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Evaluation of fluoride ion residues in black tea after fumigation with sulfuryl fluoride

Siyah çayda sülfüril florit fumigasyonu sonrası florür iyonu kalıntısının değerlendirilmesi

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ABSTRACT

Sulfuryl fluoride is a colorless, odorless gas used as a fumigant against pests during the storage of durable agricultural products. It is also one of the alternatives to methyl bromide, which is banned by the Montreal Protocol. During a fumigation, the decomposition product of sulfuryl fluoride residue can also be formed in addition to the sulfuryl fluoride residue. Fluoride is actually a natural ingredient of the tea plant. However, within the growing process of the tea plant fluoride is concentrated in the old leaves when compared with the young shoots. Investigating the variation of the fluoride content in black tea before and after sulfuryl fluoride fumigation is the subject of this study. Three different brands of black teas with different fluoride concentrations purchased from local supermarkets in 2022 were fumigated with approximately 60 g/m^3 of sulfuryl fluoride for 24 hours in a 1 m^3 fumigation chamber. The AOAC's recommended method for extraction of fluoride in plants (Method 975.04) was applied in this study. It was compared with the fluoride contents after fumigation in teas (41.4; 165.1 and 329.5 mg/kg, respectively). It is concluded that there is no statistically [$t(7)=0.284$; $t(7)=0.769$ and $t(7)=1.419$ $p>0.05$] significant difference in fluoride content in teas after fumigation.

INTRODUCTION

Fluorine, which is one of the halogen group elements in the periodic table, can be found naturally in the environment, as well as anthropogenic origin due to intense industrialization. As a nutrition, fluorine can be found in nearly every food. The highest concentration is in tea and seafood (Waldbott 1963). It has been reported that fluoride in foods can cause gastrointestinal disorders and muscle-neurological disorders and problems in teeth, bones and joints (Roholm 1937, Waldbott et al. 1978). On the other hand, when fluoride is evaluated in terms of its positive effects on human health, it has been reported that moderate fluoride intake can reduce the incidence of dental caries and support the development of strong bones under certain conditions (Doull et al. 2006, Kaminsky et al. 1990). In a clinical study conducted in this context, it was concluded that fluoride intake supplemented with suitable doses of calcium and vitamin D can improve bone mineralization (Jowsey et al. 1972). For this reason, researchers are trying to determine the optimal fluoride concentration that should be taken to reduce dental caries. It has been reported that the sharpest reduction in dental

caries occurs when the fluoride concentration in drinking water is between 0.7 to 1.2 mg/l, with little additional benefit when fluoride goes beyond this range and is also associated with increased fluorosis (Heller et al. 1997). It is also notified that fluoride intake cannot be predicted considering the individual differences in food consumption habits of consumers, as well as food processing and preparation (Waldbott 1963).

The maximum residue limits (MRL) of plant protection products are one of the food safety standards for agricultural products. According to the good agricultural practices (GAP), pesticide residues lower than the related MRLs in foods will not cause a toxicological concern. The aim of this study is to investigate the amount of fluoride residue in black teas fumigated with sulfuryl fluride and to determine its contribution to their total fluoride contents. For this purpose, three different brands of black teas with different fluoride concentrations purchased from local supermarkets in Ankara in 2022 were fumigated with approximately 60 g/m^3 of sulfuryl fluoride for 24 hours in a 1 m^3 fumigation chamber. Application dose preference is as recommended by the European and Mediterranean Plant Protection Organization (EPPO 2008).

MATERIALS AND METHODS

Samples and reagents

Three different brands black tea (*Camellia sinensis*) purchased from the local supermarket. All reagents used in this work were of analytical grade or better. Water obtained from a Milli-Q system was used to prepare all solutions.

Determination of loss in mass of tea

Mass loss in tea samples was determined according to ISO 1573-1980 method (Anonymous 1980). The nearest 0.001 g about 5 g of tea samples were kept in an oven at 103 ^{O}C until constant weight.

Fumigation technique

The fumigation process was carried out in a controlled room with 21-22 ^{O}C ambient temperature and the relative humidity is around 36-37%. Approximately 500 g of tea samples were placed in a 1 m^3 fumigation chamber and the lid was tightly closed. The valve of the pressurized steel tube containing 99.8% sulfuryl fluoride (PROPESTGAS) placed on a scale (Dikomsan UNIVERSAL, MS-RAW) was opened and approximately 60 g of gas was delivered to fumigation chamber. The gas amount in the fumigation chamber was monitored with a real time gas concentration analyzer (RIKEN KEIKI, FI-8000) at the beginning and end of 24 hours.

Fluoride calibration solution preparation

For 100 ppm F (1) Stock solution: Dried 1 g NaF 2 hours at 110 ^{O}C, after 0.2210 g NaF was dissolved in a 1 l volumetric flask with H_2O. And than for

(2) Intermediate solution 10 ppm F: dilute 10.0 ml stock solution to 100 ml with H_2O.

(3) Working solution: Prepare as in Table 1 in 100 ml volumetric flasks.

