Asian Journal of Chemistry; Vol. 27, No. 8 (2015), 2847-2850

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18243

Fluoride Contents Analysis of Tea Infusion, Mouthwash and Tooth Paste Samples of Pakistan Using Ion Selective Electrode

RABIA REHMAN* and MARIA KHALID

Institute of Chemistry, University of the Punjab, Lahore-54590, Pakistan

*Corresponding author: Fax: +92 42 99230998; Tel: +92 42 99230463, Ext: 870; E-mail: grinorganic@yahoo.com

Received: 3 June 2014; *Accepted*: 6 August 2014; *Published online*: 27 April 2015; AJC-17147

Potentiometric analysis of fluoride is carried out in tea, tooth paste and mouth wash/teeth whitener samples which are commonly used in Pakistan using fluoride ion selective electrode. Due to lack of awareness and contaminated plus adulterated food usage, dental and skeletal fluorosis increased in different areas. The analysis of locally available samples of tea, tooth paste and mouthwash indicated that the concentration of fluoride is within the threshold limits in branded samples, but their excessive use should be minimized for avoiding fluorosis.

Keywords: Fluoride, Tea, Mouthwash, Tooth paste, Ion selective electrode.

INTRODUCTION

Fluoride is the anion of fluorine belongs to halogen family. Its salts are usually water soluble and it is easily leached out in water sources form its minerals found in earth crust, like: fluoroapatite ($Ca_5F(PO_4)_3$), cryolite (Na_3AlF_6) and some types of mica[1]. Fluoride is considered beneficial for human beings for preventing tooth decay and curing dental caries. In last century, different fluoride containing dental care products came into market, which has a serious threat especially for growing children[2]. According to W.H.O., the permissible range of fluoride is 2-4 mg/day for adults[3]. Its excessive amounts lead to dental fluorosis, which is indicated by staining and mottling of teeth, and skeletal fluorosis in severe conditions, which is indicated by bony deformities. Fluoride also inhibits many enzymes activity by creating complex with the active sites metal center. So, its excessive use should be prohibited[4]. Different sources of exposure to fluoride containing commodities for human beings are categorized as followed: industries, dental care products, canned food, drinks, tea and coffee products, insecticides and pesticides. In processed foods, fluoride came from fluoridated water, pesticides residues in food, Teflon pans and mechanically debone processing, like in chicken[4].

Tea (*Camellia sinensis L*), whether green or black, is naturally rich in fluoride. Its plant takes up fluoride from ground soil and water and stores in leaves. Fluoride levels in tea ranges in between 3.2 to 400 mg/kg was reported by Fung and coworkers[5]. Fresh leaves have low fluoride contents than older, dried leaves. Dental care products like: tooth paste, gel dentifrice, mouth wash and teeth whitener were also rich in fluoride. Tooth paste compromises of 20-42 % water, abrasives, fluoride and detergents. Abrasives constitute at least 50 % of typical tooth paste. These insoluble particles help remove plaque from the teeth. The removal of plaque and calculus helps minimize cavities and periodontal disease. Examples are: aluminum hydroxide, calcium carbonate, zeolites, hydroxyapatite, ($Ca_5(PO_4)_3OH$) and powdered white mica. The polishing of teeth eliminates stains from teeth, but has nothing to do with dental health. Fluoride in various forms like NaF, olaflur, sodium monofluorophosphate and stannous fluoride is found in toothpaste[6-8].

For analyzing fluoride contents, volumetric, colorimetric, gas chromatographic and radiometric methods were used by different workers[2]. Potentiometric method has many advantages over all of them, being low-cost, selective, specific and sensitive technique. It can analyze fluoride contents up to ppb levels in presence of other ions. The influence of interfering ions and pH regulation is controlled by employing TISAB (Total ionic strength adjustment buffer). The working range of pH is 5 to 7, because fluoride selective electrode is sensitive to hydroxide ions also. So, pH adjustment is necessary before analysis[9]. This way is already successfully employed for determination of fluoride in different samples, like: water, serum[10], urine[11], pan masla[12], tooth paste, tea and fruit juices[13]. So in this study, this method is applied for fluoride analysis of different commodities, like tea, tooth paste and mouth wash samples collected from Pakistan.

EXPERIMENTAL

Fluoride analysis requires sensitive methodology. Ion selective electrode (ISE) has been used in this study. This method is easy to employ and suitable for uninterrupted monitoring. It is economical, sensitive and selective way of analyzing fluoride. It is used for the determining fluoride contents of drinking water, industrial wastes, seawater, air, aerosols, fuel gases, minerals, urine, serum, plasma, plants, food, drinks and tea. If a sample contains water-soluble or suspended organic substances in addition to its metallic cations, fluoride contents may be slightly lower than the levels in real samples due to adsorption and chelation of free fluoride[13].

