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Physics of Flouride-Ise and Its Application in the Assessment of Flouride Ions Concentration in Groundwater around Maiduguri Metropolis, Northeastern Nigeria.

Sonloye.S.A[1], Moses.I.A[2], Goni. M[3]
[1, 2, 3]*(Department of Physics, University of Maiduguri, Borno State, Nigeria).*
Corresponding Author: Sonloye.S.A

Abstract**:** *Four geographical zones in Maiduguri Metropolis were chosen for this study and twenty water samples-five samples from each zone were taken for analysis. Fluoride content of each water sample was then determined by using Lanthanide Fluoride ion Selective Electrode, LaF_3. The results show that the concentrations of fluoride ions in the groundwater samples from all the locations under investigation are far below the minimum concentration of 0.5 mg/l specified by World Health Organization (WHO) for drinking water [1]. The brown staining of permanent teeth, which may be due to dental caries, commonly seen in these areas of Maiduguri is attributed to low concentration of fluoride in drinking water in these areas. Since fluoride is essential for formation of tooth enamel in children, different methods of fluorination of drinking water are recommended. However, direct fluorination of drinking water must be done by expert as fluoride concentration above 1.5mg/l may, over a long period of time, induce dental and skeletal fluorosis [1,2]. The findings in this work is of relevance to water managers and scientists in Maiduguri and other areas where groundwater remains the major source of drinking water.*

Keywords: *Dental caries, Flouride, Groundwater, Ion-Selective Electrode, Maiduguri.*

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I. Introduction

Fluoride ranks 17th most abundant element in the earth's crust, representing 0.06%–0.09% of the earth's crust and the main source of fluoride in groundwater is basically from the rocks minerals [3]. As groundwater percolates through the weathered rock in the aquifers, it dissolves fluoride bearing minerals, hence releasing fluoride into solution. It, therefore, follows that most groundwater sources generally have higher fluoride concentrations than surface water. Fluoride is one of the important life elements. It is essential for normal mineralization of bones and formation of dental enamel [2,4]. However, Low levels of fluoride below the minimum level of 0.5mg/L can cause dental cavities while above the maximum permissible limit would cause various metabolic disturbances in animals and human being including dental and skeletal fluorosis [2, 5, and 6]. World Health Organisation, WHO sets the minimum value as 0.5mg/L and the maximum permissible limit of 1.5mg/L for Fluoride in drinking water [1]. These effects are mostly felt in developing teeth before they erupt from gums [5]. Children under nine years old, if exposed to high level of fluoride in drinking water over a long-term, can lead to skeletal fluorosis [1]. Because brown staining and/or pitting of permanent teeth, which may be due to dental caries, is commonly seen in Maiduguri, it becomes imperative that fluoride level in drinking waters in this environment needs to be monitored and strictly controlled. In typical drinking waters, the analysis of fluoride can be accomplished either by Ion Selective Electrodes (ISE) or by Ion Chromatography (IC). Electro analytical methods based on potentiometry with ion-selective electrodes seem to be the most popular and convenient method of determining the fluoride concentrations in drinking water due to its high selectivity, specificity and low detection limits [7]. Other advantages of this method include a short analysis time, elimination of sample pre-treatment, simplicity of the measuring system and relatively low instrument cost [8].

1.1Theory of Fluoride Ion-Selective Electrode

The Fluoride ISE method was invented by Frant and Ross in 1966[8,9]. This method utilizes a Fluoride Selective Membrane, which is typically a lanthanum fluoride crystal. Typically the LaF3 element is sealed into a rigid plastic tube with silicone rubber. After a settling time of several minutes, equilibrium is set up between the F^{-1} ions in the surface and in the solution resulting in a charge imbalance which is dependent on the activity and concentration of the fluoride ions under test. The fluoride activity is measured according to the following equation:

$$\mathbf{E = Eo + 2.3\ RT/\ nF\ log\ X}^{[10]} \qquad (1)$$

Where Eo = a constant for a given cell
R = the gas constant
T = the Temperature in Kelvin
n = the ionic charge
F = the Faraday constant and the expression
RT/nF is termed the Slope Factor
X= activity of the fluoride

