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Comparison of different Total Ionic Strength Adjustment Buffer Compositions for Determination of Low Level Fluoride in Environmental Water Samples with Fluoride Ion Selective Electrode

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Abstract

Fluoride content of environmental water samples collected from the vicinity of Pilanesberg National Park was determined using a Fluoride Ion Selective Electrode (F-ISE). Different Total Ionic Strength Adjustment Buffers (TISABs) EDTA, CDTA, citrate and acetate buffers, were compared for their effectiveness in releasing fluorine into the solution in its ionic form, by adjusting the pH and ionic strength of the solution, as well as by chelating polyvalent cations present in the samples. Nine water samples were collected from different sites around the park, where there is a decommissioned fluorspar mine, and an extinct volcano for fluoride content. Quantification was carried out by means of multipoint calibration covering the range of interest in all treatments. The fluoride concentration was calculated using the Nernst equation with values obtained from the calibration graph. It was found that CDTA and EDTA buffers were the best TISABs as they produced a better linearity, slope and recovery in that order, whereas the other acetate also produced better parameters and results than the untreated water samples.

Keywords: Fluoride; Environmental water samples; ISE; TISAB's; CDTA; EDTA; Acetate; Citrate; Pilanesberg

Introduction

Fluoride is considered as one of the essential microelements for humans to be healthy [1,2]. It presents in most, if not all body tissues, with the highest levels in bones, dentine and teeth. Smaller quantities in the order of 1.0mg/L in ingested water are usually considered to have beneficial effects on the rate of avoidance of dental carries, particularly among children [3,4]. However, excessive intake results in pathological changes to teeth and bones, such as mottling of teeth (dental fluorosis) followed by skeletal fluorosis [5-7]. Higher levels of fluoride lead to increases in the levels of dental mottling, and changes in bone structure, namely skeletal fluorosis [8-14]. Fluorosis is caused by intake of high fluoride predominantly through drinking water containing concentrations more than 1.0mg/L [15-17].

Neel, et al. and Linhares, et al. stated that fluoride accumulates in bones and teeth as fluorapatite and cause bones to become brittle [18,19]. Other metabolic changes also have been reported in soft tissues such as thyroid, reproductive organs, brain, liver and kidneys [20-24]. Fluoride may induce periosteal reaction, hyperostosis, osteoporosis, osteosclerosis, osteophytosis or osteomalacia in various combinations [25,26]. The effect of fluoride is also observed on plants. Excessive accumulation of fluoride in leaves results in the appearance of necrosis at the tips and margins of leaves [27-28]. Fluoride may induce changes in metabolism, decreased growth and yield, leaf chlorosis and in extreme cases plant death [29].

Hence it is imperative to monitor the amount of fluoride in water bodies as well as the soil. The content of fluoride in samples can be determined by using several techniques, including potentiometry using a Fluoride Ion Selective Electrodes (ISE), Ion Chromatography (IC), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), capillary electrophoresis, solvent-extraction coupled to fluorimetry, polarography and colourimetric techniques based on dyes. Methods based on Flow Injection Analysis (FIA), using different detection methodologies have also been reported; each method with its own advantages and disadvantages [30-32]. Potentiometry involves the usage of Fluoride Ion Selective Electrode (F-ISE), miniaturized analytical devices, which can deliver real-time and on-line information on the presence of fluoride ions in complex samples [33,34].

In potentiometry TISABs are required to adjust the pH and ionic strength of the sample solution. In addition any polyvalent cations present in the solution that might interfere with the analysis, need to be removed by complexing them [35-38]. The theoretical slope of the graph obtained from the calibration standards is 59.2mV at 25 for monovalent anions [39,40]. The slope of the calibration graph is the mV response per decade of concentration change. Measured slope generally lie in the range 54 ± 5mV/decade and will have a negative value for negative ions.

Materials and Methods

The water samples were collected from suspected areas in and around Pilanesberg National Park using previously cleaned and dried plastic sampling bottles. A total of nine water samples including rivers, shallow lakes, stagnant accumulated rain water bodies and a tap water were collected. Four different types of TISAB solutions were used for treating the samples as complexing agents (Figure 1).