Fluoride stock solution (Jenway 025 087), Ion selective electrode (Jenway ISAB-025 107) and TISAB (total ionic strength adjustment buffer, containing 58 g NaCl, 57 mL glacial acetic acid, 4 g of 1,2-cyclohexanediamine-N,N,N′,N′-tetracetic acid (CDTA) and 150 mL of 6 M NaOH) were used. Samples of tea, tooth paste and mouthwashes were collected from local markets of native town. Micropippette of 100-1000 µL Biohit (720060) and deionized water (> 18 M/cm) for dilutions

Calibration of ion selective electrode: Fluoride standard solutions range for this analysis was 20-200 µmol/L. The calibration curve was obtained by direct potentiometry with calibration standards and graph was shown in Fig. 1. For calibration, 0.7 mL of each standard solution was added to 0.3 mL of TISAB in a 5 mL glass tube, shaken well and let to stand for 2 min to allow for equilibrium. The stable reading was obtained after 1 min[10].

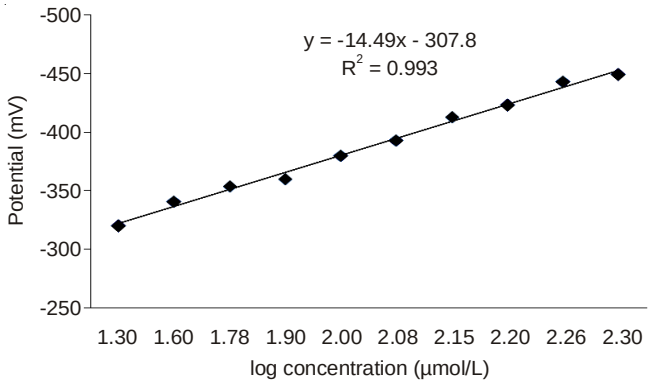

Fig. 1. Calibration line for fluoride analysis

Preparation of samples

Tea samples: Total 38 samples were collected from home town and labeled as their brand names. Then for analyzing fluoride contents this procedure was adopted for all samples. 1 g of tea sample was taken in a beaker along with 100 mL deionized water and boiled for 5-10 min. It was cooled and filtered, then diluted to 100 mL again[14-16].

Toothpaste samples: Total 15 toothpaste samples were collected and labeled as their brand names. Then 1 g of each toothpaste sample was dissolved in 100 mL of deionized water separately and boiled for 5-10 min. It was cooled and filtered, then diluted to 100 mL again for further analysis[13].

Mouth wash samples: Total 7 mouthwash and teeth whitener samples were collected and labeled as their brand names. Then 1 g of each sample was diluted to 100 mL with deionized water and heated for 5-10 min. They were cooled, filtered and the volume of filtrate was made 100 mL. Then 0.7 mL of this sample and 0.3 mL (total 1 mL) of TISAB were taken in small test tube and analyzed by ISE[8].

Analysis of fluoride contents by ion selective electrode: For this, 0.7 mL of tea filtrate and 0.3 mL of TISAB were taken in small test tubes separately for each sample and their electric potential was determined using ion selective electrode. Double distilled water is used for dilutions. Ion selective electrode (composite type) is calibrated first with standard solutions of fluoride and then all samples were analyzed subsequently. Electrode was washed and dried after dipping, so the risk of error is minimized by carefully controlled method[10,11].

Validation and reproducibility of analytical procedures for analyzing fluoride by ISE: The procedure is repeated for six measurements on the sample matrix and average values were mentioned. For standardizing the procedure, standard solution was spiked in three sample solutions of each type (*i.e*. Lipton tea, English tooth paste and Listerine mouthwas) and percentage recovery was calculated in each case using eqn. 1:

$$\text{Recovery (\%)} = \frac{\text{[Matrix spike sample result (µmol/g)]} - \text{[Parent (unspiked) sample result (µmol/g)]}}{\text{Spike amount ((µmol/g)}} \times 100 \quad (1)$$

The resulting data shown in Table-1 indicated the reproducibility of adopted method by considerably low values (below 10 %) for relative standard deviation (RSD) and good recovery range (98-101 %).

RESULTS AND DISCUSSION

Potentiometric determination of fluoride contents in tea, tooth paste and mouth wash samples were carried out using fluoride sensitive electrode and results were shown graphically in Fig. 2. It is easy, reliable and economical way of determining fluoride in variety of samples[10]. The permissible level of fluoride in drinking water is considered to be less than 1.5 mg L^{-1} (µmol/L). Up to this level, it facilitates in decreasing dental caries, but at or above 2 mg L^{-1} (105 µmol/L), it can lead to dental fluorosis, whereas at 8 mg L^{-1}, it can lead to osteopathies[11]. The concentrations of fluoride ions in 38 different samples of tea, 15 different samples of tooth paste and 7 different samples of mouthwash were analyzed.

