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Determination of Fluoride in Various Samples and Some Infusions Using a Fluoride Selective Electrode

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The determination of fluoride in some environmental samples was performed using a fluoride ion-selective electrode. Fluoride concentrations were determined in drinking waters (from different provinces, districts and villages in Turkey), fruit juices, bottled water samples, toothpastes and tooth powders, liquors of Turkish coffee, coffee, linden, rose hip, and various brand tea infusions, and dust samples collected from the Erciyes University campus car park. The average fluoride concentration in 39 drinking waters was 0.21 mg L^{-1} (0.02–1.42 mg L^{-1}); the level of dissolved fluoride in the dust samples was 1.39 $\pm$ 0.09 μg g^{-1}; the fluoride concentrations in liquors taken from tea infusions for 20 min were in the range 55 to 445 μg g^{-1}; the mean value for fluoride in fruit juices was 0.23 mg L^{-1} (0.05–0.50 mg L^{-1}). The level in bottled water samples was 0.27 mg L^{-1} (0.04–1.47 mg L^{-1}). The fluoride concentrations in toothpaste samples were between 447 and 1400 μg g^{-1}. Its value for tooth powder was 795 $\pm$ 73 μg g^{-1}. The fluoride concentrations obtained from the analyses of samples were compared with the permissible values given by the Turkish Standards for Drinking Water (TS 266) and the World Health Organization.

Key Words: Fluoride, Water, Infusion, Tea, Toothpaste, Fluoride ion-selective electrode.

Introduction

Fluoride (F^-) is an important anion, present in various environmental, clinical and food samples. Small amounts of fluoride are vital for the human organism, but it is toxic in larger amounts. For adults the lethal dose is 0.20–0.35 g F^- per kg body weight. Fluoride is widely used in various branches of industry and some fluoride compounds are formed as by-products in certain processes. Excessive amounts of fluoride in the form of different compounds can enter the human body by means of polluted air, water and the food chain. An additional source of fluoride for humans is toothpastes containing ca. 0.1% fluoride (NaF, SnF_2, Na_2PO_3F) and water fluoridation (adding fluoride in the form of NaF to drinking water)[1,2]. A small amount of fluoride is beneficial in the prevention of dental caries. Fluoride has also been used to treat osteoporosis[3]. It is very characteristic that fluoride prevents tooth decay at about 1 mg L^{-1} but causes mottled teeth

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and bone damage at around 5 mg L^{-1} when it is present in water. Fluorosis is caused by elevated intake of fluoride over prolonged periods of time. Skeletal fluorosis and dental fluorosis are the 2 main types. In dental fluorosis the structural integrity of enamel is affected and small pits are left in teeth as it breaks away. Skeletal fluorosis is the accumulation of fluoride in skeletal tissues associated with pathological bone formation[4].

Rocks, soil, water, air, plants, animals and foodstuffs all contain fluoride in widely varied concentrations. Tea leaves are usually very rich in fluoride and the tea plant (*Camellia sinensis*) takes up fluoride from the soil and accumulates it in its leaves; it is considered a major source of fluoride. A substantial amount of fluoride is released during tea infusion and nearly all (about 94.9%) of the released fluoride is available to consumers[3,5]. The common fluoride bearing minerals found in soil are fluorospar (CaF_2), cryolite (Na_3AlF_6) and chiolite ($Na_5Al_3F_{14}$)[5]. The mobility of fluoride in soil is determined by the amount of clay minerals present, the soil pH, the adsorption of positively charged complexes, and the concentrations of Ca, Fe, Al and P in soil[4]. The high solubility of F^- in soil under acid conditions (pH < 6) corresponds to the presence of cationic AlF_2^+ and AlF^{2+} complexes[4].

In all cases fluoride is found at low levels and its determination demands very sensitive methods. Ion selective electrodes (ISEs) have been used for this purpose, replacing the expensive and time-consuming chromatographic methods. ISEs are easy to use and thus are suitable for continuous monitoring. They are cost-effective, as well as sufficiently sensitive, selective and accurate[1,6]. The fluoride selective electrode is used for the determination of fluoride in drinking water[7], industrial effluents, seawater, air, aerosols, flue gases, soils and minerals[8], urine[2,9], serum[9], plasma, plants[3], food[6], beverages[10,11], tea[12], and other biological materials[5]. If a sample contains water-soluble and/or suspended organic substances in addition to its metallic cations (e.g., Si^{4+}, Al^{3+}, Fe^{3+}, Mn^{3+}, Mn^{2+}, which form stable complexes with CDTA), fluoride contents may be somewhat lower than the levels in real samples due to the adsorption and/or complexation of free fluoride[5].

