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RESEARCH PAPER

Potentiometric determination of fluoride in various brands of toothpaste

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ABSTRACT:

The potentiometric analysis of the fluoride content (as F-ion) in toothpaste suspension with an ion-selective fluoride electrode is simple, reliable and inexpensive. Very low fluoride ion concentrations (up to 10–5 mol / l) can be determined with a fluoride-selective electrode, whereby the ionic strength of a solution is regulated and the concentration of hydroxide ions and interfering metal ions is controlled. The influence of the pH value and the complex ions of metals can be successfully regulated by the Total ionic strength adjustment buffer (TISAB) solution and by maintaining the pH value in the range from 5.00 to 8.00. The fluoride concentrations of 34 different toothpaste samples of different brands are determined using an ion-selective electrode. The highest value is 1285.85 ppm from Germany (Blend a. Med) and the lowest value is 18.15 ppm from Indonesia (Formula junior). Most of the low values are from Asian countries between (18.15-514.84) ppm, which are less than 600 ppm and this concentration is insufficient for Iraqi prescriptions and World Health Organization (WHO) specifications, the highest Values are between (940.66-1285.85) ppm, from Japan, USA and Germany

KEY WORDS: Fluoride, Fluoride ion selective electrode, Toothpaste, Potentiometer.
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1.INTRODUCTION :

Fluoride (F^-) is an inorganic anion this is found in numerous dental products, consuming water, and foods. The essential reason of using Fluoride, as an additive, in ingesting water is to save human from the onset of teeth decay and the bolster enamel teeth which is used in affordable quantities (1 mg/L)(Lennon *et al.*, 2004). Dentifrices, in particular toothpastes, consist of F^- components to shield enamel in the shape of diverse dissolved salts such as: NaF, SnF_2 and Na_2PO_3F.

However, after a persistent exposure to elevated concentrations of F^-, for both youngsters and adults, fluorosis may be developed(Barmes, 1996). When fluoridated water exceeds fluoride concentrations of five mg/L, fluorosis can take various forms such as dental fluorosis reasons enamel to turn out to be mottled, and in extreme cases, you can broaden skeletal fluorosis, wherein fluoride accumulates in bones and joints inflicting pain(Zohoori *et al.*, 2015; J, 2019). With accurate concentrations in toothpaste, F^- has been proven to protect you enamel decay. Typically, many kinds of toothpaste include approximately 1350-1500 ppm F^- (Yildiz *et al.*, 2018). The quantity of F^- containing components can range in phrases in their w/v. For example, with a view to create toothpaste that carries approximately zero.15% w/v F^-, the quantities of diverse fluoride reasserts may be different due to the fact various molecular weights. In order to discover the quantity of F^- found in toothpaste, the right stoichiometric calculations have to be done.

To decide appropriately the presence of F^-, strategies and device ought to be extraordinarily touchy to the presence of ions. The greatest pH variety of the electrode is from four to seven, and the greatest

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temperature variety is from zero to eighty C(Radić *et al.*, 2020). The usage of ion selective electrodes (ISEs) is very reliably, cheaply and accurate in measuring the attention of F^{-}. Aqueous samples containing dissolved F^{-} ions can constantly be monitored by the use of an ISE(TOKALIOGLU, KARTAL and SAHIN, 2004).

the potentiomety is the method in which the ion concentration is obtained directly from the potential of an ion-selective or ion-sensitive electrode(Gao, Xie and Bakker, 2020) by using measuring electrode and reference electrode. The potential difference ΔE between the indicator and reference electrodes is determined with the help of the potentiometer. The measurement must take place without current, as otherwise, electrode reactions and a metabolism would take place at the electrodes. There are two ways to perform this current less measurement (Abramowitz, 1967):

a. Poggendorff's compensation method
A counter voltage is generated with the help of an adjustable resistor.
and this indicate to ΔE.
It is proven that any bilateral voltage divider can be operated backwards as a modern-day divider with inside the Ayrton shunt mode (Julie element). The use of Poggendorff's second ``compensation" approach in the creation of regular resistance potentiometers is surveyed. A layout of a consistent resistance potentiometer (Julie nanovolt potentiometer) the usage of a consistent contemporary supply alongside a Kelvin-Varley slide working as a Modern-day divider is defined and its benefits discussed. Applications are advised for consistent nowadays reassess used with modern dividers. These are
(1) Simplified potentiometers, (2) defection potentiometers, (3) self-balancing potentiometers, (4) servo mistakes detectors, and (5) modern-day balances(Julie, 1967).

b. High resistance
The internal resistance of the measuring device is selected so high that no more current can flow. E can then be determined directly. Both the measuring and reference electrodes must be non-polarizable and ion-selective or ion-sensitive electrodes. The ion concentration (or activity) can then be determined using Nernst's equation or read off from calibration curves.