TABLE-1
VALIDATION OF FLUORIDE ANALYSIS METHOD.

Sr. no.	Sample	Parent (unspiked) sample (µmol/g)	Spiked concentration (µmol/g)	Matrix spiked sample spiked result (µmol/g) ± S.D	RSD	Recovery (%)
1	Vital tea	1.6	2	3.62 ± 0.12	0.24	101
2	English tooth paste	2.1	2	4.11 ± 0.17	0.31	100.5
3	Listerine mouth wash	3.75	2	5.71 ± 0.14	0.23	98

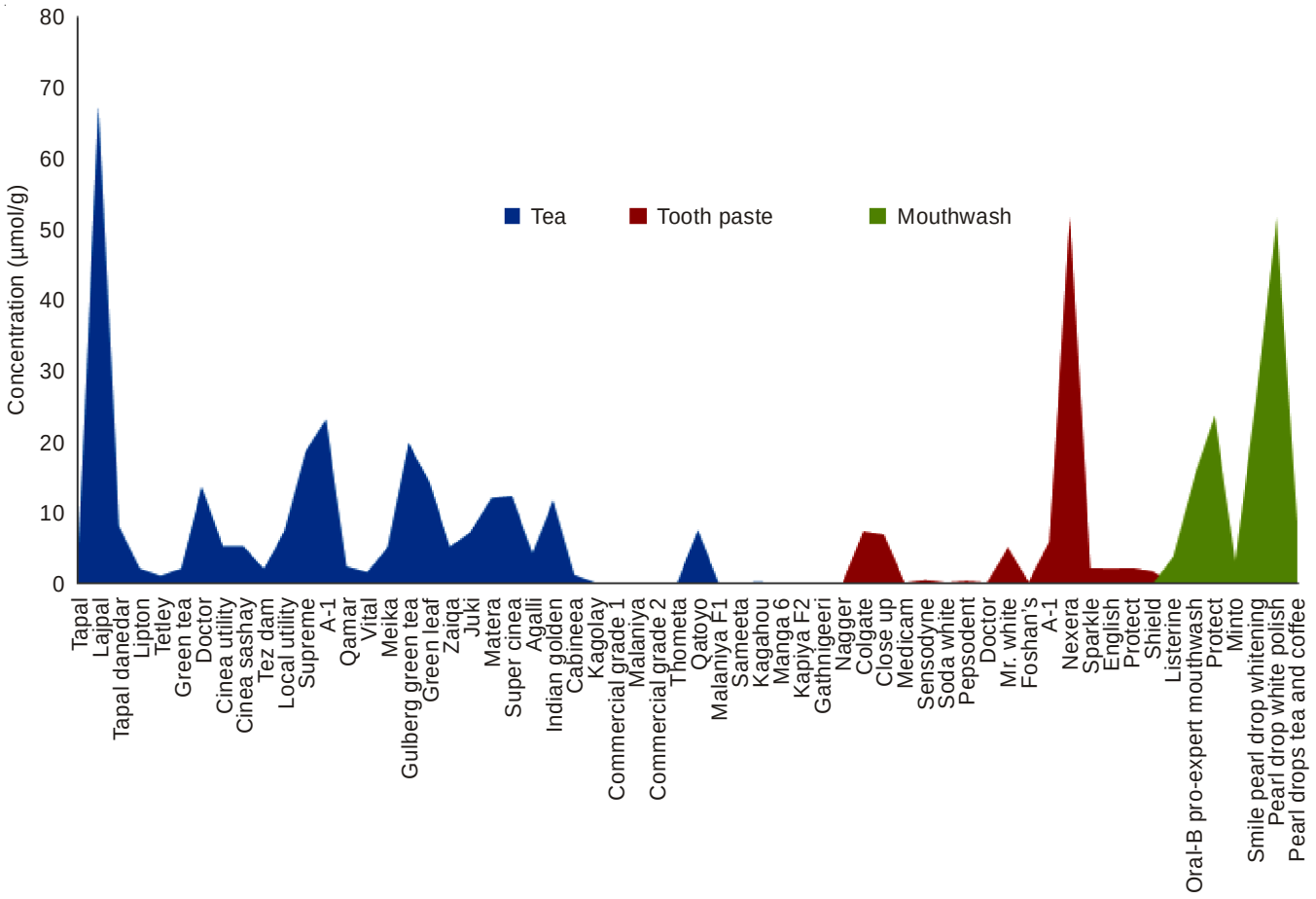

Fig. 2. Fluoride levels in different samples

Table-2 shows the concentration fluoride in different tea samples and it is observed that Lajpal tea sample contain maximum amount of fluoride (67.4 µmol/g) and Manga 6 tea sample contain its minimum amount (0.11 µmol/g). Variation in fluoride contents in tea samples can be attributed to tea type, its growing conditions, brewing conditions, like temperature, time and water taken for brewing. In all samples, the levels of fluoride are less than permissible limits, but excessive use of them on daily basis can lead to bioaccumulation of fluoride in body, which in turns lead to dissolution of calcium based structures found in body, like: teeth, bones and joints, resulting in fluorosis[17-22].

