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Determination of Fluoride and Some Metal Ion Levels in the Drinking Waters in Kayseri Province

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Fluorine is one of the most common elements in the Earth's crust. Fluoride is recognized to be the most effective caries-preventive agent. The main sources of fluoride for people are generally food and drinking water. For this reason, the fluoride and also the metal ion (Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn) concentrations in the drinking waters collected from the city center of Kayseri and its counties were investigated. In the determination of fluoride and of Na and K, an ion-meter with a combination-fluoride electrode and a flame photometer were used, respectively. The levels of Cr, Cu, Fe, Mn, Ni and Pb in the drinking waters were determined by flame atomic absorption spectrometry (FAAS) utilizing the method optimized previously, except for the Ca, Mg and Zn contents, which were measured directly by FAAS. According to the results obtained, the metal ion concentrations in the drinking waters in the studied area are within the safe drinking water regulation limits (TS 266) and also the fluoride levels (as mean 0.17 mg L^{-1}) are lower than the permissible limit for fluoride ($0.8\text{-}1.7 \text{ mg L}^{-1}$).

Key Words: Fluoride, metal ions, drinking water, preconcentration, atomic absorption spectrometry.

Introduction

Fluoride (fluorine) is a trace element. Trace elements occur in tiny amounts or traces. They play a major role in health, for even minute portions of them can significantly affect health. Since some fluoride compounds in the Earth's upper crust are fairly soluble in water, fluoride exists in both surface- and groundwaters. The fluoride concentrations in groundwater fluctuate within wide limits, e.g., from <1 to 25 mg or more per liter¹. Fluoride, bromide and iodide ions except for chloride are found in low concentrations in natural waters. The main source of the fluoride in waters is CaF_2 , which can be soluble up to 16 mg per liter at 18°C and is found in the composition of volcanic rocks. Minerals such as fluorapatite $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$, fluorspar (CaF_2), cryolite $3\text{NaF} \cdot \text{AlF}_3$ and mica also contain fluoride. Fluoride exists in volcanic gases more than in rocks².

Fluoride also is frequently added to some consumer products, such as toothpaste, toothpowder, mouthwash and vitamin supplements for various reasons. At present, different opinions exist toward the

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fluoridation applications in drinking waters in the world. These opinions are based on the experimental data having uncertainty as to whether fluoride has carcinogenic properties for humans, and also it is more toxic than Pb and less than As³. Approximately 90% of the fluoride in the body is contained in the bones and teeth. Fluoride increases the resistivity of tooth enamel against acids which cause the initiation of tooth decay. It reduces tooth decay about 40-50% in the case of a concentration approximately of 1.0 mg L⁻¹ in drinking water without any additional influences. When the fluoride concentration in drinking water is greater than 2 mg L⁻¹, it may cause fluorosis related to the concentration, to the amount of water taken up and to the amount of additional fluoride from using toothpaste and gargle, etc. When the fluoride concentration exceeds 2.4 mg L⁻¹, children under the age of four years must drink from another water source having a known suitable fluoride level or from a water treated with reverse osmosis^{2,4,5}. In the determination of the fluoride levels in various samples, different techniques have been used, such as potentiometry (with fluoride sensitive electrodes) or spectrophotometry⁶⁻¹¹.

Trace metal analyses have a gradually increasing importance due to the fact that functions of the trace elements in various areas such as biological systems, environment, and geochemistry are now understood well. Investigations on air, water and soil pollutions, especially metal contamination, for living organisms and/or materials require the determination of the trace metals¹²⁻¹⁴. Determining the trace metals directly and reliably with most instrumental methods is difficult due to the low concentrations of analytes and the interferences caused by the sample matrix. Therefore, the preconcentration and separation procedures are applied to samples both to separate the analytes from the sample matrix and to concentrate them in a small volume. By and large, trace metal enrichment methods include solvent extraction¹⁵, ion exchange¹⁶, coprecipitation¹⁷, accumulation on activated carbon¹⁸, and solid phase extraction^{19,20}. Up to now, organic based synthetic adsorbents, especially Amberlite XAD resins (XAD 2, -4, -7, -8, -16, and -1180) have been widely used as adsorbents suitable for multi-metal preconcentration from different matrices^{21,22}. One of these is Amberlite XAD-16, which is a nonionic polymeric adsorbent having excellent sorption characteristics.

