



Comparison of Cesium and silver levels in the water at the inlet to the bottled water factories and water treatment plant No. 2 in Ahvaz City and outlet water of them after the water treatment process

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Abstract

Water quality is an important issue for human health management. The aim of this study was to compare Cesium (Cs) and silver (Ag) levels in the water at the inlet and outlet to the bottled water factories and Ahvaz water treatment plant NO.2 (AWTPNO.2) by Furnace Graphite Atomic Absorption Spectrometry (FGAAS). According to the results the average Cs concentration in inlet & outlet WTPNO.2, inlet & outlet water of Byblos and Anahita factories was (0.176, 0.130), (0.214 0.210), and (0.325, 0.298) µg/l respectively. The average of Ag concentration in inlet & outlet AWTPNO.2, inlet & outlet waters of Byblos and Anahita factories had measured (1.08, 0.53), (0.457, 0.132) and (0.357, 0.288) µg/l, respectively. The purification process effectively reduces the amount of silver in the Byblus water bottle and the cesium content in the AWTPNO.2.

Keywords: Cesium, silver, Treated water, Bottled water, FGAAS

1. Introduction

The accessibility of sufficient quantities of clean water is becoming one of the major public health complications worldwide. As pointed out in the seventh UN Millennium Goal(1). Organic and inorganic contaminants in water make waters non-potable and endanger human health.(2-5). Over 1 billion people worldwide have no access to harmless drinking water(6). The first time bottle water was introduced as a placement for tap water in France by Evian in 1829. Assuming that bottled water

is safer than tap water to drink and has better taste(6-9).Although scientific studies have shown that this is not essentially true (10, 11).In addition, the sale and consumption of bottled water can have environmental and social impacts (12-14). Figure 1; Shows the *per capita* yearly intake of bottled water. Mexico is the country with the highest *per capita* consumption(7).

