

Chemical Analysis of Drinking Water Samples from Yozgat, Turkey

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Abstract

In order to ascertain water quality for human consumption, major and minor ions were evaluated in the drinking water supplied to the city of Yozgat and its surrounding villages in Turkey. Standard methods were used for determining of chemical and physical characteristics of the water samples. Cu, Fe, Pb, Ni and Mn contents of the drinking water samples were determined by atomic absorption spectrometry after preconcentration on Diaion HP-20 resin column. The data showed the variation of the investigated parameters in water samples as follows: pH 6.90-8.13, conductivity (EC) 57.3-694.5 usimens/cm, calcium 15-120 mg/l, magnesium 3-47 mg/l, chloride 11-77 mg/l, bicarbonate 180-701 mg/l, hardness 50-330 mg CaCO₃ /l, total alkalinity 150-575 mg/l, Cu 0.17-1.19 µg/l, Fe 16.11-79.30 µg/l, Pb 0.18-0.99 µg/l and Mn 0.15-2.56 µg/l. Nickel concentrations in all the drinking water samples were below the detection limit. The concentrations of investigated parameters in the drinking water samples from Yozgat were within the permissible limits of the World Health Organization drinking water quality guidelines and the Water Pollution Control Regulation of the Turkish authorities.

Keywords: trace metal ions, drinking waters, standard methods, AAS, WHO, Yozgat-Turkey.

Introduction

The natural water analysis for physical, chemical properties including trace element contents are very important for public health studies. These studies are also a main part of pollution studies in the environment [1-7]. Also, investigations of the quality of drinking water samples have been continuously performed by researchers around the world. The determinations in drinking water have been performed using classical analytical techniques including titrimetry, gravimetry and modern instrumental techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), UV-Vis spectrophotometry, etc.

Because of the low cost and easiness in usage, atomic absorption spectrometry is the main instrument for the determinations of the trace heavy metal ions in drinking waters in the analytical chemistry laboratories [8-10].

Due to relatively low levels of heavy metals, specific sample preparation involving separation/preconcentration is required for determination of these possible analytes. Solvent extraction, coprecipitation, ion exchange, solid phase extraction are some of the preconcentration/separation techniques [10-12]. Solid phase extraction (SPE) holds an important place in the techniques. In SPE, analyte ions are adsorbed on an adsorbent [13-15] such as activated carbon, silica gel, sepiolite, Amberlite XAD and Diaion HP-20 resins etc., then desorbed with a suitable eluent. The metal determinations were per-

formed in this solution. Lots of the application of the solid phase extraction for metal determination in natural water samples including drinking waters have been presented by researchers [16-18].

Yozgat is a city in the Middle Anotolia Region of Turkey. The main industries in Yozgat are textiles, food, cement, manufacturing and metallurgy. The population in Yozgat City Center and around Yozgat is approximately 100,000. Approximately 50% of the population in Yozgat City receive their drinking water from wells. Most of the water supplies are chlorinated. According to our literature review, no report has been published concerning the trace heavy metal concentrations and correlations between them in drinking water samples collected from Yozgat City and villages around Yozgat.

In the present work iron, copper, manganese, lead and nickel ions in drinking water samples from the water sources in Yozgat and villages around Yozgat were determined by graphite furnace atomic absorption spectrometry after separation and preconcentration on the Diaion HP-20 resin column. Physical and chemical properties of the samples were also determined by using standard analytical methods. Correlations between the metal concentrations were investigated.