In the present study, the levels of fluoride and the metal ions in the drinking waters taken from Kayseri province were determined potentiometrically by using the fluoride ion electrode and by FAAS utilizing sodium tetraborate after the preconcentration on a column packed with Amberlite XAD-16 resin for the metals Cr, Cu, Fe, Mn, Ni and Pb, respectively. Also, the determination of Ca, Mg and Zn was carried out directly by FAAS, and that of K and Na was carried out by flame photometry.

Materials and Methods

Sampling

Kayseri province and the locations at which the water samples were collected are shown in Figure 1. After the water samples were transported to the laboratory, the fluoride analyses were performed immediately⁶. After the determinations of fluoride were performed, the water samples were made acidic (pH ≤ 2) with concentrated nitric acid (65%, w/w), in order to minimize chemisorption and hydrolysis of metal ions, and preserved at +4°C in a refrigerator for the metal analyses²³.

Instruments and Chemicals

A Perkin Elmer 3110 model atomic absorption spectrometer with an air-acetylene burner was used in the determination of the metals (Bi, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Zn) in the drinking water samples. The instrumental parameters recommended by the manufacturer were used throughout the experimental measurements²⁴. All pH measurements were performed using a NEL digital pH-meter with a combination electrode. The fluoride analyses were performed by using a Jenway 3040 model ion-meter in conjunction with a combination fluoride electrode²⁵. In the determination of sodium and potassium and also the other metal ions after the preconcentration onto Amberlite XAD-16 resin, a Jenway PFP 7 model flame photometer and an atomic absorption spectrometer were used, respectively, except for Ca, Mg and Zn, which were determined directly by FAAS.

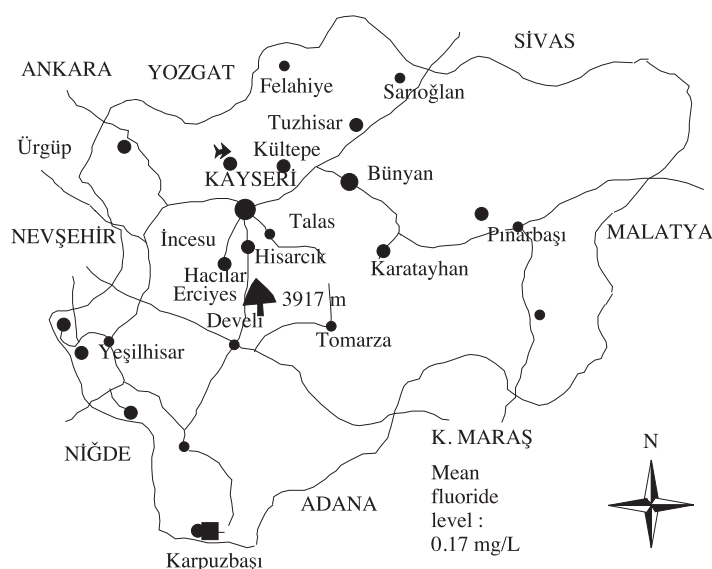


Figure 1. Map of Kayseri province and the sampling locations for the drinking water samples.

Analytical-reagent grade chemicals (Merck, Darmstadt, Germany) were used without further purification. Doubly distilled water was used throughout the experiments. The glassware was kept overnight in a 5% nitric acid solution prior to being used. Fluoride stock solution ($1000 \mu\text{g mL}^{-1}$) was prepared from sodium fluoride. Total ionic strength adjustment buffer (TISAB) solution contains 58 g of sodium chloride, 57 mL of glacial acetic acid, 4 g of 1,2-cyclohexanediamine- N,N,N',N' -tetraacetic acid (CDTA) and approximately 150 mL of 6 mol L^{-1} NaOH in a volume of 1000 mL (pH 5.0-5.5; Orion ISE 940900, 1983). At a pH below 5.0, the measurement gives low biased concentrations because of the complexation of F^- by H^+ . A high bias in the measured concentration occurs at pH values above 7.0 because of the presence of high concentrations of OH^- or HCO_3^- . Stock solutions of the metals ($1000 \mu\text{g mL}^{-1}$) were prepared by dissolving appropriate amounts as nitrate salts and diluting to 1000 mL with 1% (w/w) HNO_3 . The working solutions were diluted to the appropriate volume prior to being used. Sodium tetraborate solution (0.01 mol L^{-1}) was prepared by dissolving the appropriate amount of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in water and completing to the mark (pH 9.2).