In this study, the fluoride contents in drinking waters, fruit juices, bottled water, different brands of toothpastes, dust samples from the Erciyes University campus car park, infusions of tea, linden, rose hip, Turkish coffee and coffee samples were determined potentiometrically using a combination-fluoride electrode. The fluoride concentrations obtained from sample analysis were compared with permissible values given by the Turkish Standards for Drinking Water (TS 266)[13] and the World Health Organization[5].

Experimental

Instruments and chemicals

The fluoride analyses were performed using a Jenway 3040 model ion-meter in conjunction with a combination fluoride electrode (Orion ISE 940900). Analytical-reagent grade chemicals (Merck, Darmstadt, Germany) were used without further purification. Distilled water was used throughout the experiments. The glassware was kept overnight in 5% nitric acid solution prior to being used. Fluoride stock solution (1000 μg mL^{-1}) was prepared from sodium fluoride and stored in polyethylene labware. 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)[14,15]. The TISAB solution regulates the ionic strength of samples 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 solution[16]. CDTA forms stable complexes with polyvalent metal cations (e.g., Al(III), Fe(III) and Si(IV)), which are more stable than metal-fluoride complexes (AlF_6^{3-}, FeF_6^{3-} etc.) in solution. The CDTA preferentially complexes with polyvalent cations present in water and/or aqueous solution (e.g., Si^{4+}, Al^{3+} and Fe^{3+}). There are 6 complexing groups in CDTA and it forms metal-CDTA complexes in a metal-ligand ratio of 1:1[14], freeing the fluoride ion from its complexes with the cations. The electrode is selective for the fluoride ion over other common anions by several orders of magnitude; only the hydroxide ion appears to offer serious interference.

Sampling

Drinking water samples were taken from different provinces in Turkey. After the water samples were transported to the laboratory, fluoride analyses were performed immediately. The fruit juice, bottled water, tea, linden, rose hip, Turkish coffee, coffee and toothpaste and tooth powder samples of different brands were purchased from local markets. The dust samples were collected from the Erciyes University campus car park.

Determination of fluoride in drinking water, fruit juice and bottled water samples

A combination fluoride electrode was used to determine the fluoride concentrations in drinking water, juice and bottled water samples. The samples and fluoride standard solutions were diluted 1:1 with the TISAB. The solutions, which contained 25 mL of the sample and 25 mL of TISAB solutions, were mixed with a magnetic stirrer for 3 min. The electrode potentials of the sample solutions were directly compared with those of fluoride standard solutions.

Determination of fluoride contents in toothpaste and tooth powder samples

For the determination of fluoride in toothpaste and tooth powder samples, ~0.05 g of the sample was weighed into a 100 mL beaker. After 25 mL of TISAB solution was added to the samples, the mixture was boiled thoroughly for 2 min. The suspension was completed to 50 mL with distilled water. The fluoride contents of the samples were determined with the ion-meter. The determinations of fluoride for each sample were repeated in triplicate analyses.

Determination of fluoride in tea and coffee infusions

Ten grams of dried tea sample was placed into a beaker. Then 400 mL of boiling deionized water (containing 0.01 mg F^- L^{-1}) was poured into the beaker and 25 mL of the tea liquor was taken after 5, 10, 20, 30 and 40 min. TISAB solution was added and the fluoride contents in tea liquor were determined using the ion-meter. For the infusion of the tea bag, a tea bag was added to 400 mL of deionized water, and the steps for the determination of fluoride mentioned above were the same. Linden, rose hip, Turkish coffee and coffee samples were also infused as mentioned above. The liquors of the linden and rose hip samples were taken after 15, 25 and 35 min, while the liquors of Turkish coffee, coffee and other various brand tea samples were taken after 20 min. The fluoride contents released into the liquors were determined using the ion-meter.

Water soluble fluoride contents of car park dust samples

Two grams of the car park dust sample was weighed into a beaker and mixed with 50 mL of boiling deionized water. The mixture was filtered through a Whatman no. 42 filter paper. The fluoride concentrations in 25 mL aliquots taken from filtrate were determined.

Results and Discussion

Detection limit and accuracy

The detection limit of the method (LOD) is 0.01 mg L^{-1} ($3s_b/b$, n = 10). The quantification limit (LOQ) value was 0.033 mg L^{-1} ($10s_b/b$, n = 10), where s_b is the standard deviation of the blank determinations, b is the slope of the calibration curve and n is the number of replicate analyses[17]. An example calibration curve is illustrated in Figure 1. In validation studies, the average recovery values based on the spiked samples at 2 different fluoride levels were 99 ± 16% and 83 ± 11% (n = 4) for tap water and peach juice, respectively. Fluoride ions in peach juice may be adsorbed by the organic substances occurring in high amounts in the sample. However, the obtained recovery value may be in the sample[5].