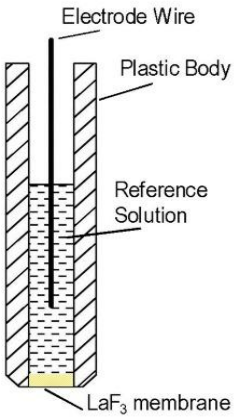

Fig.1: diagram showing LaF_3

The method is sensitive to the solution pH. At low pH, fluoride can form hydrofluoric acid, which lowers the measurement. At high pH, hydroxide can also respond to the ISE and increase the measurement. A Total Ionic Strength Adjustment Buffer (TISAB) solution is typically added to the samples to adjust the solution pH to an optimum value of 5.0 ~ 5.5. The relatively high ionic strength from the TISAB can also minimize the liquid junction potentials, provide constant ionic strength for samples and standards and it contains a chelating agent to break up metal-fluoride complexes. All negative interfering effects that can influence the method of determination are eliminated by the usage of TISAB buffer. Calibration is performed by analyzing a series of standards and plotting mV vs. fluoride concentration on semi-log paper or by calibrating the ion meter directly in terms of fluoride concentration.

Since the electrode only respond to free ions, the concentration of free ions, C_f, is given as:

$$C_f = C_t - C_b \text{ [11]} \qquad \textbf{(2)}$$

Where Ct = total ions concentration
C_b = concentration of all bond or fluoride complexed ions

II. Material and Methods

Maiduguri, also called Yerwa by its local, is the capital and the largest city in Borno State in north-eastern Nigeria. It is located within the Latitude 11^0 5'N and longitude 13^0 09'E. Koppen-Geiger climate classification classifies its climate as hot semi-arid with low rainfall [12] and average daily temperature ranging from 25°C to 35°C, with mean of the daily maximum temperature exceeding 40°C between March and June before the onset of the rains in July to September. It has mainly sandy loam soils [4]. In this study, four geographical areas in Maiduguri were chosen and Water samples collected from twenty different boreholes-five samples, 5, from each zone, in the month of May, 2015 were used for the analysis. These areas include Jiddari Polo (JPL), Gwange (GWG), Mashamari (MSH) and Moduganari (MDG).

2.1 Collection and Analysis of the water samples

Water samples were collected from twenty boreholes located at different geographical zones within Maiduguri Metropolis using clean and dried 250 ml plastic bottles for the collection of the sample. The tap ot each borehole was opened and water was allowed to flow for between 1min to 2 minutes before taken each sample. Then, the plastic bottles were filled with water up to 200 ml leaving some space to allow shaking before analysis. The collected samples were labelled as: GW (1, 2, 3, 4, 5) for the five samples collected from Gwange, JPL for samples from Jiddari Polo, MDG for samples from Moduganari and MSH for Mashamari samples. These samples were delivered to the laboratory for analysis within 30 minute of collection.

Fluoride concentration determination was carried out in the Laboratory of National Agency for Food and Drugs Administration Control (NAFDAC) Maiduguri Laboratory. Analysis was carried out using a Orion

Benchtop pH/ISE Meter 720 A Model pH Meter and ORION 96-09 BN combine Fluoride Electrode as an ion-selective electrode. The pH of each of the samples was measure immediately using pH meter. Since the method is sensitive to solution pH, a Total Ionic Strength Adjustment Buffer (TISAB) solution is added to each water sample to adjust the solution pH to an optimum value of 5.0 ~ 5.5. All negative interfering effects that can influence the result of the analysis are also eliminated by TISAB. The fluoride activity in each sample is then measured according to the equation (1) given above.