2.1. Basis of Potentiometry

2.1.1. Nernst equation

The potentiometric is based on the Nernst equation. It describes the relationship between a half-cell potential of the ion activity(Jasielec, no date).

$$E = E^{o} + \frac{R * T}{n * F} * \ln * \frac{a(ox)}{a(red)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

E = Potential Energy in volt.
E^{o} = Standard Potential in volt
n = number of electrons converted participated in the processes
R = general gas constant joule/kelvin
a = activity
T = temperature in kelvin
F = Faraday constant in coulomb

Since R, T and F are constant and ln x can be replaced by ln10 lg x, the equation can be simplified:

$$E = E^{o} + \frac{RT}{nF} \ln_{10} \lg \frac{a(ox)}{a(red)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Since both E^{0} (indicator) and E (reference) are constant quantities, they can be summarized:

$$\Delta E = E^{o} + \frac{RT}{nF} \ln_{10} \lg \frac{a(ox)}{a(red)} - E_{ref} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

$$E^{o} = E_{ind} - E_{ref} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

The equation can be simplified even further because with ion-selective electrodes either the oxidized or the reduced form of the substance to be determined as a pure phase. Pure phases have the activity a = 1.

So, it results:

$$\Delta E = E^{o} + \frac{RT}{nF} \ln_{10} \lg a(ox) \ldots\ldots\ldots\ldots\ldots\ldots 5$$

Or $\Delta E = E^{o} - \frac{RT}{nF} \ln_{10} \lg a(red) \ldots\ldots\ldots\ldots\ldots 6$

In our experiment, fluoride is measured

$$E = E^{o} - \frac{RT}{nF} \ln_{10} \lg c(F) \ldots\ldots\ldots\ldots\ldots\ldots 7$$

The experiment temperature was then 19 C^{o}

$$E = E^{o} - \frac{0.05792}{n} \ln_{10} \lg c(F) \ldots\ldots\ldots\ldots\ldots\ldots\ldots 8$$

2.1.2. Nikolsky-Eisenman equation:

The Nikolsky-Eisenman equation: is an extension of the Nernst equation for potentiometric measuring electrodes(Seguí Femenias *et al.*, 2016):

$$E = E^{o} + \frac{2.303RT}{nF} \log[ai + Kij * aj^{n/m}] \ldots\ldots\ldots\ldots\ldots\ldots 9$$

ai and aj are the activities of the two types of ions i (analyze ion) and j (interfering ion) and Kij is the selectivity coefficient, which indicates the extent of the cross-sensitivity. The term “cross-sensitivity” means that the measurement of a certain compound is falsified by other sample components, the less the selectivity coefficient kij for an interfering ion the less the cross-sensitivity during the measurement. An ideal ion-selective electrode for the ion species would therefore have a kij = 0, but practical values are between 10^{-1} and $10^{-5.}$

2.2. Calibration of an ion-sensitive electrode

With external calibration, the ion-selective electrodes are calibrated with solutions of known concentration. Thus a direct relationship is established between the potential difference and the concentration.

A dilution series of the ion to be determined is used for this process. In order to eliminate the influence of the activity coefficient, one works with constant ion strength and constant pH value. These measurement conditions can be achieved by adding a TISAB solution (total ionic strength adjustment buffer). TISAB solutions are relatively highly concentrated electrolytes that have to behave indifferently. The measured potential differences are entered in a coordinate system as a function of the negative logarithm of the concentration (-lgc)(Light and Cappuccino, 1975). The electrode slope can be taken directly from a calibration line measured in this way or the unknown concentration can be determined graphically. Furthermore, the concentration can be calculated from the straight line parameter after linear regression.

The calibration line follows the straight-line equation:

$\Delta E = a - b^{*} \lg c$

a = y intercept, b = slope

This can be obtained by transforming and defining a constant from the Nernst equation.