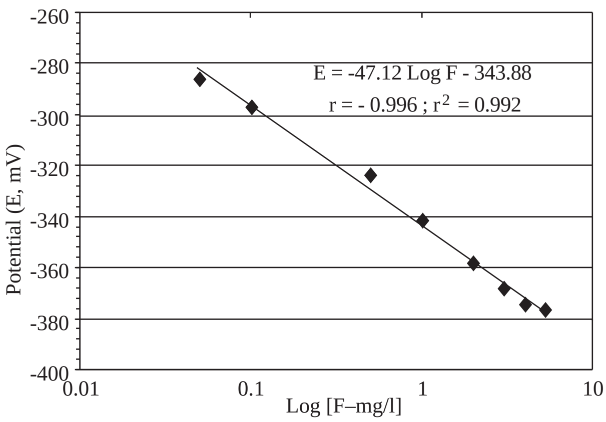

Figure 1. A sample plot of calibration curve for potentiometric determination of fluoride.

Results of fluoride analyses

The fluoride levels determined in drinking water samples collected from the cities, districts, towns and villages in different provinces in Turkey, a total of 41 different locations, are given in Tables 1 and 2. According to the Turkish National Standards for Drinking Waters[13], the recommended and maximum permissible levels of fluoride are 0.8 to 1.7 mg L^{-1} and 1.4 to 2.4 mg L^{-1}, respectively. In the drinking waters from all the sampling locations, the fluoride contents were lower than 0.80 mg L^{-1}, the minimum permissible value[13], with only 2 exceptions. As can be seen from Table 1, the highest fluoride level was observed in Kozaklı district: 1.42 mg L^{-1} for drinking water and 4.50 mg L^{-1} for ground water. The fluoride content of drinking water in İskenderun of 1.37 mg L^{-1}follows that in Kozaklı. Of the drinking waters investigated (41 sampling sites), only those from these 2 sampling locations had sufficient fluoride levels, the others had insufficient fluoride content: their fluoride contents varied between <0.01 (LOD) and 0.40 mg L^{-1} with an average of about 0.22 mg L^{-1}. The waters of these two regions probably pass through a soil or rock layer rich in fluoride in comparison with the other regions. The natural concentration of fluoride in ground water depends on such factors as the geological, chemical and physical characteristics of the water-supplying area, the consistency of the soil, the porosity of rocks, the pH and temperature, the complexing action of other elements, and the depth of wells. Owing to these factors, fluoride concentrations in ground water fluctuate within wide limits, e.g., from >1 to 25 mg or more per liter[5]. Table 2 shows the fluoride contents from Kayseri and Amasya provinces. The mean fluoride contents for drinking waters were 0.16 ± 0.06 mg L^{-1} (for 8 different sampling locations) for Kayseri and 0.14 ± 0.10 mg L^{-1} for Amasya. In our previous study[7] in the city center of Kayseri and surrounding districts, which were different from those of this study, the mean concentration of fluoride in drinking waters was 0.17 ± 0.10 mg L^{-1} (for 61 different sampling locations). When the results obtained from the previous study[7] were compared with those of this study, there was no significant difference among the results of the 2 investigations. The results obtained indicate that the fluoride levels of the drinking waters are generally low regarding drinking water standards. Consequently, most of the drinking waters (about 95%) investigated in this study have low fluoride levels. This lack of fluoride content in the drinking waters, which are one of the main sources of fluoride nutrition for humans, may cause health problems for human health, especially teeth and bone structures.

Table 1. Fluoride concentrations of drinking waters at some locations in Turkey.

Sampling location[a]	Mean concentration (mg L^{-1})	Sampling location	Mean concentration (mg L^{-1})
Halkalı - İstanbul	0.12	Bergama - İzmir	0.18
Kaynak - İstanbul	0.07	Pozantı - Mersin	0.18
Pendik - İstanbul	0.08	Çeşmeli - Mersin	0.08
Tarsus (1)	0.16	İskenderun (1)	0.09
Tarsus (2)	0.12	İskenderun (2)	1.37
Bahçelievler - Ankara	0.02	Kozaklı - Nevşehir	1.42
Keçiören - Ankara	0.06	Silifke - Mersin	0.12
Gaziantep	0.29	Turhal - Tokat	0.24
Kırıkkale	0.29	Tokat	0.09
Maraş	0.17	Gemerek - Sivas	0.23
Narlı - Maraş	0.13	Keşan - Edirne	0.12
Alanya	0.05	Malatya	< LOD[b]
Sofulubel - Adana	0.40	Adapazarı	< LOD
	Range	0.02–1.42	

[a] The fluoride levels were 0.10 and 4.50 mg L^{-1} for Kurtboğazı Dam, Ankara, and spring water of Kozaklı, Nevşehir, respectively.

