Determination of trace elements in bottled water in Greece by instrumental and radiochemical neutron activation analyses

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Four different bottled water brands sold in Greece in the winter of 2001–2002 were analyzed for a wide range of chemical elements, using neutron activation analysis (NAA). The elements Na and Br were determined instrumentally (INAA), whereas the other metals and trace elements radiochemically (RNAA). The results indicated that the mean level of all the elements determined in the samples were well within the European Union (EU) directive on drinking water and accomplish the drinking water standards of the World Health Organisation (WHO) as well as of the Food and Drug Administration (FDA).

Introduction

According to the Food and Drug Administration, bottled water can be defined as water that is intended for human consumption and is sealed in bottles or other containers with no added ingredients except that it may contain safe and suitable anti-microbiological agents. Although it seems like a relatively new idea in Europe, born during the heightened awareness of fitness and the potential water pollution of the last two decades, however, water from mineral springs has been bottled and sold far from its source for hundreds of years since it was often thought to have therapeutic and religious effects.

Recently, an increasingly worldwide concern about the quality of bottled water has been risen, which can be also measured by means of its concentration in minerals.[1–4] Minerals are chemical elements required by our bodies for numerous biological and physiological processes that are necessary for the maintenance of health. Actually, they are divided into two categories: those that are required in our diet in amounts greater than 50 mg per day, called "minerals", and those that are required in amounts less than 50 mg per day, which are called "trace elements". Despite the fact that trace elements constitute only a small fraction of the total uptaken food, recent epidemiological studies have indicated a strong association between the occurrence of several diseases in humans and the presence of trace elements considered to be toxic such as As, Cd and Pb as well as excessive or deficient levels of essential micronutrients such as Co, Zn and Se. Hence, the European Union (EU) as well as the World Health Organisation (WHO) have recommended general guidelines for the quality of water used for human consumption.[1]

In this paper, a report on the concentrations of the most common trace elements encountered in bottled water consumed in Greece, is presented. The applied method included evaporation of the water samples to dryness followed by instrumental and radiochemical neutron activation analyses (INAA, RNAA) of the obtained dry residues, considering that radiolysis of the water itself could possibly cause a release of radioactive gas or even an explosion out of the container.[5] The results were compared with the EU directive on drinking water and the international standards for drinking water as well as with the results gained for water of other countries, analyzed by other analytical methods.

Experimental

Four different brands of bottled water were bought from the local market so as to acquire a 10-liter mixture consisting of 2.5 liters of each brand. The water samples (2 l each) were then slowly evaporated till dryness in a water bath (~60 °C). After homogenization, samples of about 200–300 mg of the obtained dry residues, as well as small dry quantities of two standard reference materials (Wheat Flour SRM 1567a and Soil-7, provided by NIST and IAEA, respectively) were sealed in pre-cleaned polyethylene capsules and irradiated for 15 minutes in the research reactor of the Nuclear Research Center "Demokritos" in Athens, using a thermal neutron flux of 10^{13} n·cm^{-2}·s^{-1}. The determination of cobalt and selenium required the irradiation time of 3.5 hours, and the reference material RM IAEA-155 Whey Powder was used instead of Soil-7. The moisture content of the standard materials was determined in samples of approximately 2 to 3 g by drying for 24 hours at 85 °C, according to the procedure required by the supplier. Therefore, all elemental concentrations are reported on a dry-weight basis.

Five days after irradiation, the activated samples and standards were transferred into clean vials and the corresponding gamma-spectrum for each one was

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recorded for 900 seconds, using an HPGe detector, (Canberra, GC2520-7500S), coupled to an 8k multi-channel analyzer and a PC.

As for the gamma-spectra, the prevailing radioisotopes were ^{24}Na and ^{82}Br, and only the elimination of them would in most cases permit the simultaneous determination of many other trace elements by instrumental means. So, all the samples and standards, except Soil-7, were primarily diluted in 6M HNO_3 and transferred in a separator funnel.[5] To that solution 2 ml of 1M HCl and 3 ml of 1M NH_4Br were added, as a carrier. The addition of carriers not only reduces considerably the fraction lost by adsorption, but also causes the trace elements to behave as expected for large concentrations (macro level) and, therefore, maximizes the separation of the interfering elements from the measured ones.[6] A few drops of a saturated $KMnO_4$ solution were then added to the funnel in excess, in order to oxidized the bromine ions to Br_2. After thorough shaking, the liberated bromine was removed by extraction with three portions of 10 ml $CHCl_3$. The brownish-purple aqueous fraction in the funnel was subsequently treated with a few drops of 30% H_2O_2 in order to decolorize the solution which was finally acidified with 4 ml of 1M HCl. The chloroform fraction, containing the liberated bromine, was washed with 4 ml of 1M HCl and the separator funnel was also thoroughly rinsed with conc. HNO_3. The washed liquids were collected together with the main aqueous fraction and condensed to minimum volume.