$\Delta E = E^{\circ} + 0.05792/n * \lg a_{oxd,}$ at 19 C^{o}

The constant potentials (standard potential of the indicator electrode, potential of the reference electrode, diffusion potential at the diaphragm), the activity coefficient f and all device-constant values are combined into one constant (Const.):

$\Delta E = const + 0.05792/n * \lg c_{oxd}$

From the above equation the logarithm of the concentration C is linearly depends on the voltage difference ΔE read off

3. Types of electrodes

If the potential of an electrode is constant, even when a current is flowing, the electrode is non-polarizable. In contrast to this, the potential of polarizable electrodes changes when a current flows.

3.1. Solid membrane electrode:

Solid membrane electrodes consist of compacts or single crystals of poorly soluble ionic compounds or a homogeneous mixture of ionic compounds. If such an electrode is immersed in a solution of one of its participating ions, a potential difference that can be measured forms at the phase boundary through solubility equilibrium. The solubility equilibrium depends on the solubility product of the poorly soluble ionic compound. The membrane material may only let through the ion to be determined with the smallest radius. The most important solid-state membrane electrodes are the fluoride electrode and the silver sulfide electrode.

3.2. Fluoride electrode:

The membrane of this electrode consists of a single crystal of sparingly soluble lanthanum fluoride (LaF3 ↓). The electrode reacts specifically to free fluoride ions(Bralić *et al.*, 2001). The solubility product of LaF3 ↓ determines the concentration range for fluoride determination, which is 10^{-6} mol / l. The electrode is highly selective, the only cross-sensitivity is to hydroxide ions, as they can form sparingly soluble La(OH)3 with La3 +. It should be measured at a pH between 5 and 6. At higher pH values, the hydroxide ion concentration is too high, at pH values below 5 there is undissociated hydrogen fluoride, which then cannot be determined because the electrode only reacts to free ions. The creation of the potential is similar to that of the pH-sensitive glass electrode. The release of ions at the interfaces creates a charge according to the following equation:

$$LaF_3 \rightleftharpoons LaF_2^+ + F^-$$

4. MATERIALS AND METHODS

4.1. Reagent

Preparation of total ionic strength adjustment buffer (TISAB):

Total ionic strength adjustment buffer (TISAB) was prepared according to recommended procedure (Tzimou-Tsitouridou, Kabasakalis and Alexiades, 1985) as follows; 57 ml of glacial acetic acid, 58.44 g of sodium chloride, 029 g of sodium citrate and 61.50 g of sodium acetate were added t0 500 ml deionized water and allowed to dissolved then the pH adjusted to 5.3 with 5 molar sodium hydroxide, and then made up to 1liter volumetric flask with deionized water

Equal volumes of the sample and total ionic strength adjustment buffer (TISAB) are mixed, thereby fixing the ionic strength high enough to make the activity coefficients of unknowns and standards virtually identical. The optimal pH range for the fluoride electrode is pH 5 and is provided by the sodium acetate-acetic acid buffer. Some citrate ions are preferably added to complex metal ions such as iron and aluminum and ensure that the fluoride ion is displaced into the solution as "free" fluoride

4.2. Standard fluoride solution

A standard stock solution of 1000 mg/L ($5.263x10^{-2}$M) Fluoride has been prepared by dissolving 2.219 g sodium fluoride in 1000 ml distilled water after previously dried at 110 °C for two hours, with dissector cooled. See table 2….

4.3. Apparatus

Ion selective electrode of Fluoride (SENTEK)
Limit detection of the electrode 1*10-6 M (0.02 ppm)
TISAB buffer range (4-8)
HANNA HI 4221 PH/mV /Temperature Bench Meters, used to the measurement, measuring range (-2000, + 2000) mv
Accuracy: 0.2, resolution: 0.1

4.4. Methods

The solutions are made up in 150 ml plastic bottles, each filling up to 100 g. The density of the solutions is assumed to be approximately 1 g / cm3.

A weighed sample of toothpaste of approximately 400 mg is placed in a 150 ml beaker containing 50 g of total ionic strength adjustment buffer (TISAB). The mixture then boiled for 2 min". After cooling the solution and filled up to 100g with deionized water." The electrodes are rinsed with deionized water and dried with a tissue after each measurement

5. RESULT AND DISCUSSION

Table.1 fluoride standard solutions concentration and potential energy in (mev)

Conc.[F] M	-Log[F]	E (meV]
1.01E-08	8.00	-284.93
1.00E-07	7.00	-273.97
1.01E-06	6.00	-277.83
1.00E-05	5.00	-303.87
1.00E-04	4.00	-353.17
1.00E-03	3.00	-408.93
1.01E-02	2.00	-476.00