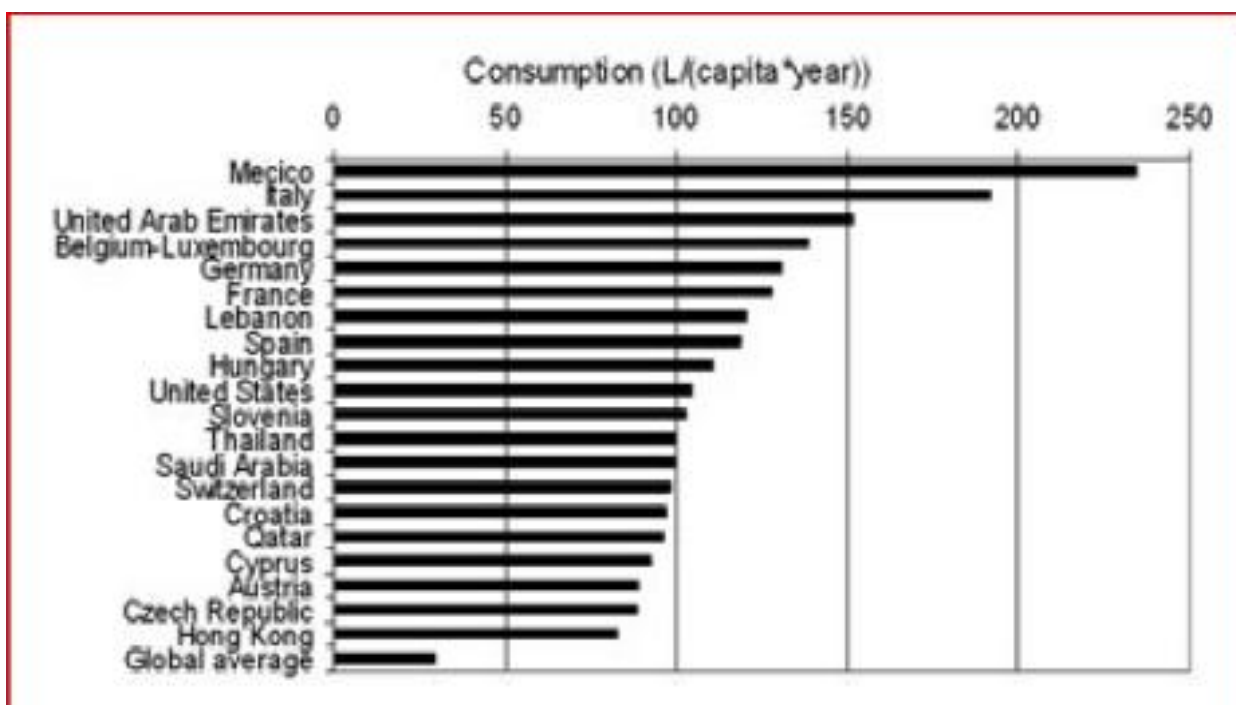


Figure 1–Per capita consumption of bottled water by countries with highest bottle water consumption and World average.

Different studies on drinking water quality have been conducted worldwide. In most studies, attention has been focused on exposure to heavy metals. There are many other metals such as silver and cesium that are used in electronics, defense, industries and medical practices which are emitted in the environment and finally to water. Silver is a relatively abundant metal and its estimated average concentration in the earth crust is about 0.044ng/m^3 (15). Silver is used both in its metallic form and for surgical prosthesis and splints, fungicides, and coinage, such as ions form have been used in treating mental illness, epilepsy, nicotine addiction, gastroenteritis, and infectious diseases (16, 17).

silver nano- particles have potential antimicrobial activity, but have the potential to cause adverse effects on the human body(18). The interaction of silver with essential nutrients, especially selenium, copper, vitamins E and B12 was recorded (19). The chronic exposure to silver causes adverse effects such as permanent bluish- grey discoloration of the skin (argyria) and eye (aryrosis) (20).

Exposure to great levels of silver and silver compounds could result in respiratory problems, skin

problems and stomach aches (21). The other element in water is Cesium. It is the 40th most abundant among the elements, it is widely dispersed in the earth's crust at very low concentrations (22). Tanco in southeastern Manitoba, Canada, is the world's largest cesium source containing nearly two-thirds of the known ore (23). After the Chernobyl nuclear accident, cesium has been recommended as a preventive therapy for radiation harming by the isotope ^{137}Cs (24). Radioactive cesium emits a β particle and is used to treat some cancers. Metallic cesium form is used in a variety of products for example, Atomic Clocks, carbon dioxide purification; and ion cesium form is used in Biotechnology and Medicine for example, purification of nucleic acids, i.e., RNA and DNA viruses (22).Cesium chloride for cancer treatment has never been approved by the US Food and Drug Administration (FDA). It may cause serious cardiac arrhythmias, prolonged QTC interval (24), hypokalemia (25) and accumulation in brain (26), and has impact on Thyroid Function(27).Silver and Cesium determination in water is performed by different methods. The present study measured the level of Cesium and Silver in drinking water by FGAAS which is a micro-amount sample analysis method with high sensitivity.

2. Experimental

2.1. Apparatus

A Model Varian AA-240-FS Atomic Absorption Spectrometer (made in Australia) equipped with a GTA120 graphite furnace atomizer, a PDS120 Programmable sample Dispenser and a circulating cooling unit were used for the determination of silver and cesium in water. Deuterium lamp background correction was employed to correct the non-specific absorbance for silver. The hollow cathode lamps of silver and cesium (Varian Australia) were used as the

radiation sources. The operating condition; for silver and cesium hollow cathode lamp were those recommended by the manufacture. Argon 99.999% (M.Y.Co., Ahvaz, Iran), with 3 L/min flow rate, was used as a protective and purge gas. For determination of cesium and silver; auto sampler took 20 μ l and 19 of all samples and calibration solutions and injected directly into the graphite tube respectively. The information recorded by software Spectra AA. The detailed graphite furnace temperature program used for the determination of Ag and Cs are shown in table1. All measurements were produced in the integrated absorbance (peak area) mode.