The effective separation of sodium from the other constituents required the use of hydrated antimony pentoxide (HAP), which was prepared by the hydrolysis of the $SbCl_5$ solution.[7,8] The resultant precipitate was filtered off, washed and dried at 270 °C for 5 hours. Then, it was powdered, sieved, and only the fraction between 100 and 300 µm was finally collected. For chromatography, HAP was initially suspended in 12M HCl and then packed into glass columns of 2 cm length and 0.7 cm diameter, with a fiberglass plug at the bottom. The condensed samples and standards from the treatment described above were eventually eluted at room temperature through the columns, which were subsequently washed with small portions (~15 ml) of 12M HCl. The yellowish effluent fractions were then subjected to gentle heating, which made them lucid, till dryness. Their corresponding gamma-spectra were finally taken for 3600 seconds.

Results and discussion

The accuracy and precision of the procedure have been evaluated by analyzing the standard reference materials used throughout this work. The precision is expressed in terms of the coefficient of variation, defined as $100s/X$, where s stands for the standard deviation and X is the arithmetic mean concentration. The accuracy can be determined by the relative percentage difference of the estimated mean concentration X, from the certified value.

In Tables 1 and 2 the elemental content of the used reference materials expressed as ($X \pm s$) are displayed, while (N) represents the number of independent determinations contributing to the mean value. As it can be seen, the majority of the elements, with the exception of sodium, were analyzed with a satisfactory precision and accuracy better than 90%.

In Table 3 the mean concentration levels of the elements determined in the analyzed samples are shown. A similar analytical technique differing on the irradiation (3.5 hours) and measuring (21,600 seconds) time was used for the determination of cobalt and selenium. Also, in that case the RM IAEA-155 Whey Powder reference material was used instead of Soil-7. Apart from the mentioned elements, a fairly large number of other elements (such as Sr, Cd, Au, Ag, etc.) were also detected in our samples, but since they did not exist in the selected reference materials, their concentration could not be measured.

Table 1. Elemental concentration of the reference material Wheat Flour when Soil-7 is used as a standard

| Element | Wheat Flour (SRM 1567/NIST) | | | | |
| | Present work | | | Certified or reported value, µg/g | Relative error, % |
	$X \pm s$, µg/g	N	Coefficient of variation		
Br					
554.30 keV	6 ± 1	2	17	6	0
776.50 keV	5.0 ± 0.8	3	16	6	2·10
K	1.24 ± 0.03[a]	3	2	1.33[a]	6.8
Zn	14 ± 6	2	43	11.6	19
Na	14 ± 1	3	7	6.1	1.3·10^2

[a] mg/g.

*Table 2*. Elemental concentration of the reference material Soil-7 when Wheat Flour is used as a standard

Element	Soil-7 (SRM Soil-7/IAEA)				
	Present work			Certified or reported value, µg/g	Relative error, %
	$X \pm s$, µg/g	N	Coefficient of variation		
Br					
554.30 keV	7 ± 1	2	14	7	0
776.50 keV	8 ± 1	3	12	7	1·10
K	13.0 ± 0.2[a]	3	1.5	12.1[a]	7.4
Zn	(9.8 ± 4.0)·10	2	40	104	6
Na	1.1 ± 0.1[a]	3	9	2.4	54

[a] mg/g.

Table 3. Elemental concentration of the bottled water, expressed in terms of mean value of concentration (X) ± standard deviation (s), where N stands for the number of independent determinations contributing to the mean value

Element	$X \pm s$, µg/l	N	Ccoefficient of variation, $s/X \times 100$, %	Range, µg/l, $X_{max} - X_{min}$
U	0.22 ± 0.08	8	36	0.38–0.10
Ba	(4.4 ± 2)·10	7	46	81.0–19.3
La	0.02 ± 0.01	7	53	0.043–0.001
Sb	0.02 ± 0.02	6	100	0.055–0.005
Ca	21.5 ± 5[a]	8	23	27.3–14.5[a]
Cr	2.6 ± 0.9	8	35	3.6–1.6
Zn	5.7 ± 1	4	18	6.7–4.2
K	0.33 ± 0.09[a]	8	28	0.46–0.17[a]
As	0.03 ± 0.02	2	79	0.04–0.01
Br	(1.0 ± 0.5)·10	9	50	(2–1)·10
Se	0.10 ± 0.04	6	40	0.16–0.06
Co	(9 ± 2)·10^{-3}	6	22	(12–6)·10^{-3}

[a] mg/l.

