. 1203–1240.

SAŽETAK

Određivanje arsena i drugih elemenata u tragovima u konzumnoj vodi iz boce metodom spektrometrije masa visoke razlučivosti s induktivno spregnutom plazmom

Željka Fiket, Vibor Roje, Nevenka Mikac i Goran Kniewald

Određivane su koncentracije arsena i drugih elemenata u tragovima u 18 različitih marki mineralnih i izvorskih konzumnih voda u bocama, u Hrvatskoj. Za usporedbu analizirani su i uzorci vodovodnih voda iz Rijeke, Lourdesa i Zagreba. Analize su provedene na spektrometru masa visoke razlučivosti s induktivno spregnutom plazmom (HR ICP-MS). Dobiveni rezultati uspoređivani su s najvećom dopuštenom količinom za elemente u tragovima u vodi za piće te mineralnim i izvorskim vodama prema hrvatskom, WHO i EPA standardu za vode. Koncentracije svih analiziranih elemenata bile su u svim uzorcima ispod najveće dopuštene količine prema hrvatskim, WHO i EPA standardima.