Table 1: preparing working standard solution of Cesium from its bulk standard solution at concentration (24 μ g/L)

Cs Standards Concentration(ppb)	Make up Volume(μ L)	Bulk Volume(μ L)	Total volume(μ L)
4	19	1	20
8	18	2	20
16	16	4	20
32	12	8	20
64	4	16	20
80	0	20	20

Table 2: preparing working standard solution of Ag from its bulk standard solution at concentration (64 μ g/L)

Silver Standards Concentration(ppb)	Make up Volume(μ L)	Bulk Volume(μ L)	Total volume (μ L)
6	11	3	14
8	10	4	14
10	9	5	14
20	4	10	14
24	2	12	14
28	0	14	14

Table 3: Instrumental parameters for Ag and Cs determination in water samples by FGAAS

Parameter	silver	cesium
Lamp current/mA	4.0	7.0
Wavelength/nm	328.1	582.1
Slit width/nm	0.5	1.0
Sample volume/ μ l	19	20
Background correction	Deuterium	BC off

All measurements were performed using the optimized temperature program listed in Table 2.

Table 4: Temperature program of atomizer for silver and cesium analysis

Step No	Silver							Cesium					
	T (°C)	hold Time (sec)	Gas flow (L/Min)	Gas flow (L/Min)	Read	Signal storage	Temp (°C)	hold Time (sec)	Gas flow (L/Min)	Gas flow (L/Min)	Read	Signal storage	
Drying	1	85	5	3	Normal	No	No	85	5	3	Normal	No	No
	2	95	40	3	Normal	No	No	95	40	3	Normal	No	No
	3	120	10	3	Normal	No	No	120	10	3	Normal	No	No
Pyrolysis	4	500	5	3	Normal	No	No	500	5	3	Normal	No	No
	5	500	1	3	Normal	No	No	600	1	3	Normal	No	No
	6	500	2	0	Normal	No	yes	600	2	0	Normal	No	yes
Atomization	7	2000	0.8	0	Normal	Yes	Yes	2200	0.9	0	Normal	Yes	Yes
	8	2000	2	0	Normal	Yes	Yes	2200	2	0	Normal	Yes	Yes
Cleaning	9	2100	2	3	Normal	No	Yes	2300	2	3	Normal	No	Yes

2.2. Reagents and solutions

All chemicals used were of analytical-reagent grade and all solutions were prepared with deionized water (obtained from the college of Pharmacy, Jundishapur University of Medical Sciences, Ahvaz, Iran). A stock standard solution of cesium (1000 mg/L) was prepared by dissolving 10 mg of cesium nitrate 99.8% (Alfa-Aesar, U.S.A Co) was dissolved in nitric acid 0.1 M in a 10 ml volumetric flask. The working standard solution (24µg/L) as bulk solution was prepared daily by serially dilution of the stock standard solution with nitric acid 0.1 M.

Stock standard solution of silver (1000 µg/L) was obtained from Chem-lab made in Belgium and stored in the dark.

Working standard solution (64 µg/L) as bulk solution was obtained by appropriate dilution of the stock standard solution. Pipettes and vessels in the experiments were kept in 1mol nitric acid for at least 24 h and subsequently washed twice with double distilled water and then with de-ionized water.

The $\text{Pd}(\text{NO}_3)_2$ 0.1% (w/v) as chemical modifier for silver analysis; was prepared by dissolving 0.01g of (Fluka U.S.A) in nitric acid 0.1 M in a 10 ml volumetric flask. Ascorbic acid as another modifier was prepared by dissolving 0.1g of ascorbic acid 99.5% (Samchun , korea) in nitric acid 0.1 M and diluted to 10 ml in a 10ml volumetric flask. Of the both chemical modifier, was used 2.5 micro liters of total volume (19µl)

2.3. Sampling

Sampling is one of the most important stages of the study. By using Gpower_{3,1} software, the number of samples required for each of inlet and outlet from AWTPNO.2, Byblus and Anahita factories was determined 42 (totally 252 water samples). Samples

were taken 7 times, each time; 6, one-liter samples were collected. The samples were then mixed and one liter composite sample was isolated and transported to laboratory. The collected water samples were filtered by passing through filter papers (0.45µm). To protect and stabilize collected water samples, pH of them were adjusted at 2 by concentrated HNO₃ and were kept at 4 °C before until analysis. 100 ml of each of collected water sample was heated on heater to 5 ml water; therefore the amount of metals in water became 20 times condensed.