As far as toxicity is concerned, the concentrations of elements considered being toxic such as arsenic (0.0253±0.02 µg/l), were found here being below the current standards for drinking water (0.05 mg/l).[1] The short half-life ($T_{1/2} = 1.097$ d) of radioarsenic, combined to the extended period between irradiation and measuring, are responsible for the failure of detecting arsenic in a large number of samples in order to achieve better precision. Also, it has been remarked that added selenium into the diet can counteract the effects of excess arsenic, as the two elements are combined.[9,10] With reference to the way of entering the aquifer, it has been suggested that large-scale withdrawal of groundwater for irrigation causes seasonal fluctuation of the water table, which in turn results the intake of oxygen into the pore waters of sediments that are arsenic-rich in the form of arsenopyrite. Oxidation of arsenopyrite (FeAsS), in analogous fashion to pyrite (FeS$_2$), may release high concentrations of arsenic into the solution:[11]

$$4FeAsS_{(S)} + 13O_{2(g)} + 6H_2O \rightleftarrows$$
$$\rightleftarrows 4Fe^{2+} + 4AsO_4^{3-} + 4SO_4^{2-} + 12H^+$$
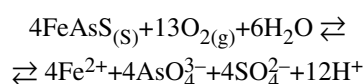
Trivalent inorganic arsenic, with its propensity for binding to the SH group of enzymes, is acknowledged to be more toxic to humans than the pentavalent.

Although some trace elements, such as chromium, cobalt and selenium are considered to be essential for human beings, their accumulation is definitely harmful. In the analyzed bottled water, the chromium concentration (2.6±0.9 µg/l) is reckoned inadequate to cover the daily needs of an adult, who requires approximately 50–200 µg.[12a] Trivalent chromium deficiency is characterized by disturbances in glucose, lipid and protein metabolism, whereas the hexavalent is placed among the toxic metals. The biologic activity of trivalent chromium is mainly focused on the regulation of glucose metabolism as a part of the glucose tolerance factor that enhances insulin activity.[13,14]

Considering that cobalt present in the diet is absorbed to the extent of 70–80%, its concentration in bottled water (0.009±0.002 µg/l) is not enough to cover the daily human needs.[12b] Cobalt is an essential micronutrient that enters the body in vitamin B$_{12}$ and subsequently participates in the formation of red blood cells and DNA.[15] No information is available on the maximum allowable level of cobalt in water since it is not a cumulative toxic.

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Table 4. Mean concentration levels ($X \pm s$) of the elements determined at the present study in bottled water in comparison with their concentration in water of other countries determined by (I): instrumental neutron activation analysis, (II): inductively coupled mass spectrometry and (III): coprecipitation with PbS, followed by neutron activation analysis, as well as the guidelines for drinking water according to the WHO, the EU and the FDA

Element	$X \pm s$, μg/l Present study	$X \pm s$, μg/l (I)*	$X \pm s$, μg/l (II)**	$X \pm s$, μg/l (III)***	EU, mg/l	WHO, mg/l	FDA, mg/l
Ba	$(4.4 \pm 2) \cdot 10$			0.5 ± 0.1	1		2
La	0.02 ± 0.01			0.04 ± 0.01			
Sb	0.02 ± 0.02	0.006		0.05 ± 0.01	0.005	0.005	0.006
Ca	$(21.5 \pm 5) \cdot 10^3$				250		
Cr	2.6 ± 0.9	0.7	1.35		0.05	0.05	0.1
Zn	5.7 ± 1	29	7	3	5		5
K	$(0.33 \pm 0.09) \cdot 10^3$			59 ± 5	12		
As	0.03 ± 0.02				0.05	0.01	0.05
Br	$(1.0 \pm 0.4) \cdot 10$			0.25 ± 0.04			
Se	0.10 ± 0.04		3.45		0.01	0.01	0.05
Co	$(9 \pm 2) \cdot 10^{-3}$	0.07	0.52	0.14 ± 0.03			

* Ref. 19.
** Ref. 20.
*** Ref. 6.

The recommended daily consumption of selenium for an adult is 55 μg, whereas its concentration in the analyzed water was estimated to be 0.10±0.04 μg/l. It has been proven that selenium is an antioxidant that neutralizes free radicals as a part of some enzymes (e.g., glutathione peroxidase) or by working in conjunction with vitamin E. So, it protects people from some kinds of cancer and heart diseases.[16–18]

In Table 4 the mean concentration levels of the determined elements, are compared with the corresponding ones of the EU, the WHO, and the FDA and in the water from other countries, which were determined by other analytical methods like: (I) instrumental neutron activation analysis of the dry residue resulting from the evaporation of drinking water,[19] (II) inductively coupled mass spectrometry applied for bottled water samples[20] and (III) coprecipitation of the metals contained in mineral water with PbS, followed by neutron activation analysis of the precipitate.[5]

Conclusions

In bottled water consumed in Greece, twelve elements were determined by instrumental and radiochemical neutron activation analyses qualitatively. Except Ca and K, which were present in relatively high concentrations (mg/l), all other elements were found to be as parts per billion or lower.

All metal concentrations were found to be within the European Union directive[1] and the World Health Organization and the Food and Drug Administration guideline limits, as well as they were consistent with the elemental composition of drinking water determined by other analytical procedures.

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