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Potentiometric Determination of % Fluoride Ion Content (w/v) in Toothpastes by Ion Selective Electrode

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Abstract

The concentration of fluoride in common dentifrices can be found using various methos. An ion selective electrode can be used to continuously measure the concentration of fluoride in various toothpaste suspensions. Using an ion selective electrode, compared to high performance liquid chromatography and ion chromatography, requires a short amount of time required for sample preparation and gathering experimental data. The quick monitoring of fluoride in toothpaste using an ion selective electrode. This can ensure that the specified fluoride content is accurate and effective against fighting cavities in teeth. If the toothpaste samples contain large amounts of fluoride, they may cause fluorosis; however, smaller amounts may not properly protect teeth. Creating suspensions of toothpaste can be used to ensure advertised fluoride contents match actual fluoride contents, while mirroring the oral environments toothpastes are used in. In this study, fluoride ion content has been measured in several different toothpaste samples by ion selective electrode. The specifications of fluoride content in the toothpastes that the study selected were between 0.14 to 0.498% (w/v). %RPD, 0.37%, and %Recovery was found 94.5%. Most results met their specifications.

Keywords: Fluoride; Ion Selective Electrode; Toothpaste

Introduction

Fluoride (F^-) is an inorganic anion that is present in several dental products, drinking water, and foods. The main purpose of F^-, as an additive, in drinking water is to prevent the onset of tooth decay and to strengthen tooth enamel when used in reasonable amounts (~1 mg/L) [1]. Dentifrices, specifically toothpastes, include F^- additives to protect teeth in the form of various dissolved salts such as: NaF, SnF_2, Olafur, and Na_2PO3F. However, after a chronic exposure to elevated concentrations of F^-, by both children and adults, fluorosis can be developed [2]. When fluoridated water exceeds fluoride concentrations of 5 mg/L, fluorosis can take two forms. Dental fluorosis causes teeth to become mottled, and in extreme cases, one can develop skeletal fluorosis, where fluoride accumulates in bones and joints causing pain [3].

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With correct concentrations in toothpaste, F^- has been shown to prevent tooth decay. Typically, many types of toothpaste contain about 1350-1500 ppm F^- [4]. The amount of F^- containing ingredients can vary in terms of their w/v. For example, in order to create toothpaste that contains about 0.15% w/v F^-, the amounts of various fluoride sources will be different because varying molecular weights. In order to find the amount of F^- present in toothpaste, the correct stoichiometric calculations must be done.

In order to accurately determine the presence of F^-, methods and equipment must be extremely sensitive to the presence of ions. The optimal pH range of the electrode is from 4 to 8, and the optimal temperature range is from 0 to 80 C [5]. The usage of ion selective electrodes (ISEs) is very effective in measuring the concentration of F^- reliably and cheaply. Aqueous samples containing dissolved F^- ions can continuously be monitored using an ISE [6]. The pollutant is in the atmosphere due to the huge industries, and it exists there, in the normal case, under tri-chromium and hexa-chromium which differ in both the transition period and the bioavailability and toxicity. Hexa-chromium was found to be more toxic than the tri-chromium. The studies showed no biological role of the chromium in the plants [1].

Materials and Method

Apparatus and chemicals

In order to carry out the experiment, the following reagents and materials were used:

- pH meter with fluoride specific ion electrode system (HI 2215 pH/ORP meter. Hanna Instruments) single junction reference electrode filled with 4 M (4N) Potassium Chloride, KCl filling Solution.(5)
- Centrifuge capable of spinning at 2000 rpm
- Magnetic stirrer
- Plastic coated stirring bar
- Timer
- 100 ml plastic cups
- Volumetric pipettes
- Volumetric glassware
- Plastic bottles with screw caps, 120 ml or larger
- 50 ml screw capped graduated plastic centrifuge tubes

Reagents

- Sodium Fluoride, USP (NaF) Alfa-Aesar, ACS, 99% min. Lot NO. W09B052
- Sodium Fluoride, Certified ACS, Fisher Chemical, Lot NO. 157879
- Sodium Hydroxide, 50% solution, Dawn Scientific Inc., ACS, Lot NO. 150212.1C

- Total Ionic Strength Adjustment Buffer solution, pH=5.32. This solution marketed commercially under the trade name TSIAB [7]. Sufficient bugger for 15-20 determinations can be prepared by mixing with stirring 57 mL of glacial acetic acid, 58 g of sodium chloride, 4 g of cyclohexylamine dinitrilotetra acetic acid, and 500 mL of distilled water in a 1 L beaker. Cool the contents in a water or ice bath, and carefully add 6M sodium hydroxide to a pH of 5.0 to 5.5. Dilute to 1 L with water, and store in a plastic bottle [8].
- Various common samples of commercial toothpastes were obtained via Amazon
- Deionized water on the day of use (**TABLE 1**).

