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Determination of Fluoride Content in Tea Infusion by Using Fluoride Ion-Selective Electrode

Josipa Giljanović[1,*], *Ante Prkić*[1], *Marija Bralić*[2], *Mia Brkljača*[3]

[1] Department of Analytical Chemistry, Faculty of Chemistry and Technology, Teslina 10/V, 21000 Split, Croatia.
[2] Department of Environmental Chemistry, Faculty of Chemistry and Technology, Teslina 10/V, 21000 Split, Croatia
[3] Department of Mediterranean agriculture and aquaculture, University of Zadar, Mihovila Pavlinovića bb, 23000 Zadar, Croatia.
[*]E-mail: josipa@ktf-split.hr.

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The fluoride content was analyzed in 43 tea infusion. The analyzed samples were the mints (family *Lamiaceae*), the mint (*Mentha piperita*) and lemon balm (*Mellissa officinalis*), green tea (*Camellia sinensis*) and pomegranate (*Punica granatum*) in tea bags, bottles and bulk purchased in local supermarkets and marketplaces in Split, Croatia, were determined. Potentiometric determination by using fluoride ion-selective electrode was applied in this work. Average F^- concentration in all tested samples was 0.116±0.211 mg L^{-1}. In order to get a better insight into the fluoride content in different plant samples, a One-Way ANOVA program R was used for statistical data analysis. Concentration of F^- follows log-normal distribution with parameters distribution of average concentration value of 3.77 mg L^{-1} and variance 3.00 mg^2 L^{-2}. F^- concentration was higher ($P < 0.001$) in infusions of green tea (0.393±0.23 mg L^{-1}) than in infusions of mint (0.011±0.004 mg L^{-1}) and pomegranate (0.008±0.002 mg L^{-1}) tea. On the other hand, F^- concentrations ($P < 0.001$) were lower in bulk samples (0.008±0.003 mg L^{-1}) than in tea bags ones (0.164±0.259 mg L^{-1}) and tea beverages (0.161±0.116 mg L^{-1}). F^- content was statistically different among same plant samples in correlation of samples packing. For green tea samples ($P < 0.001$) F^- concentration was higher in tea bags (0.558±0.12 mg L^{-1}) than in bottled green tea beverage (0.161±0.12 mg L^{-1}). We have got same situation for pomegranate tea samples, in tea bags (0.00921±0.002 mg L^{-1}) and bulk ones (0.00713±0.002 mg L^{-1}) respectively. For mint tea samples we did not find correlation between sample packing and F^- concentration.

Keywords: fluoride, tea infusion, potentiometric, determination, ion-selective electrode

1. INTRODUCTION

Fluorine is a halogen element and it is the most reactive non-metal. Its chemical behavior and properties are mainly different from other halogens elements. Fluoride is important anion too and occurs in various environmental, clinical and food samples. Fluorine is both beneficial oligoelement (needed for growth and bone tissue upholding and teeth) and toxic (for adults the lethal dose is 0.20-0.35 g F^- per kg body weight) [1]. Higher F^- concentration in the human body can be resulted by living in polluted environment and feeding with polluted food. Higher fluoride intake, above recommended levels (1.5 mg L^{-1}), leads to dental and skeletal fluorosis [2,3]. Acute fluoride intoxication can have neurological complications [4], urinary stone formation [5] and hypocalcaemia [6] as consequences on endemic patients. In recently published papers was described a link between fluoride intake and cancer [7-10].

Tea-consuming way has got a significant change in past few decades by spreading availability of instant formulations such as packed tea, powdered tea, and both bottled and canned tea beverages. Since tea (*Camellia sinensis)* is naturally rich in fluorine, the amount of fluoride consumed through these new tea ways of preparation and new philosophy of approach to the tea consumption culture [11].

It is estimated that packed tea and instant tea powder make about 30% of the total tea market, but their fluoride concentrations have not been well studied [11].

Potentiometric determination of fluoride by using fluoride ion-selective electrode (FISE) is very simple and fast method often described in similar determinations [1,11-15]

In this paper we made analysis of fluoride contents in three different plants and in different tea package for samples purchased in local supermarkets and marketplaces in Split, Croatia.

