Tanzania Journal of Science 46(3): 851-858, 2020
ISSN 0856-1761, e-ISSN 2507-7961

Total and Available Fluoride Content in Toothpastes Sold in Dar es Salaam, Tanzania

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Received 8 Aug 2020, Revised 28 Sep 2020, Accepted 16 Oct 2020, Published Oct 2020
https://dx.doi.org/10.4314/tjs.v46i3.24

Abstract

A total of eleven (11) different toothpaste brands (imported and manufactured in Tanzania) sold in Dar es Salaam were evaluated for Total Fluoride (TF) and Total Soluble Fluoride (TSF) concentrations. To protect the subject's identity, the samples were coded. Four selected toothpastes were analyzed for potentially bioavailable fluoride by examining the relationship between TSF in tooth brushing residues and in that of the toothpaste. The results indicated that measured TF of the toothpaste samples coded as TPSA, TPSC and TPSH were consistent to the one declared by the manufacturers. On the other hand, samples coded as TPSB, TPSD, TPSE, TPSF, TPSG, TPSI, TPSJ and TPSK showed discrepancies between TF declared by the manufacturers and the measured amounts. Generally, measured TSF in majority of the tested toothpastes were above the minimum required amount for dental caries prevention (≥1000 ppm). Toothpastes with amounts below minimum were, TPSF (TF = 310 ppm and TSF = 305 ppm); TPSG (TF = 350 ppm and TSF = 340 ppm); TPSI (TF = 20 ppm and TSF = 17 ppm). Significant correlations were observed between TSF in toothpastes and in that of brushing residues (r = 0.850; p = 0.0001). These findings indicate that TSF concentration that is chemically available in toothpastes could be used to estimate how much fluoride would be bioavailable during brushing. On the other hand, the necessity for the development of strict regulatory measures on amounts of fluoride concentrations in toothpastes sold in Dar es Salaam is recommended for effective caries control.

Keywords: Toothpaste; Fluoride ion electrode; Available fluoride; Total fluoride; Dentifrice; Dental caries.

Introduction

An ideal toothpaste product for dental health may be regarded as the one in which total fluoride concentration equates to the ionizable/soluble fluoride content (Walsh et al. 2010). This is because positive correlation between caries reduction benefit and total fluoride content of ≥1000 ppm in toothpastes has been established (Walsh et al. 2010). Total fluoride (TF) indicates all fluoride content present in the formulation, while Total Soluble Fluoride (TSF) means free ionic and/or ionizable fluoride present in a product. It is the TSF that has the potential to interact with enamel at the tooth surface interface to interfere with the development of caries. Thus, in order for enamel re-mineralization to be effective, a minimum of 1000 ppm of TSF should be supplied (van Loveren et al. 2005, Wong et al. 2011).

The availability of fluoride in toothpastes is usually affected by the interaction between toothpaste constituents, which may lead to insolubility of fluoride. This indicates that the compatibility of chemicals in the toothpaste is of utmost significance for maximum tooth

protection (Cury et al. 2010). Time and temperature also influence the availability of fluoride because when products are stored at 22 °C, a loss of approximately 25% of its free available fluoride after one year is expected. Approximately 35% of ionizable fluoride is lost when stored at 29 °C for a year. Therefore, toothpastes are considered to have 3-year shelf life (Benzian et al. 2012).

The potential for existence of counterfeit and overstayed products in Dar es Salaam markets, and the presence of discrepancies between the information given by manufacturers and measured amounts (Kikwilu et al. 2008, Colgate Palmolive) necessitated a need for conducting a study to evaluate TF and TSF in relation to the provided consumer information on toothpastes. Contrary to Kikwilu et al. (2008) who reported fluoride contents present in toothpastes manufactured in Tanzania only (Whitedent and Aha brands), this paper reports TF and TSF concentrations in toothpastes sold (both imported and locally produced) in Dar es Salaam, Tanzania. Also this study determined the correlation between TSF in the toothpaste and in the brushing residues.

Materials and Methods

Sample collection

Different kinds of toothpastes were purchased from local vendors at Kariakoo market and others from Mlimani City Mall (Mlimani CM) in Dar es Salaam, Tanzania (January 2019). The sampling sites were selected based on the areas where majority of people of different economic strata shop. Thus, Kariakoo was selected due to having many shops and street vendors where most of these products are sold. Mlimani CM on the other hand, was also selected due to having modernized and standard shops and absence of free-lance traders compared to Kariakoo. Toothpaste samples collected from the two shopping areas were transported to the Chemistry Department, University of Dar es Salaam. Upon arrival, the samples were stored based on manufacturer's instructions before any experiments were performed. Table 1 summarizes areas of collection, and information gathered from the toothpaste packages including declared total fluoride, manufacturer country and expiration dates.