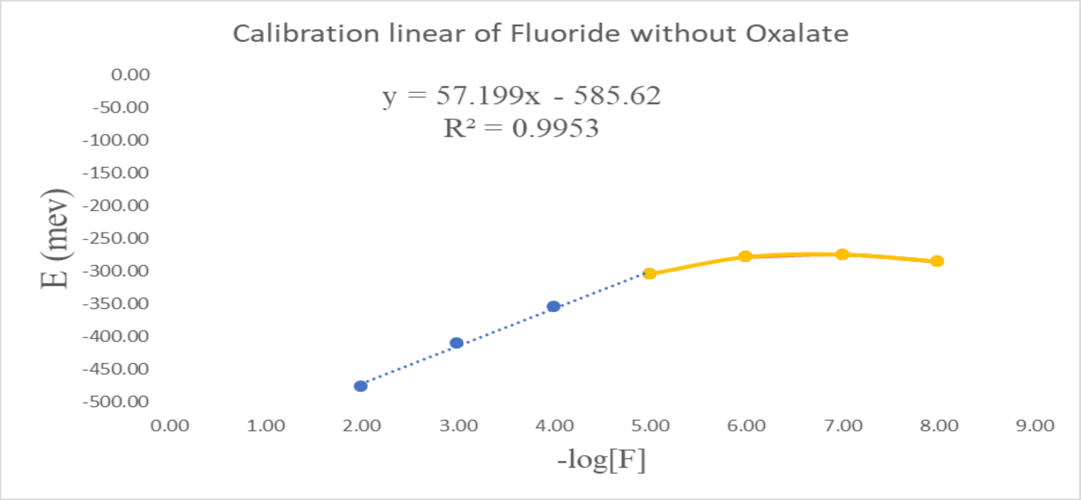

Figure 1 calibration curve of fluoride without interfering ion

Table.2. calibration of standard fluoride with 0.01M Sodium oxalate

-log {F}	E (mev)	Conc. [F] M
6.996971	-298.133	1.007E-07
5.996971	-302.433	1.007E-06
4.975104	-313.066	1.059E-05
3.997402	-352.533	1.006E-04
2.993106	-408.033	1.016E-03

1.996109	-464.166	1.009E-02

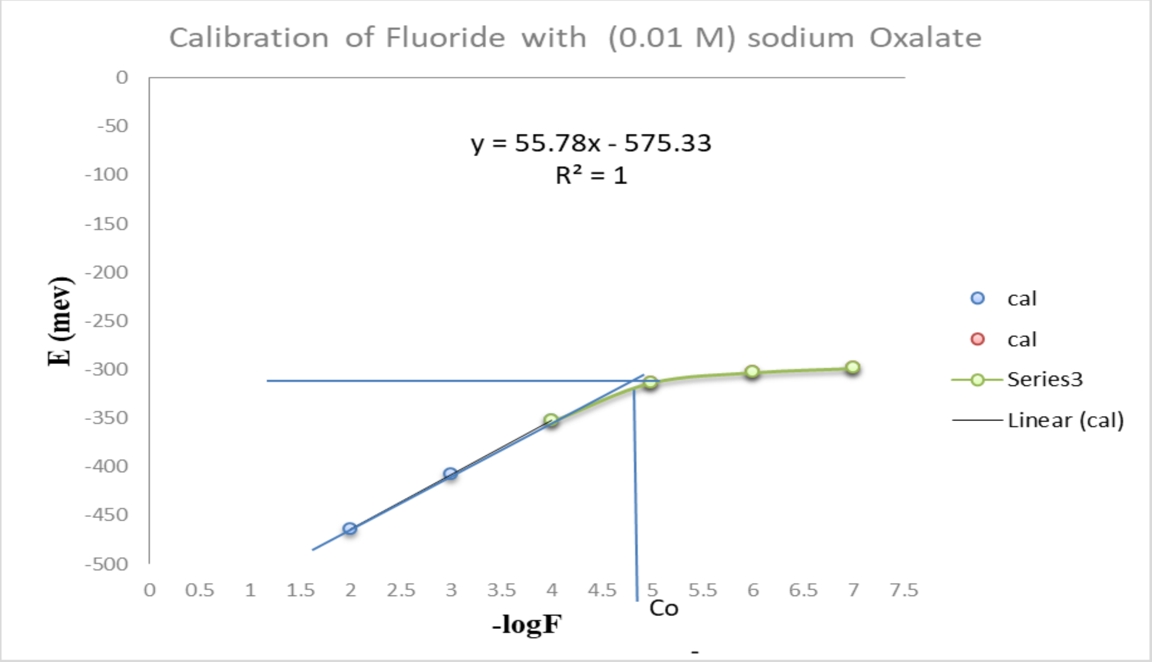

Figure.2. calibration curve of fluoride standard solutions with addition of 0.01 M sodium oxalate

