Original Research

Evaluation of Metal Levels of Drinking Waters from the Tokat-Black Sea Region of Turkey

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Abstract

The concentrations of chromium, nickel, copper, manganese, zinc, iron, cobalt and aluminum ions in drinking waters from eight sites of Tokat, Turkey, were determined by atomic absorption spectrometry. The values found the present work for the heavy metal contents of the drinking water samples of Tokat, Turkey were below the maximum tolerable limits set by the World Health Organisation (WHO) and the Water Pollution Control Regulation of the Turkish authorities.

Keywords: drinking water, atomic absorption spectrometry, heavy metals, preconcentration, pollution, Tokat, Turkey

Introduction

Because of the importance of the heavy metal ions on human metabolism, trace heavy metal analysis is an important part of public health studies [1-5]. Some transition metals at trace levels in our metabolism are important for good health. Heavy metals normally occurring in nature are not harmful to our environment, because they are only present in very small amounts. However, if the levels of these metals are higher than the levels of healthy life, the roles of these metals change to a negative dimension. The main sources of the heavy metal ions directly are food and water and, indirectly, industrial activities and traffic [6-8]. Drinking water is also an important source for heavy metals for humans. The levels of heavy metal ions in drinking water are generally at µg/l. For precise and accurate analysis of heavy metal ions in drinking water it is possible to use neutron activation analysis (NAA), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), x-ray fluorescence spectrometry, and graphite furnace atomic absorption spectrometry (GFAAS). However, these techniques are expensive and difficult to use.

The Separation/Preconcentration-Flame atomic absorption spectrometry (FAAS) combination is an important alternative for these techniques due to cheap cost and easy usage of FAAS. Concern has increased over the concentration of trace metal ions in drinking water. Organizations like the World Health Organization and the European Committee recommend limits for drinking water that require much greater sensitivity in measurement than is obtainable by flame atomic absorption spectrometry. Preconcentration-separation techniques like coprecipitation, liquid-liquid extraction, cloud point extraction and ion exchange are used prior to flame atomic absorption spectrometric determination of heavy metals in drinking waters [9-13]. Solid phase extraction based on adsorption of the traces metal ions on a suitable adsorbent including activated carbon, Amberlite XAD resins, Ambersorb resins, Chromosorb resins and other polymeric materials is one of the preconcentration technique for drinking waters [14-18]. Tokat is a developing industrial-agricultural city in central Anatolia. Tokat has a population of 114,000 and is known for some industrial plants including textile, nutrition and sugar.

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The object of the research reported is to determine the trace heavy metal concentrations of drinking water samples from eight stations in Tokat, Turkey, after separation-preconcentration procedure by solid phase extraction based on adsorption. The correlations of between metal concentrations of the investigated drinking water samples were also calculated.

Experimental

Instrument

A Perkin Elmer AAnalyst 700 atomic absorption spectrometer with deuterium background corrector was used in this study. A 10 cm long slot-burner head, a lamp and an air-acetylene flame were used. The operating conditions were as recommended by the instrument manufacturer. The atomic absorption signal was measured as a peak height mode against an analytical curve. A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase. A glass column 100 mm high and 10 mm in diameter was used in solid phase extraction studies.

Chemicals

All the chemicals used in the present work were of analytical grade and used as such from freshly opened bottles. No attempt was made to purify them further. Solid phase materials (Amberlite XAD-1180, Amberlite XAD-4 and Diaion HP-2MG) were purchased from Sigma Chem. Co., St. Louis, and were prepared with the washing steps as reported previously in literature [19-21].

Sampling

The drinking water samples were collected in prewashed (with detergent, doubly de-ionized distilled water, diluted HNO_3 and doubly de-ionized distilled water, respectively) polyethylene bottles from eight stations in Tokat and villages around Tokat in July 2004. The samples were obtained directly from the water pump after allowing the water to run for at least twenty min. The samples were filtered through a Millipore cellulose membrane with a 0.45 µm pore diameters. Then the samples were acidified to 1% with nitric acid and were stored in 1 L polyethylene bottles. The samples were subsequently stored at 4°C for as short a time as possible before analysis to minimize changes of the physicochemical form of the metals [22, 23].