Table 1: Toothpastes analyzed, areas of collection, sample codes, manufacturer country, batch numbers and expiry dates.

Sample code	Collection area	Country of origin	Batch number	Expiry date
TPSA	Mlimani CM	South Africa	150318	2021
TPSB	Mlimani CM	Kenya	141140-11	04/2020
TPSC	Mlimani CM	Kenya	141400-10	07/2020
TPSD	Kariakoo	Thailand	8085	03/2020
TPSE	Kariakoo	PRC	P18804769	12/2021
TPSF	Kariakoo	Tanzania	242	10/2021
TPSG	Kariakoo	Tanzania	014	12/2021
TPSH	Mlimani CM	Kenya	141202-01	09/2020
TPSI	Kariakoo	PRC	18	07/2021
TPSJ	Mlimani CM	UAE	1216	11/2021
TPSK	Mlimani CM	UAE	0896	08/2020

Mlimani CM = Mlimani City Mall; PRC = Peoples' Republic of China; UAE = United Arab Emirates.

Correlational studies: Participants and Experimental design

Upon their consent, a total of eight (8) volunteers living in Dar es Salaam agreed and were recruited in this research. Volunteers brushed their teeth in mornings, using one of the four selected toothpastes on each day. Therefore, the research consisted of four phases, each carried out in 1 day, for 4 days, where volunteers used TPSC, TPSD, TPSG, and TPSK (declared non fluoridated) in days 1, 2, 3, and 4, respectively to brush their teeth. Since fluoride contents in the saliva before brushing were reported to be negligible (ranged from 0.02 to 0.8 ppm), this study analyzed fluoride contents in the residues from brushings (Naumova et al. 2012). In each day, volunteers brushed their teeth with the respective toothpastes and each volunteer spitted the residues from their brushings (toothpaste slurry and saliva) in small plastic containers, followed by immediate mouth rinsing with 10 mL of water. These samples were stored in the deep freezer ready for fluoride concentrations analysis (Naumova et al. 2012). These experiments were designed to check if there is any correlation between the TSF in the toothpaste and bioavailable in the brushing residues during tooth brushing at significance level of $p = 0.05$.

Instrument used for TF and TSF concentrations determination

TF and TSF concentrations were determined using JENWAY Fluoride Ion Selective Electrode (F-ISE), Bibbly Scientific Ltd, Serial number 413887.

Preparation of fluoride buffer

To a 1 L beaker, 500 mL of distilled water were added, followed by 57 mL of glacial acetic acid (analytical grade) and mixed thoroughly. NaCl (58 g) was then added, followed by 4 g of 1,2-cyclohexylenediaminetetreacetic acid (CDTA) then stirred to mix the contents thoroughly. The beaker with contents was transferred to a cool water bath and 6 N NaOH (125 mL) solution was added slowly while stirring, until the pH of the solution reached 5.5, then diluted with distilled water to 1 L.

Sample preparation and analysis

For each toothpaste sample collected, two different fluoride concentrations (TF and TSF) were analyzed. In both experiments, before opening, the toothpaste tube was squeezed repeatedly from top to bottom to allow homogeneous distribution of the contents. The first few grams were discarded as the top part does not allow thorough mixing of the contents.

Samples were treated according to Pearce (1974) with little modification as follows: 110-120 mg of each toothpaste were added into a plastic beaker followed by addition of 20 mL of double distilled water and the contents were mixed well. Triplicates of 2.5 mL of the suspension were transferred to tubes for TF analyses. The remaining of the suspension was centrifuged at 12,000 rpm for 10 minutes to remove insoluble fluoride bound to the abrasive. Thus, triplicates of 2.5 mL of the supernatant from centrifuge were transferred to test tubes for TSF determination.

Samples for the analysis of TF and TSF concentrations in brushing residues during brushing were collected in the morning, and treated according to the method of Naumova et al. (2012). Each volunteer was supplied with 0.8 g of the selected toothpaste and brushed their teeth for about 1 min, and spitted the mixture of toothpaste slurry and saliva into a plastic container followed by immediate mouth rinsing with 10 mL of water. These were collected for TF and TSF concentration analysis (Naumova et al. 2012). The mixture of toothpaste slurry and saliva samples from tooth brushing were agitated and amounts of 2 mL were used for TF and TSF determinations. The samples for TSF determinations were centrifuged and 1 mL of the supernatant was transferred to plastic assay tubes.