2.EXPERIMENTAL

2.1. Reagents and chemicals

All needed solutions were prepared by solving certain amount of chemicals in suprapure water. Suprapure water (declared conductivity 0.04 μS cm^{-1}) was prepared by Millipore Simplicity (USA). Following chemicals were used: Sodium nitrate, $NaNO_3$, p.a., Sodium fluoride, NaF, p.a., Sodium acetate, CH_3COONa, p.a., Sodium hydroxide, NaOH, p.a., Acetic acid, CH_3COOH, p.a., Kemika (Croatia). NaF was dried at 110 °C for two hours and after cooling was used as standard solutions needed for construction of calibration curve.

2.2. Apparatus

The indicator electrode was a combined fluoride ion selective electrode (FISE) DC219 from Mettler Toledo (Switzerland) [16]. Potentiometric data were recorded in the polyethylene vessel with a

millivoltmeter (Model MA 5740, Iskra, Ljubljana, Slovenia) coupled to a personal computer and recorder, Figure 1.

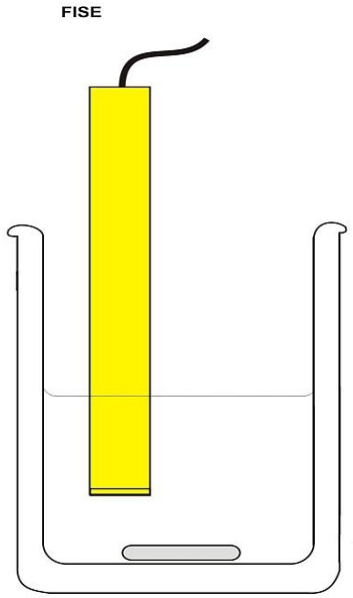

Figure 1. Potentiometric cell used for fluoride determination

In Figure 2 is given response of used DC219 from Mettler Toledo FISE in our experiment to fluoride ions at pH = 5.3.

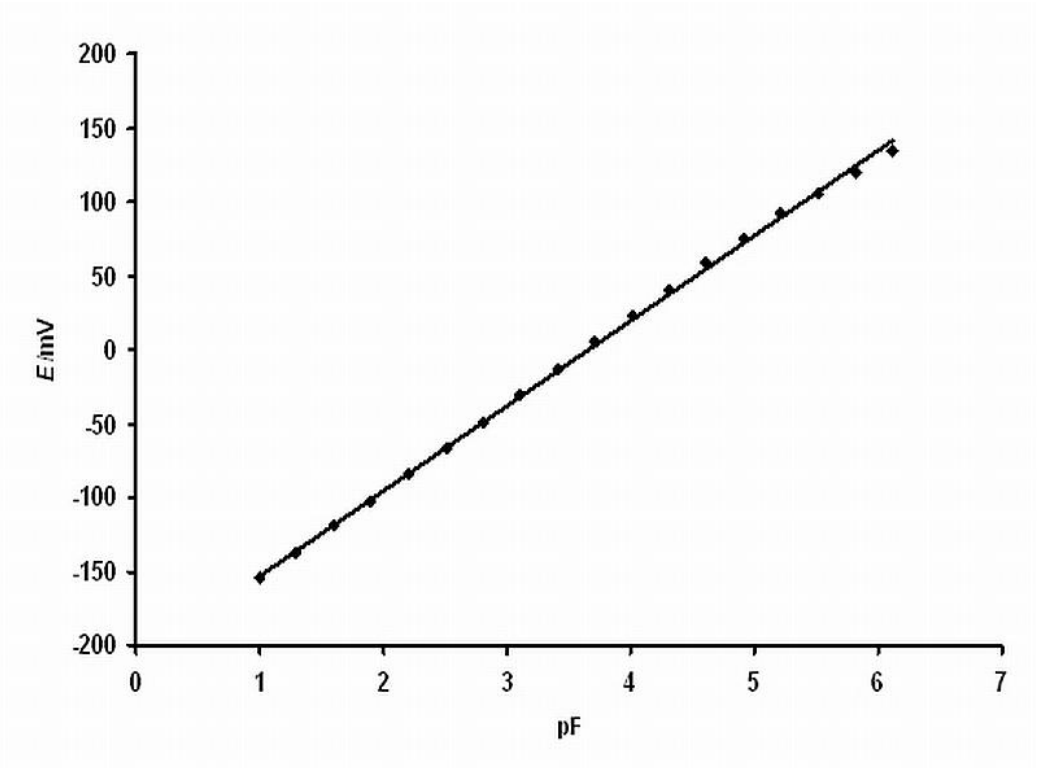

Figure 2. Response of FISE to fluoride ions at pH = 5.3

Potential change of 57.51 mV per decade of fluoride concentration change was recorded, with correlation coefficient of 0.9991, which is in good agreement with theoretical Nerstian slope for monovalent cations.