TABLE-2
FLUORIDE CONTENTS DETERMINATION IN DIFFERENT TEA SAMPLES

S. No.	Tea samples	µmol/g	RSD	S. No.	Tea samples	µmol/g	RSD
1	Tapal	3.7	0.21	20	Juki	7.26	0.16
2	Lajpal	67.4	0.86	21	Matera	12.05	0.45
3	Tapal danedar	8.1	0.28	22	Super cinea	12.36	0.31
4	Lipton	2.1	0.17	23	Agalli	4.3	0.26
5	Tetley	1.1	0.11	24	Indian golden	11.78	0.31
6	Green tea	2.1	0.16	25	Cabineea	1.27	0.12
7	Doctor	13.7	0.45	26	Kagolay	0.182	0.62
8	Cinea utility	5.3	0.31	27	Commercial grade 1	0.134	0.78
9	Cinea sashay	5.3	0.26	28	Malaniya	0.142	0.13
10	Tez dam	2.1	0.31	29	Commercial grade 2	0.173	0.24
11	Local utility	7.4	0.12	30	Thometa	0.212	0.16
12	Supreme	18.5	0.62	31	Qatoyo	7.52	0.45
13	A-1	23.2	0.78	32	Malaniya F1	0.165	0.31
14	Qamar	2.4	0.13	33	Sameeta	0.183	0.26
15	Vital	1.6	0.24	34	Kagahou	0.218	0.17
16	Meika	5.21	0.35	35	Manga 6	0.11	0.11
17	Gulberg green tea	19.84	1.2	36	Kapiya F2	0.16	0.16
18	Green leaf	14.42	0.58	37	Gathnigeeri	0.134	0.45
19	Zaiqa	5.21	0.32	38	Nagger	0.163	0.31
Minimum	Manga 6	0.11	0.07	Maximum	Lajpal	67.4	0.86

In tooth paste samples, Nexera contain maximum amount of fluoride (51.6 µmol/g) and medicam contain its minimum amount (0.137 µmol/g) as clear from Table-3. Mouthwash samples analysis is given in Table-4, indicating that maximum amount of fluoride is present in pearl drop white polish sample (51.6 µmol/g) and minimum amount is present in minto (3.2 µmol/g). Overall fluoride concentration ranges from 0-10 ppm in above all three samples. They are also within the permissible level range, but it should be tried that products containing less fluoride should be considered more for daily use, in order to avoid excessive exposure to fluoride level, especially for growing ones[23-25].

TABLE-3
DETERMINATION OF FLUORIDE CONTENT
IN DIFFERENT TOOTHPASTE SAMPLES

Sr. no	Toothpaste samples	µmol/g	RSD
1	Colgate	7.350	0.31
2	Close up	6.900	0.12
3	Medicam	0.137	0.12
4	Sensodyne	0.483	0.78
5	Soda white	0.166	0.13
6	Pepsodent	0.354	0.34
7	Doctor	0.150	0.35
8	Mr. white	5.150	1.20
9	Foshan's	0.200	0.58
10	A-1	5.900	0.32
11	Nexera	51.600	0.87
12	Sparkle	2.200	0.35
13	English	2.100	0.31
14	Protect	2.200	0.24
15	Shield	1.700	0.13
Minimum	Medicam	0.137	0.12
Maximum	Nexera	51.600	0.87

TABLE-4
DETERMINATION OF FLUORIDE CONTENT
IN DIFFERENT MOUTHWASH SAMPLES

S. No.	Samples	µmol/g	RSD
1	Listerine	3.75	0.23
2	Oral-B pro-expert mouthwash	14.8	0.37
3	Protect	23.7	0.78
4	Minto	3.2	0.13
5	Smile pearl drop whitening	25.8	0.34
6	Pearl drop white polish	51.6	0.35
7	Pearl drops tea and coffee	8.4	0.23
Minimum	Minto	3.2	0.13
Maximum	Pearl drop white polish	51.6	0.35

Conclusion

The recommended daily fluoride intake by W.H.O for children is 2 mg (105 µmol) and for adults is 2-4 mg (105-210 µmol). So the analysis of these samples indicated that overall the values are within threshold limits, *i.e* ranges for tea, tooth paste and mouth wash samples were 0.11-67.4, 0.137-51.6 and 3.2-51.6 µmol/g, respectively, but excessive use of tea or swallowing toothpaste or mouth wash samples can be injurious to health. Secondly analysis with ISE is rapid and precise results were obtained with more accuracy and sensitivity.

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