Procedure

For preconcentration-separation of investigated heavy metal ions in the drinking water samples from Tokat, 500 mL acidified water sample was neutralized and adjusted to related pH. Then the solid phase extraction procedures given in literature [19-21] were applied to the samples. Then the analyte ions were determined by atomic absorption spectrometry.

Results and Discussion

The levels of chromium, nickel, copper, manganese, zinc, iron, cobalt and aluminum in drinking water samples from Tokat were determined by atomic absorption spectrometry. The results are given in Table 1 for chromium, nickel, copper and manganese, and in Table 2 for zinc, iron, cobalt and aluminum.

Chromium concentrations in natural water, including drinking water, are usually very small. Chromium in water supplies is generally found in the hexavelant form. The chromium range was 3.14-6.08 µg/l. The lowest level of chromium was in Resadiye Station. The highest level of chromium was found in the sample from Yesilyurt Station. The mean of Cr levels was 4.40 µg/l. Maximum ac-

Table 1. Cr, Ni, Cu and Mn levels of drinking water samples from Tokat.

Station	Concentration (µg/l)			
	Cr	Ni	Cu	Mn
Tokat	4.18±0.35	2.16±0.19	4.84±0.25	2.64±0.16
Turhal	5.24±0.41	5.35±0.28	6.32±0.36	3.14±0.19
Erbaa	3.29±0.25	4.63±0.19	7.43±0.51	4.53±0.36
Zile	4.29±0.40	3.32±0.18	6.02±0.30	3.78±0.10
Niksar	5.54±0.21	4.15±0.26	7.37±0.26	5.15±0.49
Yesilyurt	6.08±0.32	3.10±0.15	5.82±0.35	4.62±0.15
Almus	3.28±0.25	3.46±0.29	5.83±0.45	3.60±0.24
Resadiye	3.14±0.20	4.36±0.33	4.44±0.40	4.34±0.36

ceptable concentration of total chromium in drinking water was 50 µg/l [24].

International regulations on water quality are lowering the maximum permissible levels of potentially toxic metals in humans. The guideline value of Ni in drinking water is 20 µg/l [24]. Nickel concentration of drinking water samples from San Luis, Argentina [25], and Xian, China [26], were 3.89 µg/l and 0.74 µg/l, respectively. The mean level of nickel in the samples from Tokat was 3.82 µg/l. Nickel values of four samples were higher than the mean value. The highest nickel level was found in the drinking water sample from Turhal (5.35±0.28 µg/l) and the lowest in the city center of Tokat (2.16±0.19 µg/l) (Table 1). This point agrees with the values of drinking water samples from various cities around the world [27-29].

Copper in the samples was in the range of 4.44-7.43 µg/l. The lowest and highest values were in Resadiye and Erbaa, respectively, but even in Erbaa, Cu was considerably below the limit of 1.0 mg/l permitted by WHO in drinking waters [23]. Mean level of copper concentration was 6.01 µg/l. Consequently, no contamination due to copper exists in the investigated drinking water samples from Tokat. It is reported that copper concentrations of drinking water samples from Northern Mexico as 0.1-319 µg/l [30]. Manzoori and Bavili-Tabrizi [31] have reported that copper concentration in water from Tabriz City, Iran, as 32 µg/l.

The highest manganese level was found in Niksar station, 5.15±0.49 µg/l, and the lowest in Tokat city center station, 2.64±0.16 µg/l. Average manganese level of the samples was 3.98 µg/l. WHO has recommended a guideline value of 0.1 mg/l of manganese in drinking water [24]. None of the drinking water samples analyzed for manganese exceeded the limit permitted by WHO, which agrees with results obtained by other authors in other countries [32, 33].