3. RESULTS AND DISCUSSION

The concentrations of fluoride ions in 15 different samples of mint tea (*Mentha piperitae folium* and *Melissa oficinalis*), 12 samples of green tea (*Camellia sinensis)* and 16 samples of pomegranate tea (*Punica granatum*) were analyzed.

All samples of analyzed tea were purchased at supermarkets and local marketplaces. The analyzed teas are commonly used by local people. Tea infusions were prepared on a customary way of tea preparation.

For all measurement suprapure water was used so that we can be sure that measured fluorides are from tea. From each tea were randomly selected five samples and dried at 80 °C for five hours and analyzed on fluoride content. The infusion was prepared using 2.0 g of tea leaves or tea bags, with 200 mL boiling suprapure water and place in water bath at 80 °C. The tea infusion was collect after 1, 5, 10, 20 min and after 24 hours and analyzed on fluoride level.

The amount of fluoride in tea infusion was analyzed by potentiometric methods using previously described FISE. Samples were prepared for analysis by adding 25 mL tea infusion with 5 mL acetate buffer, pH = 5.3 and 20 mL $NaNO_3$ to keep ionic strength and pH constant. During the measurement solutions were constantly mixing, and temperature was keep at 25 °C. All measurement was made for five samples of each tea and the final results presented here were average.

In Table 1. are given all collected information about analyzed tea as type of tea, name, geographic origin, shape and additive.

After collecting all data, we performed a statistical evaluation of collected data. An average F^- concentration was 0.116±0.211 mg L^{-1}. The pomegranate and mints had low level of fluoride ranging from 0.0016 mg L^{-1} to 0.016 mg L^{-1} F^- and from 0.0614 mg L^{-1} to 0.746 mg L^{-1} F^-, respectively. In order to get a better insight into the fluoride content in different plant samples, a statistical data analysis using the program *R* was performed.

Since all samples collected failed normality test, we performed nonparametric analysis on individual samples to compare the group of plant species samples or samples from each packaging type.

Plant species were compared as multiple independent samples while package of each tea species was performed by Kolmogorov-Smirnov test of two independent samples (Figure 3). Fluoride concentration was higher ($P < 0.001$) in infusions of green tea (0.393±0.23 mg L^{-1}) than in infusions of mint (0.011±0.004 mg L^{-1}) and pomegranate (0.008±0.002 mg L^{-1}) teas. We confirmed higher levels of fluoride in green tea than other plant species used for preparation of tea.