For all the TF and TSF determination tubes, 2 M HCl were added and after 1 hour at 45 °C, the samples were neutralized by using 1 M

NaOH solution, followed by buffering with TISAB II.

Calibration of the instrument was achieved using sodium fluoride standard solutions ranging in concentrations from 0.0625 ppm F to 12.5 ppm F, which were prepared with the same reagents used to prepare the samples (Cury et al. 2010). Blank sample solutions were prepared in a similar way, except there was no sample addition. Therefore, to correct reagent impurities, a reagent blank sample was analyzed, and subtracted from the toothpaste samples readings.

Recovery tests were performed by spiking the recovery samples with standard solutions, and the same procedure used in sample treatment was used. Therefore, the amount of fluoride in the sample was determined before and after spiking, and the percentage recoveries were established using the following formula:

$$\% \text{ Recoveries} = \frac{[\text{spiked}] - [\text{unspiked}]}{[\text{added}]} \times 100\%$$

These experiments were repeated for each toothpaste, and the results were used for determination of accuracy and precision of the method. Therefore, recoveries at 95-110% and precision relative standard deviation of <5% was considered suitable.

The concentration of fluoride in the samples was obtained using the following formula (Ideriah et al. 2016):

$$[F^-]_{(ppm)} = \frac{[F^-]\ \text{Toothpaste reading} - [F^-]\ \text{Blank reading}}{\text{Volume used x weight of sample (g)}} \times 1000$$

Statistical analysis

Data for TF and TSF concentrations were analyzed by using Microsoft excel, and the results are presented as mean values ± standard deviation. Analyses of correlation tests between the TSF concentrations in toothpastes and in tooth brushing residues were performed on SPSS® statistics 20 software (IBM SPSS, statistics 20.0) and the level of significance set at 5%.

Results

Eleven toothpaste samples were analyzed for TF and TSF contents, the results are presented in Table 2. Figure 1 provides comparisons between the TF declared by the manufacturer company and the measured one. Therefore, toothpastes coded as TPSF and TPSG showed discrepancies in the declared TF and the measured amount. TPSB, TPSD and TPSE showed small difference between the declared TF and the measured one.

Table 2: Amounts of declared TF, measured TF and TSF in toothpaste samples collected from Dar es Salaam

Sample code	Fluoride agent	Abrasive agent	Fluoride declared (ppm)	Mean TF (ppm): n = 3	Mean TSF (ppm): n = 3
TPSA	NaF	Hydrated silica	1450	1467 ± 0.14	1460 ± 0.06
TPSB	NaF	Hydrated silica	1450	1177 ± 0.02	1170 ± 0.09
TPSC	NaF	Hydrated silica	1450	1379 ± 0.02	1370 ± 0.07
TPSD	NaF	Hydrated silica	1450	1100 ± 0.03	1090 ± 0.08
TPSE	NaF	Hydrated silica	1450	1100 ± 0.02	1090 ± 0.03
TPSF	NaMFP	$CaCO_3$	1000	310 ± 0.06	305 ± 0.02
TPSG	NaMFP	Hydrated silica	1000	350 ± 0.08	340 ± 0.02
TPSH	NaF	Hydrated silica	1450	1400 ± 0.01	1390 ± 0.08
TPSI	NaMFP	$CaCO_3$	ND	20 ± 0.01	17 ± 0.00
TPSJ	ND	ND	NF	7 ± 0.00	7 ± 0.00
TPSK	ND	ND	NF	7 ± 0.02	7 ± 0.01

ND = Not defined; NF = Non fluoridated; NaMFP = Sodium monofluorophosphate; NaF = Sodium fluoride.