The main industrial uses of zinc are galvanization and preparation of alloys. The main source of zinc in natural waters including drinking waters may be galva-

nized pipes. The guideline value for zinc in drinking-water is given as 5.0 mg/l by WHO [23]. Zinc concentration ranges from 4.16 to 8.44 µg/l (lowest in Almus, highest in Niksar). The mean level of zinc is 6.12 µg/l. While zinc levels in drinking water from Xian, China have been reported as 21.84 µg/l [26], zinc concentration of drinking water sample from Tehran, Iran, was found by Yamini et al. [16] to be 220 µg/l.

Iron in drinking water is present as Fe^{2+}, Fe^{3+} in suspended form [34]. While the lowest iron level was in the Niksar water sample as 14.5±0.1, the highest iron concentration was in Resadiye water samples as 34.6±0.3 µg/l. WHO has proposed a guideline value of 0.3 mg/l for drinking-water [23]. The average values of iron in all samples are below the maximum allowable concentration.

Cobalt concentration was found to be below the detection limit of the method in only one sample (Erbaa Station). The highest level of cobalt was in the sample from Niksar (2.45±0.09 µg/l) and the lowest level of Co was Tokat city center (1.07±0.06 µg/l). However, even in Niksar Station, Co was below 10 µg/l, the limit permitted by WHO [23]. Cobalt levels of drinking water samples from Xian, China [26], and Kayseri, Turkey [29], were 0.32 µg/l and 6.4 µg/l, respectively.

Aluminum is among the most abundant elements in the earth's crust, it is present only in trace concentrations in natural waters. A mean aluminum level of drinking water of Tokat is 6.38 µg/l. The highest level of Al was in a sample from Almus station (8.54±0.30 µg/l) and the lowest level of aluminum was Turhal station (4.26±0.36 µg/l). The maximum permissible content of Al in drinking water is 0.2 mg/l [35]. In drinking water samples collected from the water supplies at different locations in Granada, Spain, aluminum levels ranged from 4.2 to 134.1 µg/l [36].

Lead and cadmium contents of all the water samples investigated from Tokat city were below 5 µg/l and 2 µg/l, respectively. These levels of lead and cadmium were below the limit of WHO [23, 37].

Table 2. Zn, Fe, Co and Al levels of drinking water samples from Tokat.

Station	Concentration (µg/l)			
	Zn	Fe	Co	Al
Tokat	6.12±0.24	29.6±0.2	1.07±0.06	7.50±0.50
Turhal	4.64±0.37	16.2±0.1	1.25±0.07	4.26±0.36
Erbaa	5.42±0.22	32.1±0.3	< 1	5.20±0.42
Zile	7.60±0.17	26.3±0.1	1.22±0.08	6.21±0.30
Niksar	8.44±0.77	14.5±0.1	2.45±0.09	8.25±0.66
Yesilyurt	6.52±0.54	17.6±0.2	1.67±0.10	5.54±0.52
Almus	4.16±0.27	25.1±0.2	1.69±0.08	8.54±0.30
Resadiye	6.02±0.56	34.6±0.3	2.17±0.16	5.50±0.32

Table 3. Correlations between metal concentrations.

	Cr	Ni	Cu	Mn	Zn	Fe	Co	Al
Cr	1.000							
Ni	-0.038	1.000						
Cu	0.280	0.452	1.000					
Mn	0.208	0.296	0.493	1.000				
Zn	0.443	-0.243	0.203	0.507	1.000			
Fe	-0.881	-0.168	-0.460	-0.196	-0.243	1.000		
Co	0.025	0.340	0.270	0.861	0.362	-0.142	1.000	
Al	-0.105	-0.551	0.004	0.020	0.230	-0.078	0.281	1.000

Relationships between Concentrations of Metal Ions

A linear regression correlation test was performed to investigate correlations between metal concentrations. All data were subjected to statistical analysis and correlation matrices were produced to examine the inter-relationships between the investigated metal concentrations. Correlations between metal concentrations in water samples have been widely studied by a number of authors [27-29, 38, 39]. The values of correlation coefficients between metal concentrations are given in Table 3. According to the data given by literature [30, 35], these correlations were not significant except correlations between Cr-Fe, Ni-Al and Mn-Zn. In conclusion, no correlations were found between metal concentrations in the drinking water samples.

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