Table 1. Characteristic of analyzed tea samples and found fluoride content

	Plant species (Tea type and name)	Plant part (Tea form)	Package type	Country of origin	Country packed in	F^-/mg L^{-1} $n = 5$	F^-/mg kg^{-1} $n = 5$
Mint							
1.	*Mentha piperita*	leaf	bags	Austria	*Austria*	0.013	1.34
2.	*Mentha piperita*	leaf	bags	Croatia	*Croatia*	0.012	1.22
3.	*Mentha piperita*	leaf	bags	Croatia	*Croatia*	0.002	0.19
4.	*Mentha piperita*	leaf	bags	Croatia	*Croatia*	0.015	1.52
5.	*Mentha piperita*	leaf	bags	Croatia	*Croatia*	0.016	1.61
6.	*Mentha piperita*	leaf	bags	Poland	*Germany*	0.012	1.17
7.	*Melissa officinalis*	leaf	bags	Poland	*Germany*	0.011	1.11
8.	*Mentha piperita*	leaf	bags	China	*UK*	0.009	0.87
9.	*Mentha piperita*	leaf	bulk	Croatia	*Croatia*	0.009	0.89
10.	*Mentha piperita*	leaf	bulk	Croatia	*Croatia*	0.010	0.98
11.	*Mentha piperita*	leaf	bulk	Croatia	*Croatia*	0.007	0.69
12.	*Mentha piperita*	leaf	bulk	Serbia	*Croatia*	0.013	1.27
13.	*Mentha piperita*	leaf	bulk	Croatia	*Croatia*	0.014	1.38
14.	*Melissa officinalis*	leaf	bulk	Croatia	*Croatia*	0.013	1.27
15.	*Melissa oficinalis*	leaf	bulk	Croatia	*Croatia*	0.002	0.16
Green tea							
1.	*Camellia sinensis*	leaf	bags	China	*Croatia*	0.638	63.8
2.	*Camellia sinensis*	leaf	bags	China	*Croatia*	0.363	36.3
3.	*Camellia sinensis*	leaf	bags	Austria	*Austria*	0.609	60.9
4.	*Camellia sinensis*	leaf	bags	China	*Croatia*	0.746	74.6
5.	*Camellia sinensis*	leaf	bags	China	*Croatia*	0.556	55.6
6.	*Camellia sinensis*	leaf	bags	China	*UK*	0.464	46.4
7.	*Camellia sinensis*	leaf	bags	China	*Croatia*	0.533	53.3
8.	*Camellia sinensis*	leaf	bottled	China	*Croatia*	0.091	-
9.	*Camellia sinensis*	leaf	bottled	China	*Austria*	0.177	-
10.	*Camellia sinensis*	leaf	bottled	China	*Croatia*	0.354	-
11.	*Camellia sinensis*	leaf	bottled	China	*Croatia*	0.123	-
12.	*Camellia sinensis*	leaf	bottled	China	*China*	0.061	-
Pomegranate tea							
1.	*Punica granatum*	cuttings	bags	Croatia	*Croatia*	0.016	1.59
2.	*Punica granatum*	cuttings	bags	Croatia	*Croatia*	0.009	0.91
3.	*Punica granatum*	cuttings	bags	Croatia	*Croatia*	0.011	1.11
4.	*Punica granatum*	cuttings	bags	Croatia	*Croatia*	0.010	0.99
5.	*Punica granatum*	cuttings	bags	Croatia	*Croatia*	0.010	1.03
6.	*Punica granatum*	cuttings	bags	Croatia	*Croatia*	0.008	0.75
7.	*Punica granatum*	cuttings	bags	Croatia	*Croatia*	0.102	1.03
8.	*Punica granatum*	cuttings	bags	Croatia	*Croatia*	0.007	0.75
9.	*Punica granatum*	cuttings	bags	Croatia	*Croatia*	0.007	0.72
10.	*Punica granatum*	cuttings	bags	Croatia	*Croatia*	0.007	0.71
11.	*Punica granatum*	cuttings	bags	Croatia	*Croatia*	0.007	0.69
12.	*Punica granatum*	cuttings	bulk	Croatia	*Croatia*	0.008	0.74
13.	*Punica granatum*	cuttings	bulk	Croatia	*Croatia*	0.007	0.64
14.	*Punica granatum*	cuttings	bulk	Croatia	*Croatia*	0.006	0.69
15.	*Punica granatum*	cuttings	bulk	Croatia	*Croatia*	0.007	0.73
16.	*Punica granatum*	cuttings	bulk	Croatia	*Croatia*	0.007	0.72

Table 2. Fluoride content in tea infusions from pomegranate, mint and green tea (mg L^{-1})

Plant	Mean	Minimum	Maximum	Standard deviation	Median	No. of samples
	mg L^{-1}					
Pomegranate	0.0104	0.00160	0.0161	0.00431	0.0117	15
Mint	0.393	0.0614	0.746	0.235	0.414	12
Green tea	0.00843	0.00640	0.0159	0.00243	0.00735	16
All	0.116	0.00160	0.746	0.211	0.0111	43

Comparison of samples packaging revealed that F^- concentrations ($P < 0.001$) were higher in tea bags samples (0.164±0.259 mg L^{-1}) and bottled ones (0.161±0.116 mg L^{-1}) than in bulk samples (0.008±0.003 mg L^{-1}). F^- content was statistically different among packing type of the same plant species, only for green tea samples. F^- concentration was higher ($P < 0.001$) in tea bags (0.558±0.12 mg L^{-1}) than in bottled green tea beverage (0.161±0.12 mg L^{-1}). Probably size of tea pieces used has high effect on levels of fluoride in infusion, as tea material is finer the extraction of fluoride would be higher. That should be considered when higher daily tea consumption is expected. For mint tea samples and pomegranate tea samples F^- concentration was not affected by sample packing type being tea bags and bulk tea leaves, see Figure 3.