Experimental

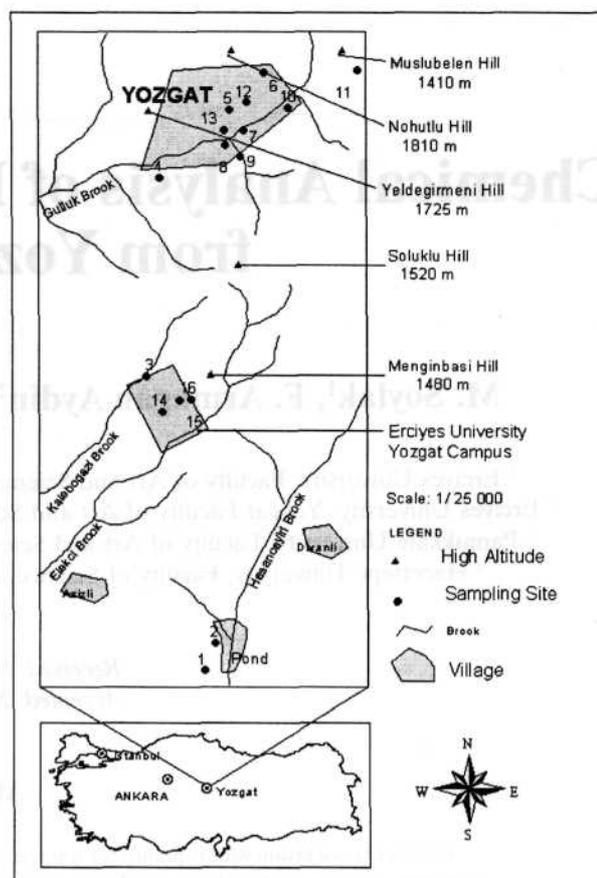
Reagents and Solutions

Analytical reagent-grade chemicals were employed for the preparation of all solutions. Freshly prepared doubled distilled water, from a quartz still, was used in all experiments. All chemicals used were the same as previously described in literature [19]. A 1.0×10^{-2} M solution of oxine was prepared by dissolving the required amounts of oxine in a water/methanol (75/25, v/v) mixture immediately before use. Diaion HP-20 resin (Sigma Chem. Co., St. Louis) was prepared with the washing steps reported previously [20].

Apparatus

Prior to analysis, all instruments were calibrated according to manufacturer's recommendations. pH was measured by using Nel pH 900 digital pH meter with combined glass electrode. Conductivity was determined using a Jenway PCM1 portable conductivity meter. Chloride was determined using the Volhard Argentometric Method. Determination of hardness, bicarbonate and total alkalinity were done by titrimetric measurement [9]. Calcium and magnesium with a Perkin Elmer 3110 model flame atomic absorption spectrometer were determined directly [10].

A Perkin-Elmer Analyst 100 model atomic absorption spectrometer equipped with deuterium background correction and HGA-800 graphite furnace was used for the heavy metal determinations. Twenty microliters of sample were introduced into the graphite tube using an Eppendorf pipette. A glass column 60 mm high and of 10 mm diameter was packed with 400 mg of Diaion HP-20 resin.



Station No	Station Name	Station No	Station Name
1	Ataturk Cesmesi	9	Hastane Karsisi
2	Golet Cesmesi	10	Polis Evi
3	Osmanli Cesmesi	11	Muslubelen
4	Kader Cesmesi	12	Yozgat Sebeke I
5	Meydan	13	Yozgat Sebeke II
6	Karayollari	14	Muhendislik Faculty
7	Pazar Yeri	15	Fen Ed. Faculty
8	Bakircilar Cesmesi	16	Dekan Cesmesi

Fig. 1. Map of the Sampling Stations.

Sample Collection

The drinking water samples were collected in pre-washed (with detergent, doubly de-ionised distilled water, diluted HNO_3 and doubly de-ionised distilled water, respectively) polyethylene bottles from 16 stations in Yozgat and villages around Yozgat in May 2000. The sampling stations were shown in Figure 1. pH and conductivity of the samples were measured while collecting the samples. Two liters (one liter for the determinations of main ions and one liter for metal determination) of each water sample was taken in duplicate at two different sampling periods approximately 1 month apart. The determinations of the major ions of the water samples were performed within one week after sample collection.

Table 1. The physical and chemical properties of the drinking water samples from Yozgat, Turkey.