A discussion of the limit of detection in potentiometric should start with a practical example; to emphasize that arbitrary definition of this quantity can be very misleading. The IUPAC recommended definition of limit of detection for an ion-selective electrode is obtained, as shown in Diagram 2, by extrapolating the linear portions of the calibration graph until they meet(Midgley, 1987; Bereczki *et al.*, 2006)

$$E = E^{0} + \frac{RT}{nF} \ln_{10} \lg \left(a_i + K_{ij} \bullet a_j^{n/m}\right)$$

$C_o = Ki\, j^{*} a^{n/m}$ [16]

ai =[F]

$E = a - b^{*}\log [F + (c_o)]$

-Log Co = 4.8 log co = -4.8

Co=LOD = anti log Co= 1.584E-05

[Oxalate]= 0.01

$E = a - b^{*}\log [F + kj^{*}(oxalate)^{1/2}]$, Co = kj*(oxalate)1/2]

$Kj = Co/(oxalate)^{1/2}]$, Kj = 1.584 E-05 /0.1 = 1.58E-4

Table 3 Concentration of fluoride measured in various tooth paste

ID	Box Contain [F] in ppm	Manufacture	Brand	E (meV)	[F] in mol/l measured	[F] in ppm measured
S1	1450	Germany	Prokudent	-379.77	2.52E-04	1196.38
S2	500	Germany	Elmex	-350.6	7.78E-05	359.48
S3	1450	Germany	odol-med3	-379.73	2.51E-04	1141.05
S4	1450	Germany	today dent	-377.77	2.32E-04	1089.49
S5	Not mention	Indonesia	formula-juni	-275.9	3.85E-06	18.15
S6	1450	Germany	denta gard	-381.27	2.67E-04	1243.56
S7	0.0032	China	smart mout	-341.97	5.50E-05	256.83
S8	1053	Iran	alpha dent	-333.2	3.86E-05	179.13
S9	0.0022	Indonesia	life buoy	-329.6	3.34E-05	159.15
S10	Not mention	China	Air sun	-328.97	3.26E-05	154.69
S11	Not mention	China	coafe up	-344.07	5.98E-05	275.74
S12	0.001	Italy	Capitano	-357.2	1.02E-04	461.88
S13	free fluoride	China	LMZnerbal	-330.7	3.49E-05	165.56
S14	Not mention	Switzerland	Emoform	-328.73	3.23E-05	147.16
S15	Not mention	China	dental docto	-328.6	3.21E-05	155.78
S16	0.008	Germany	herbal aloe	-330.37	3.45E-05	163.2
S17	1450	Egypt	close up	-331.47	3.60E-05	169.56
S18	1450	Germany	Signal	-373.73	1.98E-04	940.66
S19	1450	Turkey	Sanino	-381.13	2.66E-04	1261.39
S20	1450	Germany	oral-B	-380.67	2.61E-04	1230.56
S21	1450	Germany	Denivit	-378.97	2.44E-04	1149.63
S22	1450	USA	aqua fresh	-381.5	2.70E-04	1261.42
S23	1450	USA	Sensitive	-380.57	2.60E-04	1209.76

S24	Not mention	Thailand	fresh white	-358.97	1.09E-04	515.38
S25	1450	China	clesan up	-329.37	3.31E-05	154.78
S26	Not mention	Iraq	Amber	-344.63	6.12E-05	289.18
S27	Not mention	China	Dentix	-329.83	3.37E-05	160.62
S28	1450	Japan	Sensodyne	-380.67	2.61E-04	1222.55
S29	500	Germany	Zendium	-359.4	1.11E-04	514.84
S30	1450	Germany	blend.a.mec	-381.53	2.70E-04	1285.85
S31	1400	Germany	Meridol	-377.8	2.33E-04	1109.95
S32	1450	Germany	Dontodent	-377.57	2.30E-04	1084
S33	0.00243	Germany	Crest	-302.2	1.11E-05	52.63
S34	1450	Germany	Colgate	-379.2	2.46E-04	1168.12