[b] Detection limit.

Figure 2 shows the release of fluoride into tea liquor during infusion for 3 Turkish tea samples (tea 1, tea 2 and tea 3) and an imported one (tea 4). The fluoride contents released into the liquor from the tea were closely related to the duration of tea infusion. There were significant differences in fluoride contents released among all the time intervals for imported tea. The imported tea has a higher fluoride content (408–456 μg g^{-1}) than the Turkish teas (67–148 μg g^{-1}). The fluoride contents released from the linden at 15 and 25 min of infusion were 0.37 ± 0.04 and 0.68 ± 0.02 mg L^{-1} and at 35 min for rose hip were 0.19 ± 0.01, 0.30 ± 0.02 and 0.59 ± 0.06 mg L^{-1}, respectively. After Turkish coffee, coffee and the other various brand tea samples were infused, fluoride levels were determined in liquors taken at 20 min of infusion. The values obtained were 0.096 ± 0.004 and 0.17 ± 0.01 μg g^{-1} for Turkish coffee and coffee; 55 ± 6 and 127 ± 8 μg g^{-1} for 2 Turkish tea samples; 0.30 ± 0.03 μg g^{-1} for sage tea; and 142 ± 2, 56.4 ± 0.8 and 195 ± 12 μg g^{-1} for 3 imported tea samples.

Table 2. Fluoride concentration in drinking waters from Kayseri and Amasya (n = 2).

Sampling locations in Kayseri	Mean concentration (mg L^{-1})	Sampling locations in Amasya	Mean concentration (mg L^{-1})
Merkez	0.12	Yeşildere	0.17
Talas	0.11	Akdağ	0.06
Hisarcık	0.11	Derinöz	0.03
Sümer	0.23	Şeyhcui	0.29
Düvenönü	0.16	İlyas	0.24
Bünyan garajı	0.16	Ziyere	0.06
Tomarza	0.26[a]	Karasenir	0.11
Sarız -Yedioluk	0.09		
Mean ± sd	0.16 ± 0.06	Mean ± sd	0.14 ± 0.10

[a]The level of fluoride found in 2000[7], 0.23 ± 0.10 mg L^{-1}.

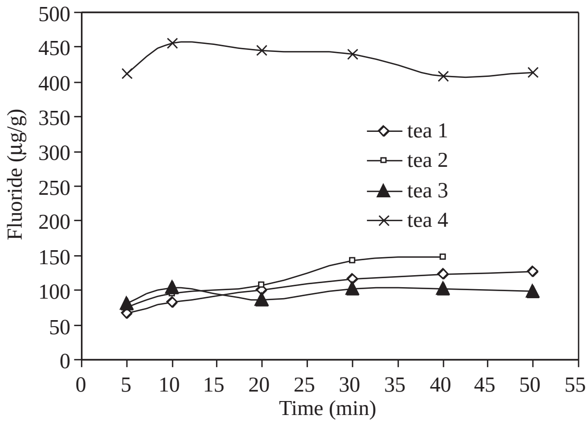

Figure 2. Water-soluble fluoride concentrations in tea liquors prepared by infusion.

Tea leaves are usually very rich in fluoride, and levels ranging from 3.2 to 400 mg kg^{-1} by weight in dry samples have been reported. The mean fluoride concentration of tea brewed with water containing fluoride at 0.1 mg L^{-1} was 0.85 mg L^{-1} in the literature[5], the upper level being 3.4 mg L^{-1}. In another study, fluoride concentrations varied from 0.4 to 2.8 mg L^{-1}in tea infusions prepared from 12 different brands of tea[5]. Fung et al.[3] reported that the highest fluoride contents are found in fallen leaves, followed by mature leaves, young leaves, branches and roots. Fluoride accumulated in old leaves over 2000 mg kg^{-1} and young leaves ranged from 250 to 360 mg F per kg.