To protect and stabilize collected water samples, pH of them were adjusted at 2 by HNO₃ concentrated and were kept at 4 °C before until analysis. The volume of 100 ml of each of water samples was evaporated on heater until reached to 5 ml water; therefore the amount of metals in water samples became 20 times concentrated.

2.4 Procedure

For drawing the calibration curve for Ag and Cs, bulk solutions were pre sequentially with concentrations 24 and 64 µg/L auto-sampler provided for Ag standard solutions 6.8.10.20.24.28 and Cs standard solution 4.8.16.32.64.80 automatically were injected into atomizer and peak absorbance was recorded. The measurement was repeated three times and the obtained signals were averaged. The ranges of linearity for silver and cesium were 0-3 and 0-80 µg/L with correlation coefficient R =1 for both silver and cesium using this method, the lowest limit of detection for our analysis were determined to be for Ag 1.8 and for Cs 1.2 parts per billion (ppb) for measurements water sample search 42 water sample was transferred into the auto-sampler cup. Volume of 20 µl for cesium and 19 µl for silver to auto-sampler were injected into the atomizer, then the information recorded by software spectra AA.

2.5 Statistical Analysis

Statistical analyses were performed using spss₂₀. The distribution of silver concentration in investigated water samples was not normal (p-value = 0.01), according to One-Sample Kolmogorov Smirnov test; so in order to compare the mean concentration of silver in the studied water samples Kruskal-Wallis test was used. One-Sample Kolmogorov Smirnov test showed that Concentration of cesium in water samples had normal distribution (p-value = 0.695) therefore for comparing the cesium mean concentration between investigated water samples; One-way analysis of Variance

(ANOVA) was used. All results were significant at the $p < 0.05$.

Results

The GFAAS method for Ag and Cs measurement was patterned by recovery test and the achieved results are summarized in Table 2. Descriptive statistics, found concentrations of the measured silver and cesium in 42 samples from inlet and outlet AWTPO.2, Byblos factory and Anahita factory are presented in table3 For silver And table4 for cesium.

Table 5: The repeatability of measurements, expressed with the relative standard deviation (RSD) (n= 5)

Cs Std. Con.(ppb)	Mean	SD	RSD%	Ag Std. Con.(ppb)	Mean	SD	RSD%
4	0.494	0.000	0.000	6	0.0091	0.0000	0.000
8	0.09	0.0009	2.9	8	0.0119	0.003	6.4
16	0.2265	0.0001	0.2	10	0.015	0.0000	1.4
32	0.5477	0.0018	0.9	20	0.0316	0.0006	4.3
64	0.9106	0.000	0.000	24	0.0375	0.009	57
80	1.0488	0.0239	5.2	28	0.04	0.008	4.4

Table 6: Descriptive statistic of Ag and Cs concentrations in investigated water samples and comparison their mean with limit set by EPA (U.S) and ADWG (100µg/l for Ag) and by ADSTR2004(1µg/l for Cs)

Type water	Silver					Cesium				
	Min.	Max.	Mean	SD	Sig*.(2-tailed)	Min.	Max.	Mean	SD	Sig.**(2-tailed)
Inlet of AWTPO.2	.134	2.56	1.08	1.094	0.000	ND	0.46	0.17	0.173	0.000
Outlet of AWTPO.2	.04	1.64	.53	0.577	0.000	ND	0.26	0.13	0.101	0.000
Inlet to byblos factory	ND	.866	.457	0.352	0.000	ND	0.431	0.214	0.173	0.000
Outlet from Byblos factory	.035	.256	.132	0.068	0.000	0.027	0.417	0.210	0.131	0.000
Inlet to Anahita	ND	1.35	.35	0.467	0.000	0.004	0.551	0/32	0.207	0.000
Outlet from Anahita	ND	.969	.288	0.391	0.000	0.007	0.66	0.298	0.247	0.000

*Comparison their mean with limit set by EPA (U.S) and ADWG (100µg/L Ag)

**Comparison their mean with limit set by ADSTR 2004(1µg/L for Cs)

Discussion

Results showed that the maximum mean concentration of Ag belonged to inlet of AWTPO.2 (1.08 µg/L) and the highest mean concentration of Cs belonged to inlet waters of Anahita factory (0.325 µg/L). The lowest mean concentration of Ag was seen in outlet waters of Byblos is 0.132 µg/L and the lowest mean concentration of Cs was seen in outlet water samples of water treatment plants NO.2 is 0.130 µg/L.