III. Results and Discussion

The results obtained from the analysis of 20 samples of drinking water collected from four different locations in Maiduguri are given in the table below:

Table 1: Shows concentration of Fluoride ions in Groundwater Samples from Different Locations in Maiduguri Metropolis.

GWG (mg/l)	JPL (mg/l)	MDG (mg/l)	MSH (mg/l)
0.2	0.2	0.02	0.01
0.1	0.1	0.01	0.05
0.1	0.1	0.04	0.02
0.1	0.1	0.03	0.01
0.1	0.2	0.01	0.02

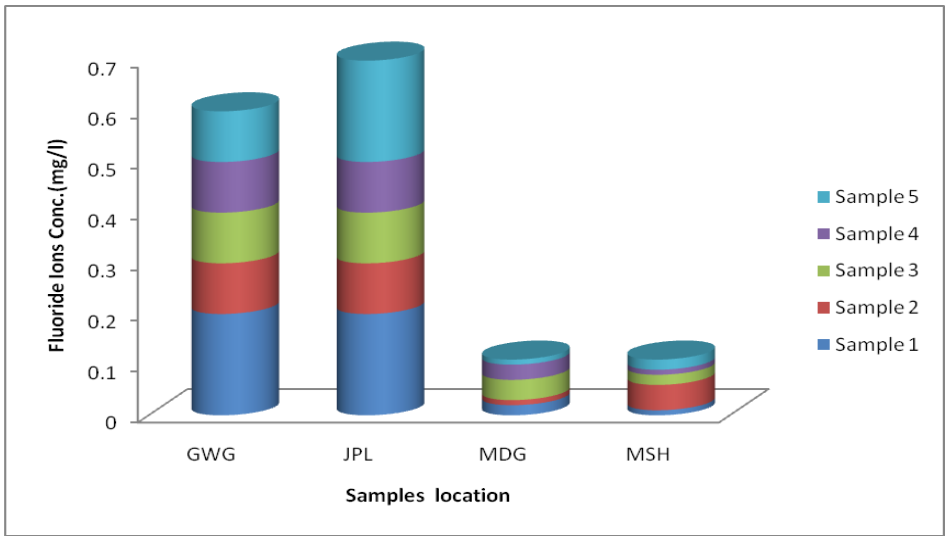

Figure 2: Graph showing concentration of Fluoride ions (mg/l) against Groundwater Samples from Different Locations in Maiduguri Metropolis.

Table 2: Shows concentrations of Fluoride ions and pH of each Groundwater Samples in Maiduguri Metropolis

SAMPLES	CONCENTRATION (mg/l)	pH
GWG 1	0.2	7.9
GWG 2	0.1	6.2
GWG 3	0.1	7.7
GWG 4	0.1	7.5
GWG 5	0.1	6.9
JPL 1	0.2	6.9
JPL 2	0.1	6.3
JPL 3	0.1	6.3
JPL 4	0.1	6.1
JPL 5	0.2	7.0
MDG 1	0.02	8.3
MDG 2	0.01	7.5
MDG 3	0.04	6.9
MDG 4	0.03	7.7
MDG 5	0.01	9.1
MSH 1	0.01	7.3
MSH 2	0.05	7.2
MSH 3	0.02	7.0
MSH 4	0.01	7.2
MSH 5	0.02	7.6