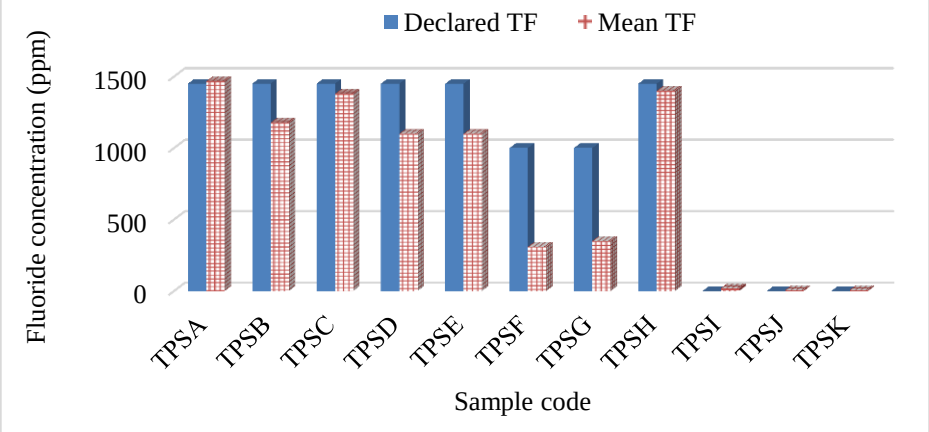

Figure 1: Comparisons between declared and measured TF in toothpastes samples collected in Dar es Salaam.

Figure 2 provides the comparison of the measured TF and the TSF for effectiveness of caries control, thus, all toothpastes involved in the study showed comparable values of TF and TSF. Figure 3 illustrates the measured TF and TSF from the brushing residues (mixture of toothpaste slurry and saliva) samples. This study was designed to check if there is any correlation between the TSF in the toothpaste and bioavailable in the brushing residues during tooth brushing.

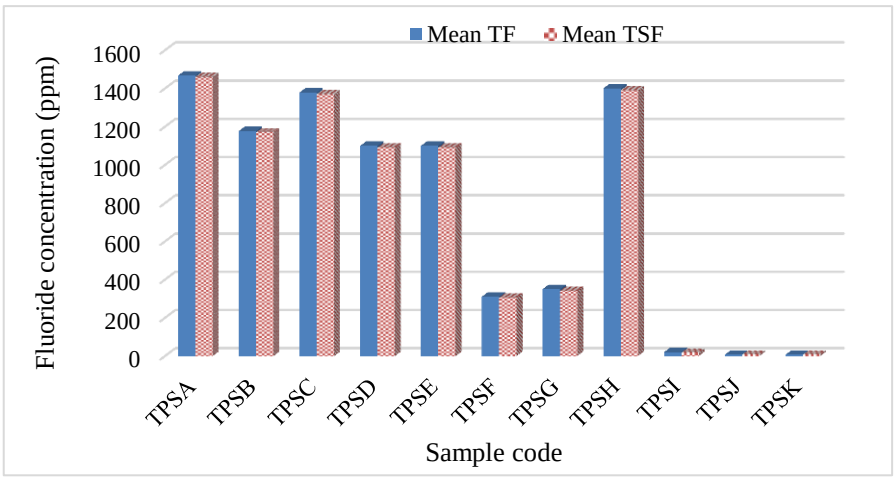

Figure 2: Comparisons between measured TSF and TF in toothpastes collected in Dar es Salaam.

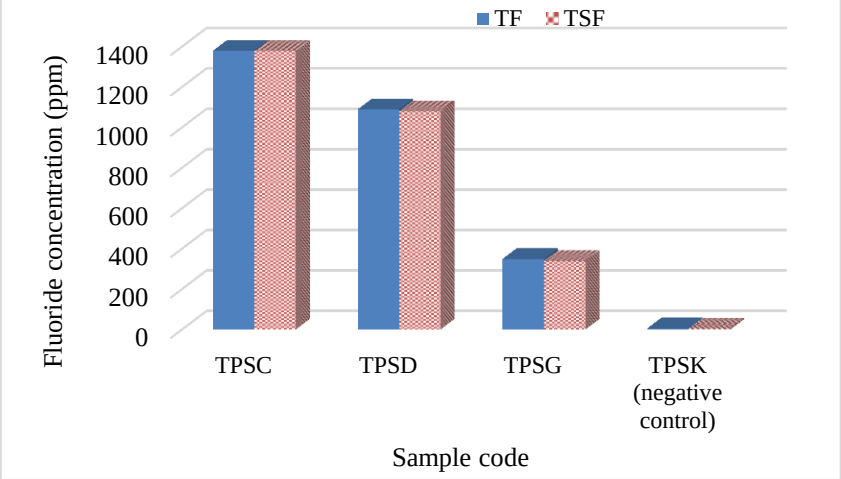

Figure 3: TF and TSF in tooth brushing residues (toothpaste slurry and saliva).