Station No	Station Name	pH	EC ($\mu\text{s/cm}$)	Ca (mg/l)	Mg (mg/l)	Cl ⁻ (mg/l)	HCO ₃ ⁻ (mg/l)	Hardness mg CaCO ₃ /l	Total Alkalinity (mg/l)
1	Ataturk Cesmesi	7.02	280.0	16 ± 1	18 ± 1	11 ± 1	380 ± 12	100 ± 2	150 ± 4
2	Golet Cesmesi	7.72	441.2	80 ± 3	18 ± 1	16 ± 1	503 ± 15	280 ± 3	413 ± 6
3	Osmanli Cesmesi	7.02	176.7	16 ± 1	15 ± 1	11 ± 1	180 ± 9	100 ± 4	150 ± 3
4	Kader Cesmesi	7.60	636.6	82 ± 2	17 ± 1	44 ± 2	701 ± 10	280 ± 6	575 ± 14
5	Meydan	7.63	377.2	60 ± 2	30 ± 2	77 ± 3	518 ± 20	280 ± 7	425 ± 7
6	Karayollari	7.61	279.0	40 ± 2	18 ± 1	53 ± 2	412 ± 15	180 ± 2	338 ± 5
7	Pazar Yeri	7.33	536.1	80 ± 3	24 ± 2	35 ± 3	381 ± 21	300 ± 3	313 ± 6
8	Bakircilar Cesmesi	7.42	316.9	50 ± 2	36 ± 3	39 ± 2	458 ± 30	180 ± 2	375 ± 7
9	Hastane Karsisi	7.57	221.1	52 ± 2	5 ± 1	53 ± 4	351 ± 21	150 ± 6	288 ± 6
10	Polis Evi	7.47	343.5	48 ± 1	22 ± 1	39 ± 2	336 ± 18	180 ± 2	275 ± 9
11	Musulubelen	7.61	393.1	68 ± 3	3 ± 1	67 ± 5	488 ± 12	180 ± 7	400 ± 7
12	Yozgat Sebeke I	7.88	694.5	120 ± 4	6 ± 1	35 ± 1	671 ± 16	330 ± 2	550 ± 6
13	Yozgat Sebeke II	7.99	242.1	83 ± 4	25 ± 1	70 ± 2	305 ± 8	310 ± 4	*
14	Muhendislik Faculty	8.13	157.0	58 ± 2	47 ± 2	60 ± 2	281 ± 9	240 ± 9	*
15	Fen Ed. Faculty	7.32	104.7	50 ± 2	6 ± 1	39 ± 2	214 ± 10	150 ± 8	175 ± 8
16	Dekan Cesmesi	6.90	57.3	15 ± 1	4 ± 1	46 ± 3	281 ± 10	50 ± 1	*

* Not determined, N = 3, $\bar{x} \pm \text{SD}$: mean \pm standard deviation

The distances from Yozgat City to the stations are approximately 30 km. The samples were obtained directly from the water pump after allowing the water to run for at least twenty minutes. The samples for metal determinations were filtered through a Millipore cellulose membrane of 0.45 μm pore size and were stored in 1 liter polyethylene bottles and acidified to 1% with nitric acid. These samples were subsequently stored at 4°C for as short a time as possible before analysis to minimize physicochemical changes [21, 22].

Preconcentration Procedure for Water Samples

For preconcentration-separation of nickel, lead, manganese, copper and iron in the drinking water samples taken from Yozgat-Turkey, the 500 ml acidified water sample was neutralized and adjusted to pH 9. The Diaion HP-20 column was preconditioned by passing buffer solution. Then 10 ml of 1.0×10^{-2} M of oxine was added. After five minutes, the metal/oxine solution was passed through the column at a flow rate of 5 ml/min with the help of a vacuum aspirator, then the column was rinsed twice with 10 ml of water. The retained metal ions were eluted with an 7-8 ml volume of 1 M HNO₃ in acetone. The eluent was evaporated over a hot plate to near dryness at 35°C in a hood and was diluted to 5 ml with 1 M HNO₃. The eluent was analyzed by GFAAS for the determination of investigated metal concentrations in separate injections.