Determining of Fluoride in Drinking Waters

A combination fluoride electrode was used to determine the fluoride concentrations in the drinking waters. The drinking water samples and the fluoride standard solutions were diluted 1:1 with a total ionic strength adjustment buffer solution. TISAB solution equals the ionic strength of sample and standard solutions and adjusts the pH, and also avoids interferences by polyvalent cations such as Al(III), Fe(III) and Si(IV), which are able to complex or precipitate with fluoride and reduce the free fluoride concentration in the solution¹⁰. The mixed solutions were stirred with a magnetic stirrer for 5 minutes. The electrode potentials of the sample solutions were directly compared with the electrode potentials of fluoride standard solutions. A calibration curve for determining fluoride in the drinking waters, prepared by the least squares method, is given in Figure 2.

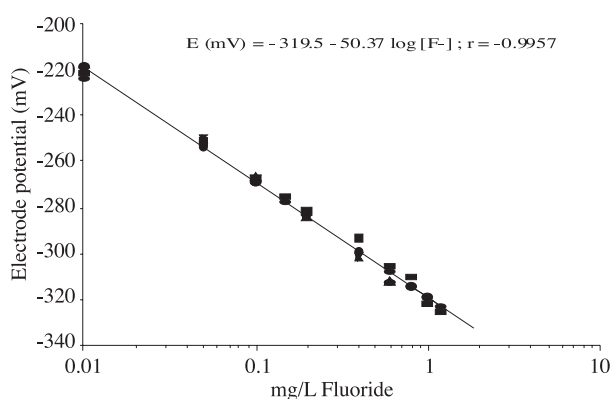


Figure 2. A calibration curve for determining fluoride in the drinking waters.

Optimal Conditions for Column Procedure

The optimal conditions for the column procedure were previously examined elsewhere in detail¹⁴. The quantitative recoveries (%) for the elements Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb were obtained at pH 9.2 with the borate buffer. The maximum sample volume was 500 mL for the elements studied with the method used. The recovery values (%) of the method were in the range 98-100 and the relative standard deviations (RSD%) were in the range 1.1-2.4 for Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb. The detection limit of the method was 0.177, 0.002, 0.008, 0.038, 0.007, 0.067, 0.015, 0.054, and 0.022 mg L⁻¹ for Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, and Pb, respectively. The matrix effects were investigated for NaCl, KCl, MgCl₂, Ca(NO₃)₂ and Na₂SO₄. The method gave quantitative analytical results ($\geq 95\%$) for the levels of interfering species less than or equal to 500 mg L⁻¹ Ca⁺² (≤ 10 mg L⁻¹ for Mn), 1000 mg L⁻¹ K⁺, 250 mg L⁻¹ Mg⁺² (≤ 10 mg L⁻¹ for Mn), 10000 mg L⁻¹ Na⁺, and 200 mg L⁻¹ SO₄²⁻ and for less than or equal to 500 mL of the model solution¹⁴.

Application of the Column Procedure for Trace Metal Analysis in Drinking Waters

In order to determine the metal ions (Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb) found in the drinking water samples by using the column filled with Amberlite XAD-16 resin, the column procedure which had been previously optimized with model solutions was used. For this purpose, the pH of an aliquot of 450 mL of the drinking water sample was adjusted to 9.2 using sodium tetraborate reagent (about 1.71 g) and then the solution obtained was passed through the column at a flow rate of 1 mL min⁻¹ with the aid of a vacuum pump. The metals (Cr, Cu, Fe, Mn, Ni and Pb) retained on the column were eluted with 1 mol L⁻¹ HCl in acetone and then the eluate was evaporated to incipient dryness. The residue was taken into a volume of 2 mL with 1 mol L⁻¹ HCl. The measurement of the metals was performed by FAAS using the injection method²¹, in which an aliquot of 100 µL of the sample solution was used. Here, the contents of the Bi, Co and Cd could not be determined because of their low levels in the drinking water samples. Calcium, magnesium and zinc concentrations were also determined directly by FAAS after diluting the samples when necessary.

Results and Discussion

The fluoride levels determined in the drinking water samples collected from the central county, counties, towns and villages in the province of Kayseri, a total of 14 different locations, are given in Table 1. In the drinking waters in all the sampling locations, which are fed by snow originating from Erciyes Mountain, the fluoride contents were found to be lower than 0.80 mg L⁻¹, the minimum permissible value²⁶. As can be seen in Table 1, the highest fluoride level (0.46 mg L⁻¹, n=3) was observed in Hacilar county. The waters of this region probably pass through a soil or a rock layer which is a little richer in fluoride than the other regions; this may be the reason for this high level. This region is close to Erciyes Mountain (about 15 km), and the fluoride levels of the three water samples taken from this region are very close to each other (s.d.: ± 0.02 mg L⁻¹).