Table 3 shows fluoride concentrations in the fruit juice and bottled water samples. The fluoride content in juices was between 0.05 and 0.50 mg L^{-1} and its value was between 0.04 and 1.47 mg L^{-1} in bottled water samples. The standard deviations of fluoride concentrations in the juice samples varied from 0.001 to 0.015 mg L^{-1}. This range for bottled water samples was from 0.0002 to 0.0096 mg L^{-1}. The fluoride levels for 2 mineral waters were 0.98 and 0.41 mg L^{-1}. According to the WHO[5], juices prepared with fluoridated water contain 0.9–1.3 mg F L^{-1}, whereas juices prepared with water including low fluoride (< 0.2 mg L^{-1}) contain 0.2–0.5 mg F L^{-1}. The mineral waters may contain fluoride levels higher than 1 mg L^{-1}.

Table 3. Fluoride in fruit juice and bottled water samples (n = 2).

Fruit juice (J) samples	Mean concentration (mg L^{-1})	Bottled water (BW) samples,	Mean concentration (mg L^{-1})
J1[a]-orange	0.37	BW1[b]	0.05
J1-apricot	0.35	BW2	0.08
J2-morello	0.05	BW3	0.07
J2-apricot	0.13	BW4	0.05
J2-peach	0.16	BW5	1.47
J2-orange	0.06	BW6	0.04
J3-morello	0.50	BW7	0.14
J3-apricot	0.36		
J4-peach	0.17		
J4-morello	0.13		
Range	0.05–0.50	Range	0.04–1.47

[a,b]Numbers show fruit-juice and bottled water samples of different brands, respectively.

The fluoride contents of 4 different brands of toothpaste and 1 of tooth powder are illustrated in Table 4. Concentrations of fluoride in tooth paste samples were between 447 and 1400 μg g^{-1} and for tooth powder was 74.5 ± 0.9 μg g^{-1}.

Table 4. Fluoride in toothpaste and tooth powder (n = 3).

Toothpaste (TP) samples	$\bar{X} \pm$ sd, (μg / g)
TP1[a]	1342 ± 34
TP2	1252 ± 36
TP3	1400 ± 128
TP4	447 ± 19
Tooth powder	795 ± 73

[a]Numbers show toothpaste samples of different brands.

Dissolved fluoride in soil is important for studying correlations between the environment and human health, because only water-soluble fluoride is transferred to water or absorbed by plants, after which it can be transferred to humans[8]. Car park dust samples were chosen as they cause health problems when inhaled by humans, especially in windy weather, and they occur in particle sizes of a few micrometers or less. Car park dusts originate mainly from soils, although atmospheric wet- and dry-deposition and traffic emission contributions occur. They also contain fluoride–bearing minerals found in soil, which are sparingly soluble in water such as fluorospar, cryolite and chiolite[5]. Fluoride from insoluble or sparingly soluble substances is less efficiently absorbed[5]. In this case, the soluble fraction of fluoride in the dusts is more important than their total fluoride content. For this reason, only the water-soluble fluoride contents of the dust samples analysed were taken into consideration. The concentration of water-soluble fluoride in 8 dust samples collected from Erciyes University campus car park was between 1.52 and 1.24 μg g^{-1} (see Table 5). According to the

WHO[5], the mean fluoride content of mineral soils is 0.2–0.3 g kg^{-1}, whereas that of organic soils is usually lower. However, in soils that have developed from fluoride-containing minerals, it may range from 7 to 38 $\mu g\ g^{-1}$.

Table 5. Water-soluble fluoride in dusts from Erciyes University campus car park (n = 2).

Soil samples (S)	$\bar{X} \pm$ sd, (μg/g)
S1	1.36 ± 0.10
S2	1.38 ± 0.02
S3	1.40 ± 0.02
S4	1.33 ± 0.01
S5	1.48 ± 0.06
S6	1.40 ± 0.02
S7	1.24 ± 0.04
S8	1.52 ± 0.04
Mean ± sd	1.39 ± 0.09

Conclusions

Measuring performed potentiometrically using a fluoride selective electrode is simple and inexpensive. Possible matrix effects can be easily eliminated by the addition of TISAB. Traces of fluoride can be determined directly in the liquid media studied (no laborious and time-consuming operations of sample preparation such as analyte enrichment are required).

According to the WHO, the optimum fluoride intake for humans ranges from 2 to 4 mg per day. The total daily intake of fluoride that may cause fluorosis in adults is over 13.0–14.5 mg per day[4]. Fluoride concentrations in tea infusions of 9 different brands of Turkish teas and imported ones ranged from 0.64 to 3.55 mg L^{-1}. As can be seen from the results, if daily tea consumption is too high, and intake of fluoride from other sources is excluded, tooth fluorosis due to the uptake excessive of fluoride may result. In addition, the authors suggest that the fluoride concentrations of food and beverage products be clearly declared by the producer on the product.

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