Results and Discussion

Physical and Chemical Properties of the Samples

The main physical and chemical properties of the drinking water samples including pH, electrical conductivity, calcium, magnesium, chloride, bicarbonate, hardness and total alkalinity from Yozgat-Turkey were given in Table 1. The pH values were in the range of 6.90-8.13 (lowest in Dekan Cesmesi, highest in Muhendislik Faculty). The ranges for electrical conductivity were 104.7 to 694.5 $\mu\text{S/cm}$ except in Dekan Cesmesi (57.3 $\mu\text{S/cm}$). Calcium and magnesium in the investigated water samples were found in the range of 15-120 mg/l and 3-47 mg/l, respectively. While lowest level of the chloride in Ataturk Cesmesi and Osmanli Cesmesi as 11 mg/l, the highest level of the chloride was found in Meydan Station as 77 mg/l. The ranges for bicarbonate in the samples were 180-701 mg/l (Table 1). The hardness of the samples were in the range of 50-330 mg CaCO₃ /l. The highest level of the calcium bicarbonate and hardness in the drinking waters may reflect the limestone formation in the Yozgat District. The ranges for total alkalinity were 150 to 575 mg/l. The major ion contents of the drinking water samples content was well below the permissible limits given by the Water Pollution Control Regulation of Turkish Authorities [23].

Table 2. The concentrations of trace metal ions in the drinking water samples.

Station No	Station Name	Concentration, $\mu\text{g/l}$				
		Cu	Fe	Pb	Mn	Ni
1	Ataturk Cesmesi	0.17 ± 0.02	29.4 ± 0.8	0.30 ± 0.02	0.79 ± 0.04	BDL
2	Golet Cesmesi	0.20 ± 0.01	20.9 ± 0.5	0.99 ± 0.08	BDL	BDL
3	Osmanli Cesmesi	0.66 ± 0.04	22.9 ± 1.1	0.95 ± 0.05	BDL	BDL
4	Kader Cesmesi	0.66 ± 0.03	39.4 ± 2.1	0.42 ± 0.02	BDL	BDL
5	Meydan	1.19 ± 0.12	79.3 ± 0.9	0.29 ± 0.01	0.43 ± 0.02	BDL
6	Karayollari	0.50 ± 0.02	44.9 ± 2.3	BDL	0.16 ± 0.01	BDL
7	Pazar Yeri	0.66 ± 0.04	40.4 ± 1.9	0.19 ± 0.01	0.19 ± 0.01	BDL
8	Bakircilar Cesmesi	0.25 ± 0.01	29.6 ± 1.3	0.27 ± 0.02	0.79 ± 0.05	BDL
9	Hastane Karsisi	0.53 ± 0.03	71.5 ± 3.4	0.29 ± 0.01	BDL	BDL
10	Polis Evi	0.62 ± 0.03	56.9 ± 0.8	BDL	0.15 ± 0.01	BDL
11	Muslubelen	0.57 ± 0.05	42.3 ± 1.3	0.36 ± 0.01	BDL	BDL
12	Yozgat Sebeke I	0.29 ± 0.01	30.6 ± 1.3	BDL	0.24 ± 0.02	BDL
13	Yozgat Sebeke II	0.78 ± 0.05	16.1 ± 0.3	0.18 ± 0.01	1.76 ± 0.08	BDL
14	Muhendislik Faculty	1.00 ± 0.09	30.5 ± 0.3	0.51 ± 0.03	1.27 ± 0.09	BDL
15	Fen Ed. Faculty	0.95 ± 0.08	61.8 ± 2.5	0.19 ± 0.1	2.56 ± 0.11	BDL
16	Dekan Cesmesi	0.98 ± 0.06	48.2 ± 2.9	0.38 ± 0.02	0.72 ± 0.07	BDL

BDL: Below the detection limit; N = 3, $\bar{x} \pm \text{SD}$: mean \pm standard deviation.