Table 1. Preparation of working solution

	ml solution to be diluted to 100 ml			
Concentration (ppm)	0.4 M KOH_3	0.8 M Na citrate	100 ppm F solution	10 ppm F solution
10	10.0	5.0	10.0	0.0
2	10.0	5.0	2.0	0.0
0.5	10.0	5.0	0.0	5.0
0.2	10.0	5.0	0.0	2.0
0.1	10.0	10.0 ml Na citrate solution containing 1 ppm F		

Sample preparation

The AOAC's recommended method for extraction of fluoride in plants (Method 975.04) was applied in this study. Tea samples were ground using a laboratory mill (Retsch ZM200) and sieved from a No. 40 sieve. 0.5 g powdered samples were weighed in 100 ml polyethylene vessels, 20 ml of 0.05 N HNO_3 was added, and the mixture shaken for 20 min on a rotating shaker. Next, 20 ml of 0.1 N KOH was added, and agitation was continued for an additional 20 min. Afterward, 5.0 ml of 0.4 M sodium citrate solution containing 1 ppm fluoride adjusted to pH 5.5 was added, and the mixture was vortex mixed for 1 min. 5.0 ml of 0.2 N HNO_3 was added and vortex mixing was repeated for 1 min. The mixture was then filtered through Whatman No. 40 filter paper.

Measurement of fluoride

Fluoride ion selective electrode (Orion Fluoride Electrodes 9609BNWP) was immersed in the solutions and readings on the ion analyzer (Orion Star A324 pH/ISE Portable Multiparameter Meter) were recorded. The fluoride concentration was determined using the standard curve (Figure 1) and calculated according to the equation:

$$\text{ppm F} = (C-0.10)x50/w$$

Where C=ppm F from curve; 0.10 =ppm background F; 50= ml final solution; w=g test portion.

Data analysis

The data obtained as a result of the study was primarily tested whether it showed a normal distribution. No transformation was adhered to the normally distributed data. Then, using the SPSS (IBM Corp., Armonk, NY) program, the differences between the treatments were made according to the paired-t test ($P<0.05$).

RESULTS AND DISCUSSION

The mass loss of the teas and sulfuryl fluoride measurements in the fumigation chamber

The mass loss of the teas and sulfuryl fluoride measurements in the fumigation chamber at the beginning and end of the fumigation are in Table 2. There was no significant difference in the mass loss measurements of the teas nor in the sulfuryl fluoride concentration during fumigation. One of the most important quality parameters for dry granulated tea is the moisture content it contains. Considering the weight losses of the tea samples before and after fumigation, it can be concluded that tea samples were not absorb the humidity of the environment during fumigation.

Table 2. The mass loss of the teas and sulfuryl fluoride measurements

	Before Fumigation	After Fumigation	Initial Measurements	After 24 hours
	% The mass loss ±SD* (n=3)		Sulfuryl fluoride (g/m³)	
Brand 1	6.67±0,08	6.77±0,05	60.5	60.5
Brand 2	3.91±0,04	3.93±0,06	61.1	61.0
Brand 3	5.14±0,08	5.11±0,06	59.8	59.7

*SD: Standard deviation

Linearity of the standard curve

Using fluoride ion selective electrode and working solution just like Table 1 sodium fluoride solutions, a standard curve for the fluoride concentration was obtained (Figure1). Excellent linearity achieved in the 0.1-10 mg/l fluoride range. The measured potential from fluoride ion selective electrode corresponding to the level of fluoride ion in solution is described by the Nernst equation (Nernst 1907):

$$E = S\log C + {}^{\circ}E$$

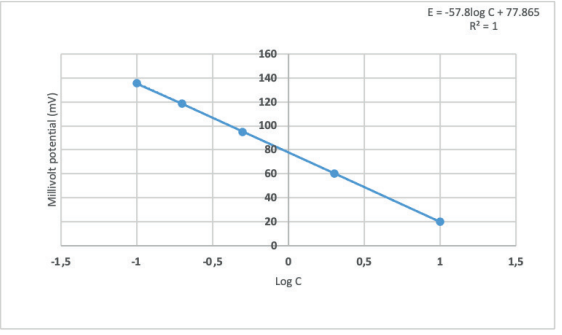


Figure 1. Standard calibration curve of fluoride

Where C is the mg/l fluoride yielding a millivolt potential of E, S is the slope, and °E is reference potential. A slope range 54 to 60 mV is recommended in the user manual (Anonymous 2016). In this study, it was obtained as 57.8 mV The calibration curve was generated for each measurement with $R^2=1$.

Fluoride content of teas

The fluoride contents of three different tea brands before and after fumigation are shown in Table 3. According to these data, there is no statistically significant difference in fluoride content of tea samples with three different fluoride contents before and after fumigation.