TABLE 1. **Toothpaste Composition**

Sample NO.	Specified F^- Content	Fluoride Source	Inactive Ingredients
1	0.15% w/v fluoride ion	NaF Sodium fluoride 0.24%	sorbitol, water, hydrated silica, sodium lauryl sulfate, flavor, PEG-12, tetrasodium pyrophosphate, cocamidopropyl betaine, cellulose gum, sodium saccharin, xanthan gum, titanium dioxide, FD&C blue no. 1, FD&C yellow no. 5.
2	0.14% w/v fluoride ion	Na_2FPO_3 Sodium monofluorophosphate 0.76%	glycerin, hydrated silica, water, sodium bicarbonate, PEG-12, sodium lauryl sulfate, flavor, sodium hydroxide, cellulose gum, carrageenan, sodium saccharin, FD&C blue no. 1, D&C yellow no. 10.
3	0.15% w/v fluoride ion	Na_2FPO_3 Sodium monofluorophosphate 0.76%	dicalcium phosphate dihydrate, water, glycerin, sodium lauryl sulfate, cellulose gum, flavor, tetrasodium pyrophosphate, sodium saccharin.
4	0.16% w/v fluoride ion	SnF_2 Stannous fluoride 0.454%	glycerin, hydrated silica, sodium hexametaphosphate, propylene glycol, PEG-6, water, zinc lactate, flavor, trisodium phosphate, sodium gluconate, sodium lauryl sulfate, carrageenan, sodium saccharin, stannous chloride, xanthan gum, titanium dioxide, mica, blue 1.
5	0.15% w/v fluoride ion	NaF Sodium fluoride 0.24%	water, hydrated silica, sorbitol, glycerin, cocamidopropyl betaine, PEG-12, titanium dioxide, cellulose gum, flavor, sodium benzoate, sodium saccharin, red 40.

6	0.498% w/v fluoride ion	NaF Sodium fluoride 1.1%	fumaric acid, hydrated silica, mica, PEG-12, poloxamer 338, sodium benzoate, sodium carboxymethylcellulose, sodium lauryl sulfate, sodium saccharin, sorbitol, titanium dioxide, tricalcium phosphate, water, xanthan gum. This product also contains flavor, FD&C Blue No. 1
7	0.498% w/v fluoride ion	NaF Sodium fluoride 1.1%	fumaric acid, hydrated silica, mica, PEG-12, poloxamer 338, sodium benzoate, sodium carboxymethylcellulose, sodium lauryl sulfate, sodium saccharin, sorbitol, titanium dioxide, tricalcium phosphate, water, xanthan gum. This product also contains flavor, FD&C Red No. 33
8	0.15% w/v fluoride ion	Na_2FPO_3 Sodium monofluorophosphate 0.76%	glycerin,water,calcium carbonate,hydrated silica,xylitol,natural flavor (peppermint oil and other natural flavor),sodium lauryl sulfate,carrageenan,sodium bicarbonate,zinc citrate.
9	0.15% w/v fluoride ion	NaF Sodium fluoride 0.243%	water, sorbitol, hydrated silica, disodium pyrophosphate, sodium lauryl sulfate, flavor, cellulose gum, sodium hydroxide, sodium saccharin, carbomer, mica, titanium dioxide, blue 1.
10	0.1% w/v fluoride ion	NaF Sodium fluoride 0.22%	treated water, sorbitol, carbopol, sodium lauryl sulphate, flavor, polyethylene glycol 1500, sodium saccharin, precipiated silica, sodium carboxy methyl cellulose, methylparaben, propylparaben.

Analysis for Total Soluble Fluoride (TSF) and Total Fluoride (TF)

Preparation of Standard Solutions: Dissolve 0.2210 g of sodium fluoride in 100 mL deionized water to create a 100 ppm F^{-} stock solution.

Use the previously created stock solution to prepare 100 ml solution containing 4 ppm, 2 ppm, 1 ppm, 0.5 ppm, and 0.2 ppm F. Store solutions in high density polyethylene (HDPE) or Teflon bottles to avoid corrosion. **(FIG. 1.)**

Preparation of Sample Solution: Create a suspension of the toothpaste sample by thorough shaking in 100 mL of deionized water. Transfer 50 mL into graduated plastic centrifuge tubes, and use centrifuge at 2000 rpm for 10 minutes to create a suspension. Keep solution in a HDPE or Teflon bottles to avoid corrosion [9] (**TABLE 2-4**).

TABLE 2. **Preparation of fluoride standard stock solution**

Stock std.	0.1105	m NaF (g)	Na	22.9890
Volume	0.5000	V L	F	18.9980
Conc.	100	[F^-] mg/L	F/NaF	0.45250
Std.	10		NaF	41.9970

TABLE 3. **Serial standards for calibration curve**

Volume of Working Standard Solution (mL)	Diluted to total volume (mL)	Standard F^- Concentration (mg/L)
2.0	100	0.2
5.0	100	0.5
10.0	100	1.0
20.0	100	2.0
40.0	100	4.0

TABLE 4. **Calibration Curve Measurements**

Series of Std	**[F^-] mg/L**	**Log [F^-]**	**E/mV**	
Blank	0.000	N/A	200.3	
0.2	0.200	-0.6990	132.4	
0.5	0.500	-0.3010	110.6	
1.0	1.000	0.0000	93.2	
2.0	2.000	0.3010	75.6	
4.0	4.000	0.6021	57.6	
		RSQ	R^2	0.9997
		dE/dlog[F^-]	m	-57.5538
		E for [F^-]=	b	92.8765