The concentration of cesium and silver in 42 water samples range was <LOD-0.66µg/L, <LOD-1.64 µg/L,

respectively. The comparison of the mean concentrations of Ag in water samples that were examined and those established by EPA.U.S Limit and there was no significant difference ($p > 0.05$). Concentrations of cesium in water samples in this study were below the typical concentrations in drinking water (1µg/L) established by the ATSDR 2004a.cesium and silver in this study 7%and 14%were below the limit of detection, respectively.

According to ANOVA test, there was no significant difference between mean concentration of cesium in studied waters ($p = 0.37$).

The results of Kruskal-Wallis test showed that there was no significant difference between the mean concentration of silver in the studied waters ($p = 0.241$).

Median silver and cesium concentrations were higher in the present study than 172 samples of drinking waters, a range of location in western Australian (median <0.005 range $<0.005-7.43$ $\mu\text{g/l}$), (median 0.074 range $<0.01-0.94$), respectively. The highest concentration of silver in drinking waters, a range of locations in western Australian (7.33 $\mu\text{g/L}$) was higher of highest amount of silver measured in the present study (2.68 $\mu\text{g} / \text{L}$) which belonged to Inlet waters to AWTPNO.2. The highest concentration of cesium in drinking waters, a range of location in Western Australia (0.94 $\mu\text{g/L}$) was higher than the highest amount of cesium measured in the recent study (0.66 $\mu\text{g/L}$) that Belonged to outlet waters of the Anahita. factory(28).

There are limited studies available, the concentration of stable cesium in both seawater and drinking water appears to be below 1 $\mu\text{g/L}$ in general, while the total dietary intake usually is below 30 $\mu\text{g/day}$ (29).

Gabriela concha et al analyzed 31 different elements in drinking water collected in San Antonio de los Cobres and five surrounding Andean villages in Argentina, and in urine of the inhabitants, using ICP-MS. elevated cesium concentration(320 $\mu\text{g/L}$) in the drinking water. There was higher of maximum amount of cesium measured in the present study (0.66 $\mu\text{g/L}$).

The concentration of silver in all water samples that were investigated by Gabriela concha et al was less than their detection method (0.01 $\mu\text{g/L}$), but in the present study, only 14% of the samples were less than the detection method(30).

Sandarin millour et al. of the 1319 food samples analyzed, only 18% of Ag values were quantified, with 82% found to be below the LOQ (0.084 mg/kg) and 53% below the LOD (0.042 mg/kg_1). The silver maximum mean levels were found in "Fish and fish products" (2.37 mg/kg_1 , $n = 83$) followed by "Ice cream" (0.193 mg/kg_1 , $n = 2$), "Meats and offal" (0.119 mg/kg_1 , $n = 213$) and "Sweeteners, honey and confectionery" (0.105 mg/kg) (31). According to the results of the present study; the content of silver in 86% of investigated water samples was higher than the detection method (1.8 $\mu\text{g/L}$).

Peters et al reported a mean dissolved silver concentration in fresh water to be 6.1 ng/L and the maximum 19.8 ng/L (32). The mean concentration of silver in water of Karun River was 1.08 $\mu\text{g/L}$ and maximum concentration of silver was reported 2.56 $\mu\text{g/L}$.

Conclusions

According to the findings of this study, Ahvaz treatment plant No. 2 has been more effective in reducing the amount of cesium and Byblos factory to reduce the amount of silver in water, and the level of silver and cesium in drinking water In all water samples, there was less than the admissible Limit set by U.S EPA and ADSRT. The bottled waters were produced by the Anahita and Byblos factory is not superior to the level of silver and cesium compared to the tap waters in Ahvaz city.

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Conflict of interest:

The authors declare that there are no conflict of interest.

Compliance with Ethics Requirements:

This article does not contain any studies with human or animal subjects.

Conclusion:


The bottled water produced by the Anahita and Byblos factory was not superior to the amount of silver and cesium compared to the tap waters in Ahvaz city.

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