Table 3. Fluoride content of teas

	N		Mean (mg/kg) ±SD* (Max-Min)	t test t	t test P
Brand 1	Before Fumigation	8	41.4±2.4 (44.9-37.6)	0.284	0.784
	After Fumigation	8	41.8±4.0 (49.8-37.4)		
Brand 2	Before Fumigation	8	165.1±5.4 (172.4-154.6)	0.769	0.467
	After umigation	8	166,5±6.9 (176.3-156.1)		
Brand 3	Before Fumigation	8	329.5±13.7 (353.2-310.9)	1.419	0.199
	After Fumigation	8	338.7±17.3 (361.2-316.3)		

*SD: Standard deviation

Tea (*Camellia sinensis*) is the most consumed beverage in the world after water (Vinson 2000). Therefore, its effects on health are significant. The natural content of fluorine in tea has been known for a long time (Lockwood 1937, Reid 1936). While it accumulates in the leaves of the tea plant due to the growing conditions, fluorine is higher in old leaves than in young shoots (Shu et al. 2003). Hudaykuliyev et al.

(2005) reported the average fluorine content of black tea produced in Türkiye as 156.3±34.76 mg/kg (87.6-289.2 mg/kg) of black tea. Lu et al. (2004) reported that fully fermented black tea has a fluorine content of 44 to 141 mg/kg in China. Furthermore, Ashenef and Engidawork (2013) reported that the fluoride concentration in tea samples ranged from 35±1.71 to 929.33±16.77 mg/kg, and that Ethiopian teas contained higher amounts of fluorine compared to teas from other origins they evaluated in their research. From these studies, the level of fluorine in granulated black tea can reach very high levels, but there is a gap in information about how much it should contain.

Sulfuryl fluoride (SO_2F_2) is an alternative fumigant to methyl bromide which is prohibited by the Montreal Protocol (Anonymous 1987). Sulfuryl fluoride is used to control pests within the post-harvest period of durable

agricultural products. Therefore, fumigation may leave considerable amounts of fluoride ion residues as a break-down product. Also significant residues of fluoride ion can be present from various sources, and separate MRLs for fluoride ion should be proposed based on background levels (EFSA 2021).

Due to the European Union Standards the allowed upper limit for fluoride ion residue in black tea products is 350 ppm. However, this upper limit is applied as 400 ppm since February 21, 2023 (Anonymous 2022). The recommendation of this MRLs for the fluoride ion in foods is still contraversial. According to the results of this study, the background fluoride concentrations in black tea samples that were examined have not been affected by the fumigationW with sulfury fluoride. Suggesting individual MRLs for the fluoride ion based on background levels is not possible due to current analysis techniques. Therefore, it can be considered as the answer to the question of how much the tolerance limit for fluorine in the natural content of granulated black tea should be. In addition, for the definition of residue, it may be more accurate to express it as a total inorganic fluoride ion instead of fluoride ion.

The Adequate Intake (AI) of fluoride recommended by European Food Safety Authority (EFSA) for both children and adults (covering all sources) is reported as 0.05 mg/kg-bw/day (EFSA 2013). The results of this study might be useful to predict whether the total fluoride intake is lower than the adequate intake level (0.05 mg/kg-bw/day) for the top tea consumers. Tea consumption can be recommended to people as the most natural and measurable way to get fluorine. For this purpose, it is of great importance to know the fluoride concentrations in tea products, especially for people who consume large amounts of tea in their daily lives. The choice of tea preparation and serving affects the fluoride content. Therefore, it should be considered in the amount's evaluation of daily fluoride intake.

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ÖZET

Sülfüril florit, tarım ürünlerinin depolanması sırasında zararlılara karşı fumigant olarak kullanılan renksiz, kokusuz bir gazdır. Ayrıca Montreal Protokolü ile yasaklanan Metil bromitin alternatiflerinden biridir. Fumigasyon sırasında gıdalarda Sülfüril florit kalıntısına ek olarak bozunma ürünü olan flor iyonu kalıntısı da oluşabilmektedir. Çayın doğal içeriğinde bulunan florür uzun zamandan beri bilinmektedir ve çay bitkisinin yetişme şartlarından dolayı genç sürgünlere göre yaşlı yapraklarda daha fazla bulunmaktadır. Sülfüril florit fümigasyonundan sonra siyah çaydaki florür içeriğindeki değişim bu çalışmanın konusunu oluşturmaktadır. 2022 yılında yerel süpermarketlerden satın alınan farklı florür konsantrasyonuna sahip üç farklı ticari markalı siyah çay örneği, 1 m^3'lük fümigasyon odasında 24 saat boyunca yaklaşık 60 g/m^3 Sülfüril florit ile fümigasyona tabi tutulmuştur. Bu çalışmada florür ekstraksiyonu için AOAC'ın bitkisel ürünlerde önerdiği yöntem (Metot 975.04) kullanılmıştır. Fumigasyon öncesinde sırasıyla 41.4; 165.1 ve 329.5 mg/kg olarak belirlenen florür içerikleri fumigasyon sonrası florür konsantrasyonları ile karşılaştırılmış ve istatistiksel olarak anlamlı bir fark olmadığı [t(7)=0.284; t(7)=0.769 ve t(7)=1.419 P>0.05] sonucuna varılmıştır.

Anahtar kelimeler: florür, kalıntı, siyah çay, sülfüril florit, fumigasyon, iyon seçici elektrot, yeterli florür alımı

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