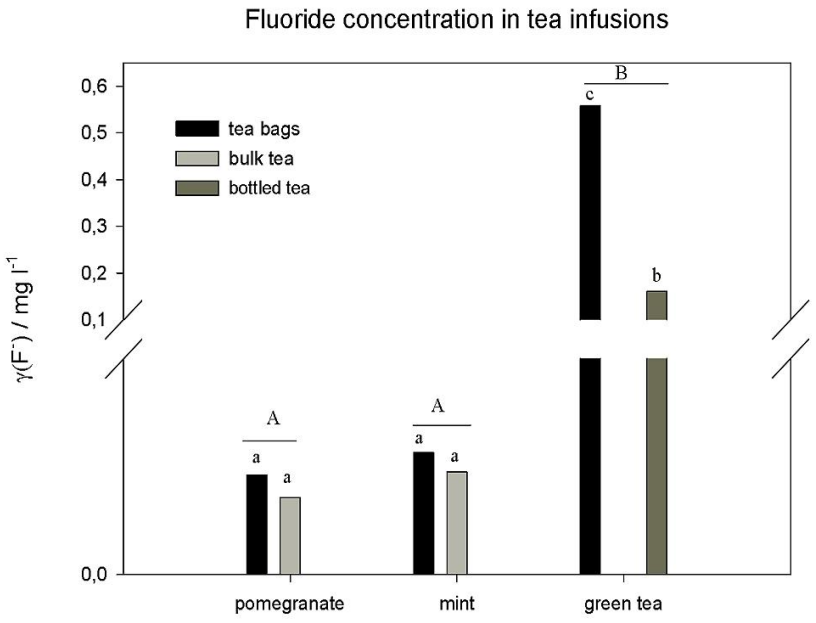

Figure 3. The effect of plant species and package on fluoride concentrations in tea infusions.

Plant species (upper cases) and package of each tea species (lower cases) were compared by nonparametric statistical test. The different letters indicate statistical difference at 0.01 level of significance.

When we compare our results of fluoride content for green tea samples with ones from similar investigations [1,11-15, 17-21], it can be seen a small difference. The difference can be explained by origin of green tea and producing ways. In China fluoride content in soil is higher than in Austria and probably has difference for each region in China (see Table 1.). It is known that plants absorb fluoride from soil during the growth. Mainly of the absorbed fluoride in plants are stored in the leaves and the leaves are common plant parts for tea preparation because of easily harvesting, handling and brewing. For most mint and all pomegranate teas we were not able to find suitable data for comparison. It is interesting to compare our results for fluoride content in mint teas with ones from Serbia [22]. Fluoride content for cultivated mint is very similar likewise in our work, but there is significant difference (around ten times higher concentration) for wild mint, what is probably caused by difference in soil types. We are stressing that most of mint (67 % of samples) and all pomegranate tea samples were cultivated in Croatia. Water in Croatia is not being fluorinated and for all purposes (eg. drinking, agriculture and industry) is used natural spring water.