The frequency distributions (%) of the fluoride levels against their concentration ranges for 61 drinking waters are illustrated in Figure 3. In the determination of fluoride levels, about a quarter of the results (23%) were between 0.10 and 0.15 mg F⁻ L⁻¹. In about 80% of all the measurements, the concentrations were found to be less than or equal to 0.25 mg L⁻¹. In another study²⁷ previously performed in the city center of Kayseri province, the concentrations of fluoride in drinking waters were determined to be between 0.2 and 0.34 mg L⁻¹. In most drinking waters in which the determination of fluoride was performed in Turkey, the fluoride concentrations were observed to be below 1.0 mg L⁻¹. According to the Turkish National Standards for drinking waters²⁶, the recommended and the maximum permissible levels of fluoride are in the range of 0.8-1.7 mg L⁻¹ and 1.4-2.4 mg L⁻¹, respectively. In the light of the results obtained, the fluoride levels of the drinking waters are rather low regarding the drinking water standards recommended for fluoride²⁶.

The levels of some metal ions determined in the same drinking waters are given in Table 2. In Table 2, one can see that there is no potential metal pollution for the drinking waters. The concentration of chromium, found to be 1.9 µg L⁻¹ on average, was based on the measurements of the total chromium. The mean chromium concentration is about one twenty-fifth of the maximum permissible level of Cr⁶⁺ (50 µg L⁻¹ Cr⁶⁺) according to TS 266. Chromium (VI) salts, CrO₄²⁻ and Cr₂O₇²⁻, are more toxic than Cr³⁺

salts, and also have carcinogenic properties.

Table 1. The fluoride concentrations determined in the drinking water samples (mg L⁻¹).

Sampling location	Mean conc. ± sd ^a (mg L ⁻¹)	No. of samples ^b	Range
City center	0.20 ± 0.03	6	0.17 - 0.24
Talas	0.10 ± 0.07	4	0.04 - 0.17
Özvatan	0.34	1	-
İncesu	0.26	1	-
Tomarza	0.23 ± 0.10	8	0.05 - 0.32
Hacılar	0.46 ± 0.02	3	0.44 - 0.48
Develi	0.13 ± 0.05	10	0.04 - 0.21
Felahiye	0.20 ± 0.02	3	0.19 - 0.22
Pınarbaşı	0.13 ± 0.05	6	0.09 - 0.23
Yeşilhisar	0.17 ± 0.04	3	0.12 - 0.21
Sarıoğlan	0.24 ± 0.09	3	0.15 - 0.33
Yahyah	0.09 ± 0.01	4	0.07 - 0.10
Bünyan	0.14 ± 0.03	6	0.11 - 0.18
Sarız	0.054 ± 0.002	3	0.05 - 0.06
Mean	0.17 ± 0.10	61	0.04 - 0.48

^aStandard deviation, ^bThe number of water samples taken from different locations.

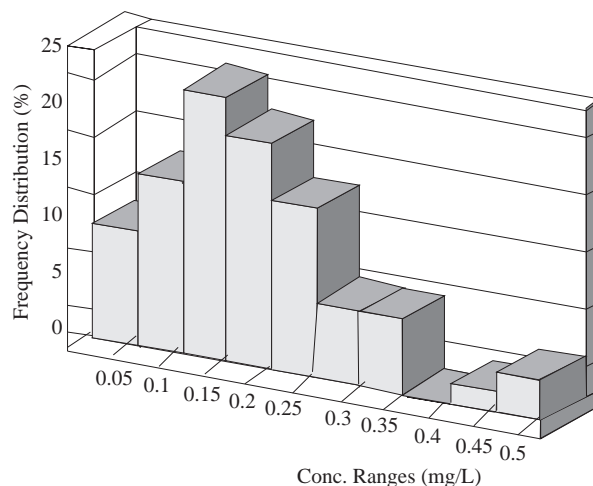


Figure 3. The frequency distributions of the fluoride levels.