Table 3: TF and TSF in tooth brushing residues (mean ± SD)

Fluoride Concentration	TPSC	TPSD	TPSG	TPSK (negative control)
TF (ppm)	1380 ± 0.3	1090 ± 0.9	350 ± 0.7	7 ± 0.5
TSF (ppm)	1378 ± 0.5	1080 ± 0.8	340 ± 0.2	6 ± 0.8

Discussion

Among the solutions that have contributed positively to the decline of dental caries in the last few decades is the wide spread use of fluoridated toothpastes (Marinho et al. 2003). Tooth brushing by using fluoridated toothpastes is therefore an important public health measure towards overcoming dental caries problems. Upon regular supply of fluoride, protection on the tooth surface is enhanced due to fact that fluoride enhances mineralization of incipient lesions, reduces enamel solubility, and prevents mineral dissolution and production of acid by plaque bacteria. For the effectiveness and efficiency of the fluoridated toothpastes, it is important that an adequate amount of fluoride be available (≥ 1000 ppm). Majority of toothpastes involved in this study contained higher declared TF than the measured amounts; therefore, with an exception of TPSA, TPSC and TPSH the rest of the toothpaste samples had discrepancies between declared TF and the measured ones. It is worth mentioning that the measured TF for TPSF and TPSG samples were lower, almost one-third (⅓) of the declared TF.

The amounts of TSF for majority of toothpaste samples reported herein are above effective dental caries prevention doses (≥1000 ppm) (Wong et al. 2011), except for TPSF and TPSG, the TF and TSF reported herein coincide with those reported by Kikwilu et al. (2008). This report and Kikwilu's indicated insufficient amounts of fluoride, well below optimum level for dental caries prevention. On the other hand, toothpaste coded as TPSI with sodium monofluorophosphate as a fluoride agent contained no declared amounts of TF, however, experimental results indicated insufficient levels of TF and TSF. This can be implicated to their respective ability in reducing dental caries. These results therefore, call for routine monitoring and controlling of these products for effective prevention of dental caries.

Table 3 and Figure 3 show the TF and TSF concentrations in brushing residues of the selected toothpastes. With respect to TF and TSF, the three toothpastes (days 1-3) were

found to be statistically different from the non-fluoridated toothpaste, TPSK (day 4). Moreover, toothpastes that presented lower TF and TSF also showed low TF and TSF in the brushing residues. A significant correlation was observed between TSF concentrations in the toothpastes and in tooth brushing residues (r = 0.850; p = 0.0001). These results support the idea that TSF in toothpastes is potentially available to be released for teeth protection during brushing. It is clearly established that the maximum and minimum TF concentrations for fluoridated toothpastes to contain are 1,500 ppm and 1000 ppm, respectively. However, since TSF concentration is the one involved in protection against caries, then, it is recommended that estimated maximum and minimum TSF concentrations (influenced by temperature and time) be indicated in the package for consumers to decide (Cury et al. 2015).

The performed correlational studies show the relationship between fluoride from toothpaste and the one produced in the oral cavity. Therefore, fluoride concentration produced in the oral cavity during tooth brushing is more important than the concentration in the toothpaste. TF in the toothpaste is spread in the oral cavity through saliva, and only chemically total soluble fluoride (TSF) interacts with enamel at the tooth surface interface to interfere with the caries process. Therefore, if TSF is below 1000 ppm, protection against caries will be minimum (Duckworth and Morgan 1991, van Loveren et al. 2005, Cury and Tenuta 2008, Cenci et al. 2008, Zamataro et al. 2008, Tenuta et al. 2009, Cury et al. 2010, Wong et al. 2011, Tenuta and Cury 2013).

Although this study reports the inconsistencies between the declared TF and the measured amounts, it is critical to note that the sample size in this study cannot represent all toothpastes of brand names mentioned herein, thus, generalization is highly discouraged until further analyses are conducted. It should also be noted that the results presented herein should not be used to draw conclusions regarding toothpaste's clinical efficacy, since more studies concerning their efficacy for caries control need to be carried out. Therefore, despite the factors stated above, this paper sounds the alarm on the problem areas that are concerned with toothpaste quality assessments in Tanzania.

Conclusion

This paper reports some discrepancies between the declared and the measured TF, although they were measured in different environments. Some toothpastes involved in this study had lower TF and TSF than the recommended for caries prevention, these included samples coded as TPSF (TF = 310 ppm and TSF = 305 ppm); TPSG (TF = 350 ppm and TSF = 340 ppm); TPSI (TF = 20 ppm and TSF = 17 ppm). Significant correlations were observed between TSF in toothpastes and in that of brushing residues (r = 0.850; p = 0.0001).

Acknowledgement

Author would like to thank Dr. Ilomo Ophery of Chemistry Department, University of Dar es Salaam for technical assistance during these analyses.

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