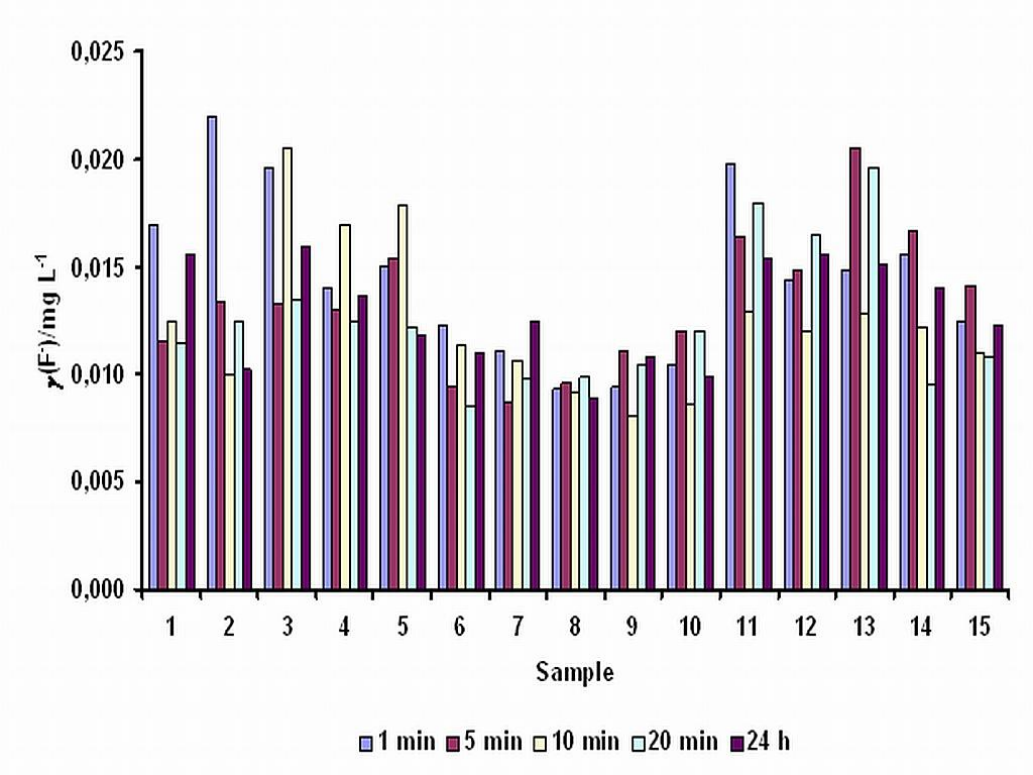

Figure 4. The changing of fluoride concentrations in mint tea infusions

We examined how brewing time affects at fluoride concentration for tested tea samples. We found out that in most cases fluoride concentration reaches maximum in 10 to 20 min, especially for mint and pomegranate tea samples. We are able to say that there is a correlation between fluoride concentration change in time and tea packing form. Extraction of fluoride is very well connected with size and plant form. Extraction is better for finely and smaller plant cuttings, what is reasonably because such samples have larger specific surface for contact with solution. On the other hand, it can be seen a relation of fluoride concentration and brewing time with country of origin for same packing form (mint tea samples 1-8). The same situation was seen in similar investigation [1,11-15] what was