A matrix which gives a connection between the fluoride and the metal levels determined in the drinking water samples is shown in Table 3. Linear correlation coefficients (r)²⁸ are significant as follows: r=0.38 (n=26), r=0.30 (n=41), r=0.29 (n=43), r=0.27 (n=51), r=0.26 (n=53), r=0.25 (n=61) at 95% confidence level. The fluoride shows a weak correlation with Na (r=0.26). The correlations between Mn and both Cu and K are weak, that is, r=0.24 and r=0.25, respectively. Na is correlated weakly and negatively between Ca, Mg and K. A remarkable point seen in Table 3 is negative correlations among the Na and the elements of Ca and Mg, which may be related to the solubilities of their minerals in soil. The correlations between Cr-Ni; Pb-Zn; Cu-Fe, Mn-Zn and Na-Pb are weak, but meaningful. The observed binary correlations between

Na-Ni, K-Mg, Cu-Pb, Ca-Mg and Fe-Mn range from 0.45 to 0.66, and they are moderately strong and meaningful. The correlation coefficient of 0.66 observed between Fe and Mn is an expected value because of the abundance of these elements in soils. In general, low and sometimes negative correlations observed among the elements may be explained by the chemical structures and solubilities of minerals in which the waters passing through different soil and rock layers can dissolve these minerals.

Table 2. The mean concentrations, standard deviations, number of samples, and permissible values (TS 266) of elements in the drinking water samples.

Element	Mean			Regulation limits (mg L ⁻¹) (TS 266)	
	concentration (µg L ⁻¹)	Range	No. of samples, n	Permissible	Maximum permissible
Ca	36 ^a	2 - 101	53	75	(200)
Cr	1.9	0.04 - 5.6	41	-(Cr ⁶⁺) ^b	(0.05)
Cu	2.0	0.22 - 13.2	51	1.0	(1.5)
Fe	45	0.93 - 517	53	0.3	(1.0)
F	0.17	0.04 - 0.48	61	0.8-1.7	(1.4-2.4)
K	22.8 ^a	0.05 - 415	53	- ^c	- ^c
Mg	16.0 ^a	2.0 - 70	53	50	(150)
Mn	0.94	0.15 - 4.44	41	0.1	(0.5)
Na	60 ^a	27 - 111	26	- ^c	- ^c
Ni	4.5	0.53 - 9.9	53	- ^c	(0.1)
Pb	2.9	0.13 - 20.4	43	- ^c	(0.05)
Zn	0.55 ^a	0.01 - 2.0	43	5	(15)

^aConcentration: mg L⁻¹, ^bOccurrence undesirable, ^cNot indicated.

Table 3. The linear correlation matrix of the elements.

	Cr	Ca	Cu	Fe	F	K	Mg	Mn	Na	Ni	Pb
Ca	a										
Cu		0.19									
Fe	-0.10		0.38								
F		-0.16		0.13							
K	-0.18	0.17		0.15	0.20						
Mg		0.60	0.20			0.47					
Mn		0.10	0.24	0.66	0.13	0.25	0.16				
Na	0.32	-0.28	0.12	-0.10	0.26	-0.30	-0.25	-0.17			
Ni	0.31	-0.13			0.20	-0.20	-0.19		0.46		
Pb		0.12	0.49	0.15				0.15	0.38		
Zn			0.13		0.12			0.35	0.31	0.20	0.30

At confidence level 95% ; r=0.38 (n=26), r=0.30 (n=41), r=0.29 (n=43), r=0.27 (n=51), r=0.26 (n=53), r=0.25 (n=61).

^aThe correlation coefficients lower than ± 0.10 are not indicated.

Conclusions

This study was performed at the request of the Health Management of Kayseri province within the limits of “the fluoridation project” proposed by the Ministry of Health for of fluoridation of drinking waters with low fluoride contents. In addition to the determination of fluoride levels, the concentrations of elements such as Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn were measured in the same drinking waters. It was observed that the metal contents did not exceed the threshold values given in TS 266.

The results of this investigation indicate that the drinking waters in Kayseri province are insufficient in fluoride content. The use of fluoride tablets for children at the age of 6 months or older (until 4 years) in the counties selected as pilot regions (Bünyan, Develi, Felahiye, Yahyalı, Tomarza, Yeşilhisar, Pınarbaşı and Talas) was commenced under the supervision of dentists in July 1997. Each fluoride tablet (dentifluor) contains 0.25 mg F⁻ and this amount is equivalent to 0.553 mg of sodium fluoride. A daily dose of fluoride is only one tablet for each child. From July 1997 to April 2000, about 13630 tablets were distributed and the project is continuing.

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