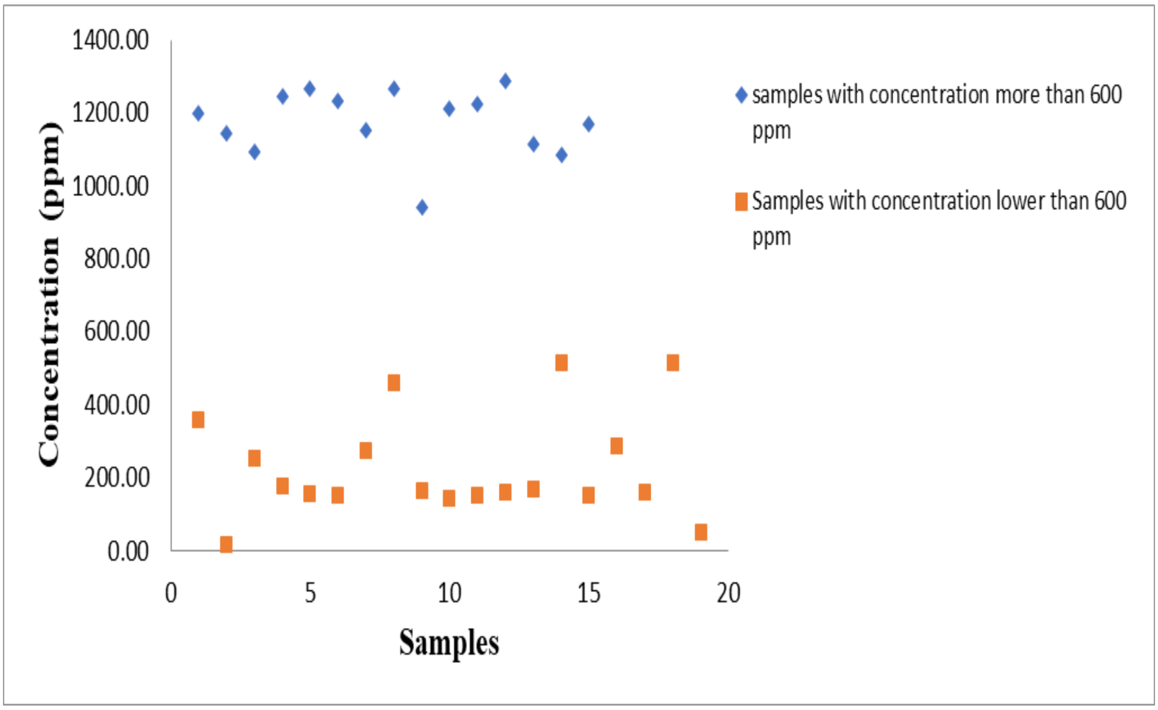

Diagram 3. Relationship between concentration of fluoride (ppm) and their samples ID

According the mentioned results as shown above, the selectivity of the LaF_3 electrode is high.

Interference from oxalate (Ox^{-2}) occurs in the solution only at low fluoride concentrations. It is suspect that this is due to the following reasons: charge, solubility. Since oxalate has two negative charges, it could react with La and create a compound of $La_2(C_2O_4)_3$

Because the solubility the lanthanum oxalate does not stay long as LaF3 ↓. i.e. the solubility of oxalate is low in fluoride, so oxalate does not form a great of interference.

The calibration line shows only a linear area in which a fluoride determination can be possible; so at [F] = 1.584E-05 …. Which are in the range of the detection limit, below that one can no longer determine the concentration of fluoride ions. Clearly fluoride can be determined easily and quickly, which other analysis techniques hardly allow.

By comparing the calculated slope with the theoretical slope (57.93) at (19 C^o, it is obvious that there is a deviation of (1.27 %.) in the determined sample content differs with the manufacturer's information with a deviation of (2 %.)

By comparing the fluoride analysis in toothpaste with ion-selective electrode with different methods such as spectroscopic and ion chromatographic methods, , it was already established that all methods are close to each other's, as shown in the literature reviews (Michalski and Mathews, 2006; Chakraborty, Pandey and Pandey, 2017)

Conclusion

The most important conclusions which are gained from the study is that most of the toothpastes in various brands contain a small amount of fluoride, which is less than 600 ppm, and this concentration is insufficient for Iraqi prescriptions and WHO specifications(Barmes, 1996).

On the other hand, the toothpastes that contain more than 600 ppm fluoride are made in USA, Japan and Germany (except toothpaste Elmex = 359.48 ppm) that produced for Kids

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