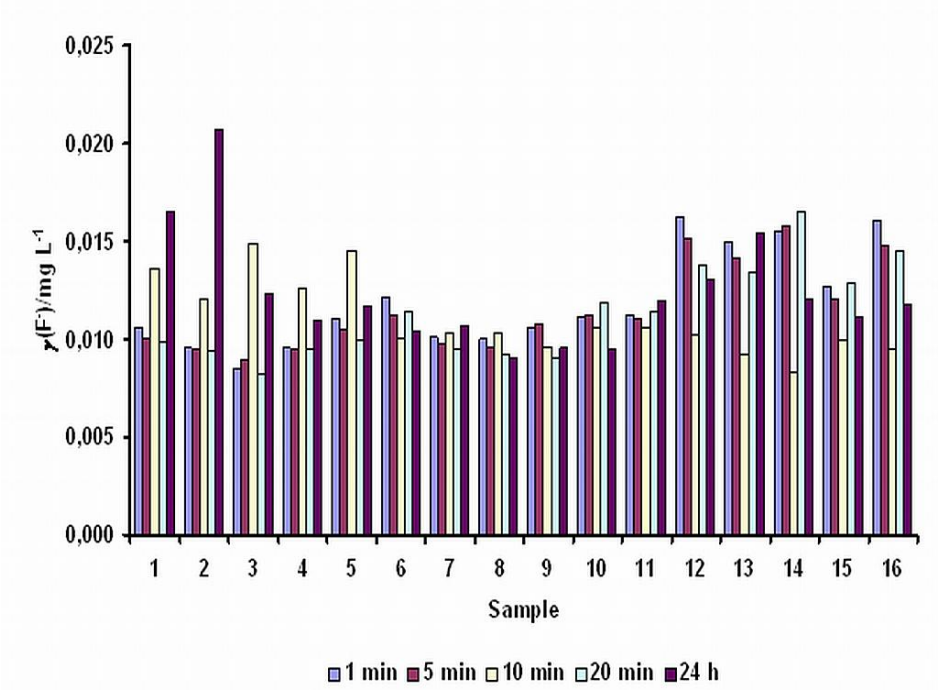

Figure 5. The changing of fluoride concentrations in pomegranate tea infusions

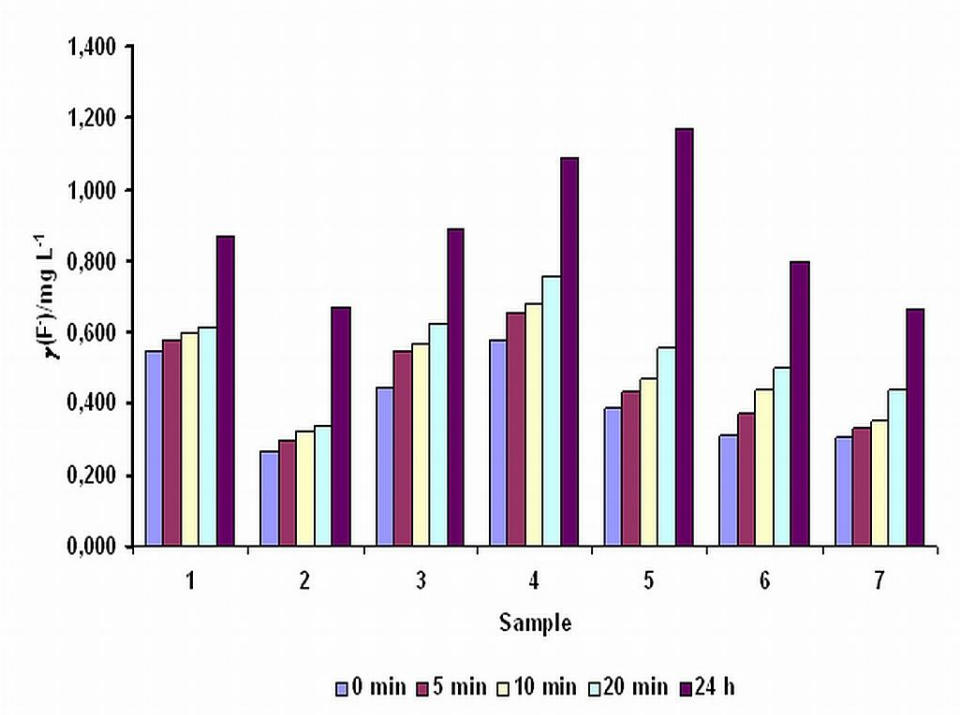

Figure 6. The changing of fluoride concentrations in green tea infusions

explained by adsorbing of fluoride at tea bags. There is no significant F^- concentration increase depending on brewing time for mint and pomegranate tea samples. The completely different situation was for green tea samples, where we found a continuous increase of F^- concentration. When we

compared fluoride concentration for green tea samples in the beginning of measurement and after 24 h, fluoride concentrations were doubled and for samples 4 and 5 it was almost same to maximum daily allowed fluoride intake (1.1 and 1.2 mg L^{-1} versus 1.5 mg L^{-1}). This interesting fact gave us a new idea of measuring fluoride content in bottled green tea samples (samples 8-12). Bottled teas are very common and popular beverages with very wide aroma palette (green tea, peach, lemon, orange, green, etc.) Hence, we performed measurement for such investigation and all samples were manufactured by local companies. We found out constant fluoride concentration in measurements lasted for 5 min. according the tested bottled tea samples, we can conclude that there is no significant F^- concentration rise and such teas are safe for human health. We are stressing that we tested a limited number of bottled teas samples. This can be part of our future investigations. Results are shown in Figures 4.-6.

4. CONCLUSION

Maximum of found fluoride concentration in analyzed samples is about 3 times lower than maximum allowed daily intake (0.558 versus 1.5 mg L^{-1}). Green tea samples have significantly higher fluoride concentration compared with ones for mint and pomegranate tea what was expected according information about fluoride accumulation in green tea. We found the effect of sample's package on fluoride levels, but only for green tea samples. Higher levels were found in tea samples packed in tea bags than in bottled ones, for green tea samples concentration in tea bags was 0.558±0.12 mg L^{-1} and in bottled green tea beverage was 0.161±0.12 mg L^{-1}. Results show that F^- concentration depends both on brewing time and leaching fluoride from tea, but does not happen in same way. Would fluoride concentration increase or decrease, it depends on how fine are plant cuttings (in fact on specific surface and for smaller cuttings it would be greater) and on country of origin, soil type, respectively. According the results, we would not suggest anyone drink a tea after 24 h of preparation, especially green tea, because fluoride concentration can be very high and/or above recommended maximum daily intake of fluoride. In normal way of dinking, for tested samples, people would obey manufacturer's recommended procedure for tea preparation and assure themselves of possible fluoride poisoning.

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