Preconcentration Procedure for Metal Ions in Drinking Water Samples

The drinking water samples collected from the sixteen water taps in Yozgat and villages around Yozgat were analysed by atomic absorption spectrometry in triplicate to determine iron, copper, manganese, lead and nickel contents using the preconcentration and separation procedure given in the experimental section. For this purpose, the method given in literature [19] was used. The concentrations, which are given in Table 2, have been calculated on the assumption of 100% recovery of the metal ions.

The lowest and highest levels of elements detected ranged between $0.15 \mu\text{g/l}$ for manganese and $79.30 \mu\text{g/l}$ for iron. The highest levels of total trace heavy metal ions were found in the water sample from Meydan Station. As can be seen in Table 2, in this station Cu, Fe, Pb, Mn and Ni concentrations were found to be $1.19 \mu\text{g/l}$, $79.3 \mu\text{g/l}$, $0.29 \mu\text{g/l}$, $0.43 \mu\text{g/l}$ and BDL (below the limit of detection), respectively. However, the concentrations for Hastane Karsisi Station were below the permitted levels of the World Health Organization (WHO) and the Water Pollution Control Regulation of the Turkish Authorities [23, 24]. The lowest level of total heavy metal contents in the drinking water samples from Yozgat was found in the Golet Cesmesi Station.

Copper concentrations in the drinking water samples were in the range of 0.17 - $1.19 \mu\text{g/l}$. The lowest and highest values were in Ataturk Cesmesi and Meydan Station,

respectively, but even in Meydan Station Cu was considerably below the limit of 1.0 mg/l permitted by WHO [24] in drinking water. Consequently, no contamination due to copper exists in the drinking water samples from Yozgat.

The highest iron level was found in Meydan Station as $79.3 \mu\text{g/l}$ and the lowest in Yozgat Sebeke II station as $16.1 \mu\text{g/l}$. None of the drinking water samples analyzed for iron exceeded the limit permitted by WHO [24], which agrees with results obtained by other authors in other countries [25-27].

The levels of lead in the samples were in the range of 0.18 - $0.99 \mu\text{g/l}$ (minimum in Yozgat Sebeke II, maximum in Golet Cesme). Lead concentrations in 19% of the samples were BDL. The action level for Pb recommended by the Environmental Protection Agency (EPA) is $15 \mu\text{g/l}$. The levels of lead in all stations were below this level. A major source of environmental Pb, particularly in urban areas, is due to the combustion of leaded petrol. Lead is discharged by vehicles into air, then adsorbed from the air by environmental samples such as soil and plants [27-28]. Pb then enters the waterways from soil, thus affecting the levels of lead in natural waters.

Average manganese levels were found to be in the range of 0.15 - $2.56 \mu\text{g/l}$. Manganese content in five out of sixteen (31%) water samples were below the detection limit. Also, the level of nickel concentrations in all investigated drinking water samples were below the detection limit of nickel.

Relationships between the Concentration of Metal Ions

A linear regression correlation test was performed to investigate correlations between metal concentrations. The whole 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 [26, 27, 29]. The correlations between Cu-Fe, Cu-Pb, Cu-Mn, Fe-Pb, Fe-Mn and Pb-Mn were found as 0.49, -0.05, 0.41, -0.38, -0.03 and 0.06, respectively. According to the data given by literature [30, 31], these correlations were not significant.

In conclusion, the concentrations of the investigated major ions and metal ions in the drinking water samples from Yozgat/Turkey were found below the guidelines for drinking waters given by the World Health Organization (WHO) and the Water Pollution Control Regulation of Turkish Authorities [23-24]. No correlations were found between metal concentrations in the drinking water samples.

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