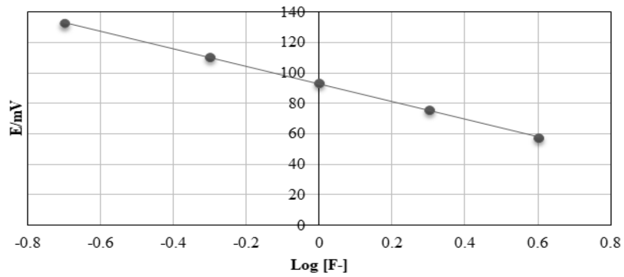

FIG. 1. **Calibration Curve**

Procedure for determination of Total Fluoride

Transfer 10 mL of each standard solution and sample supernatant into plastic beakers containing a stirring bar, add 10 mL of TISAB, and mix solution by stirring. Measure the potential (mV) of each solution using a fluoride electrode – reference electrode system [10] (**TABLE 5**).

Results and Discussion

Many of the samples that were tested matched their specified fluoride contents (**TABLE 6**). The accuracy of the specified fluoride content on toothpastes labeled was maintained, allowing for users to properly protect teeth while minimizing the risks of fluoride in the body.

Although most the samples tested did match their specified fluoride content, there were exceptions. The percent recoveries on some of the samples were relatively low. The low recovery may be attributed to the fact that the samples were not digested with acid before measuring the fluoride content with the ISE. The fluoride sources in some of the samples containing NaFPO3 and SnF2, a larger amount of free fluoride ions would be present in the solution. Thus, if the toothpaste samples were digested with an acid, the percent recovery would have most likely been higher, and closer to the specified amount.

Additionally, the elevated fluoride levels in some of the sample can be explained by the process in which the centrifuge stratified the components of the toothpaste. The solid particulates in the toothpaste sank to the bottom while many of the fluoride ions were dissolved in the upper layer of the suspension. When using the ISE to measure the fluoride content, the upper layer of the suspension was used without shaking the fluid after it had come out of the centrifuge. Due to this practice, only the upper, a more concentrated layer of the suspension was used to calculate the fluoride content of the toothpaste. If the lower layer of the suspension containing solids was used to calculate fluoride content in the experiment, the concentration of fluoride in the toothpaste would be lower than the results from this experiment because the same amount of fluoride would be distributed over a larger volume.

TABLE 5. **mV Conversion to [F^-]**

Identity	E/mV	[F-] mg/L	DF	Corr [F^-]	W mg
Blank	200.3	0.000	1	0.000	0.000

2.0 mg/L independent	39.0	8.632	1	8.632	N/A
Sample 1	12.3	25.120	1	25.120	1742.5
Sample 2	20.2	18.313	1	18.313	1752.5
Sample 3	7.9	29.955	1	29.955	1774.9
Sample 4	17.6	20.320	1	20.320	1777.9
Sample 5	14	23.468	1	23.468	1444
Sample 6	-36.3	175.570	2	175.570	1776.3
Sample 7	-35.7	171.405	2	171.405	1753.4
Sample 8	13.8	23.657	1	23.657	1751.2
Sample 9	-11.8	65.881	1	65.881	1787.8
Sample 10	-24.6	109.941	1	109.941	5012.2
Duplicate	-24.6	109.941	1	109.941	5012.2
Spiked	-25.7	114.888	1	114.888	5011.9
Spiked Duplicate	-25.7	114.888	1	114.888	5011.9
%RPD: 0.37			MS	% recovery	94.50%
			MSD	% recovery	94.50%
Average Reported Value (mg F- / L): 110.1615 mg/L					
mL of spiking solution: 0.5 mL					
Concentration of spiking solution: 100 mg/L					
Sample volume: 10 mL					

TABLE 6. **Fluoride Content**

Sample Number	**F^- Content**		**Sample (mg)**	**Volume of Solution (mL)**
	Spec. (w/v)	**Found (w/v)**		
1	0.15%	0.14416%	1742.5	100
2	0.14%	0.10450%	1752.5	100
3	0.15%	0.16877%	1774.9	100
4	0.16%	0.11429%	1777.9	100
5	0.15%	0.16252%	1444.0	100
6	0.498%	0.49420%	1776.3	100
7	0.498%	0.50468%	1753.4	100

8	0.15%	0.01234%	1751.2	100
9	0.15%	0.18425%	1787.8	100
10	0.1%	0.09925%	5012.2	100
10 Duplicate	0.1%	0.09925%	5012.2	100
10 Spiked	0.1%	0.10372%	5011.9	100
10 Spiked Duplicate	0.1%	0.10372%	5011.9	100

Calculate the TOTAL FLUORIDE in ppm from the equation:

Total Fluoride = F × V/W

Where TF=total fluoride in sample, mg/L

F=the F^{-} value obtained by interpolating sample mV in standard curve OR direct reading using machine celebrated with standard solution.

W=weight of sample, in milligrams

V=volume of sample

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