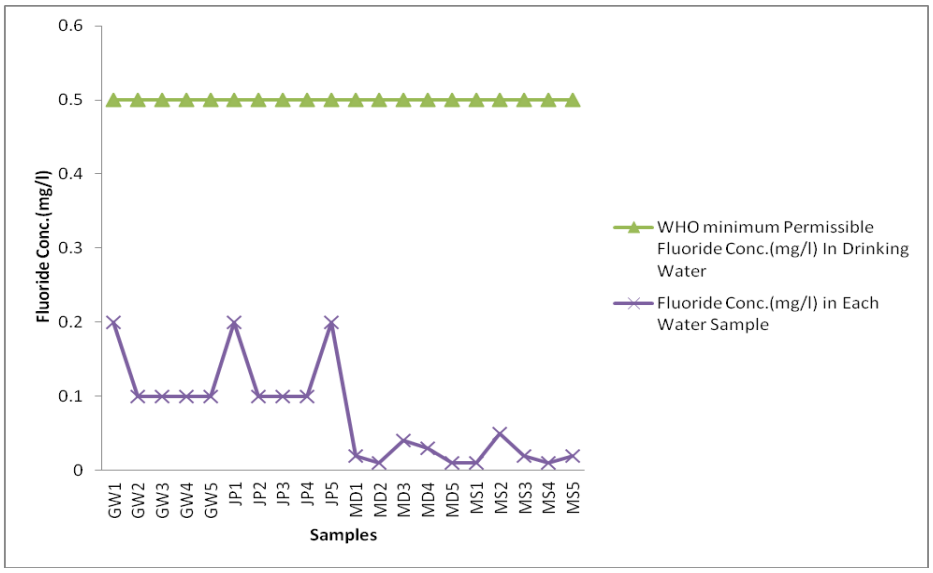

Figure 3: Shows graphs of Fluoride ions concentrations (mg/l) against Groundwater Samples from each location in Maiduguri Metropolis

Tables 1 and 2 above show the concentrations of fluoride ions, F^-, present in groundwater at different locations in Maiduguri metropolis. Table 1 particularly shows fluoride ions concentration in each of the samples from Gwange (GWG), Jiddari Polo (JPL), Moduganari (MDG) and Mashamari. While table 2 shows the concentration of fluoride ions concentration and the corresponding pH of each of the water samples. Both table 1and 2 show that there is significant amount of fluoride ions, F^-, in groundwater samples from Gwange (GWG) and Jiddari Pollo (JPL) areas of Maiduguri while fluoride ions concentration in groundwater samples from Moduganari (MDG) and Mashamari (MSH) is very very low. Moreover, fig. 2 and fig.3 above show that concentrations of fluoride ions present in all the groundwater samples from all the locations under investigation in Maiduguri metropolis is highly variable and are dependent upon the individual geological environment from which the water is obtained. Also, the fact that the concentrations of fluoride ions in the groundwater samples from all the location are far below the lemon line graphs in fig.3 clearly shows that none of the groundwater samples from all the locations under investigation meet the minimum permisible level of fluoride concentration in drinking water as specified by the World Health Organisation, WHO[1].

IV. Conclusion

Lanthanide Fluoride Ions Selective Electrode has proven to be a very effective instrument for investigating the fluoride ions concentration in drinking water due to its high selectivity, specificity and low detection limit. The analysis of groundwater samples from all locations under investigation in Maiduguri metropolis gives evidence that fluoride concentrations in these samples are far below the minimum allowed concentration of 0.5 mg/l specified by World Health Organization (WHO) [1]. The brown staining and/or pitting of permanent teeth, which may be due to dental caries, commonly seen in these areas of Maiduguri, may be attributed to this very low level of fluoride in drinking water in all the areas under investigation. Since fluoride is an essential element for the formation of healthy tooth enamel, adequate fluoride ingestion is helpful to avoid caries [2]. Fluorination of the groundwater for the purpose of drinking in these areas is, therefore, recommended to prevent tooth decay especially in children. This can be done in different ways such as direct fluorination of drinking water in the areas, the use of NaF tablets, fluoridated milk and milk powder, use of fluoridated cooking salt and direct application of tooth fluoride varnish and pastries. However, fluorination of drinking water must be done by the expert in Public health as Fluoride ions concentration above 1.5mg/l, over a long period of time, may induce dental and skeletal fluorosis, which may result in malfunction of the bone and joint system [7, 10]. Therefore, determination of fluoride ion in water samples is of great significance for human health because of daily consumption in certain amounts. The findings in this work is of relevance to water managers and scientists in Maiduguri as well as other areas where groundwater remains the major source of drinking water.

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