Ethylene Di Amine Tetra Acetate (EDTA) buffer, sodium acetate buffer, tri-sodium citrate buffer and Cyclohexylene Di Amine Tetra Acetate (CDTA) buffer were used. All the standards and sample solutions were treated with the same amount of TISAB in all cases. The recipes for the preparation of the TISABs were obtained from the literature.

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Figure 1: Map of pilansberg national park.

The TISAB solutions were prepared using the following procedure

Acetate buffer was prepared by dissolving 0.75 M sodium acetate, 0.01M sodium citrate, 58.0g sodium chloride and 57 mL glacial acetic acid in approximately 500 mL de-ionised water. The pH of the resulting solution was adjusted to 5.5 with 5M sodium hydroxide solution. The solution was diluted to a volume of 1L with de-ionized water. EDTA buffer was prepared by dissolving 4g di-sodium EDTA in approximately 500mL water; 57mL of glacial acetic acid and 58.0g sodium chloride were added and stirred until completely dissolved. The pH of the resulting solution was adjusted to 5.5 with 5M sodium hydroxide. The solution was diluted to a volume of 1L with de-ionized water.

Citrate buffer was prepared by dissolving 0.3g tri-sodium citrate in approximately 500mL deionised water. 58.0g sodium chloride and 57 mL glacial acetic acid were added to the solution. After cooling the solution to room temprature, the pH of the solution was adjusted to 5.5 with 5M sodium hydroxide. The solution was diluted to a volume of 1L with de-ionized water. CDTA buffer was prepared by dissolving 4.0g CDTA in 500 mL water. 57 mL glacial acetic acid and 58g sodium chloride were added to the solution and mixed well. After cooling to room temprature, the pH was adjusted to 5.5 with 5M sodium hydroxide and made up to 1L with de-ionized water.

The standard fluoride solution was prepared using the following procedure

A 1000mg/L fluoride solution was prepared by weighing 2.210g of sodium fluoride; dissolved in deionised water and made up to the 1000mL mark. The working standard solutions with concentration 0.01, 0.02, 0.05, 0.1, 0.5, 1, 2, 5, 10 and 100mg /L were prepared from the stock solution by dilution on the day of analysis. The instruments used in the analyses were a DC219 Metler Toledo fluoride combination electrode (Columbus Ohio, USA), Metrohm fluoride ion selective electrode and Metrohm Ag/AgCl reference electrode (Herisau, Switzerland), a Metrohm 744 pH meter (Herisau, Switzerland), a Metler Toledo S30 SevenEasy ion meter (Columbus Ohio, USA) were used for potentiometric measurements.

Statistical analysis was performed using Statistica software one way Analysis Of Variance (ANOVA) at 95% confidence level. In addition, non-parametric Krouskal-Wallis ANOVA and t-Tests were performed to determine any significant differences between the analytical procedures. In all analyses certified quality check standard fluoride solution (Fluka, Steinheim Switzerland) was run alongside the samples.

4.3 Sample Preparation

The water samples were mixed with TISABs in a 1:1 proportion; 50mL of water sample was mixed with 50mL of the respective TISAB solution.

Results and Discussion

The amount of fluoride in the water samples was calculated using the Nernst equation.

E0=m log [F-]+E

Where: E0 is the potential difference reading from the ionalyser

m is the slope of the calibration graph

Log [F-] is the logarithm of the concentration of fluoride ion

The calibration parameters obtained for the different treatments are given in Table 1.

As is evident from the parameters, the slopes of the calibration graphs are in the acceptable range, the lowest -53.7 and the highest -59.1mV/decade. The linearity (R2) is also good, (0.9955 to 0.9999). Results for the water samples are reported in Table 2.

The fluoride content in the same sample shows considerable difference with different treatments (TISABs). In the majority of the cases (7 out of the 9) CDTA produced a higher fluoride content, whereas in all cases the non-treated sample produced the lowest fluoride content. Recovery tests were also done on all of the samples and the percentage recovery for each treatment is given in Table 3.

Sample ID	Fluoride content, mg/L (Result ± SD, n=3)				
	Treatment				
	No Buffer	EDTA Buffer	CDTA Buffer	Citrate Buffer	Acetate Buffer
1	1.79 ± 0.17	1.98 ± 0.12	2.06 ± 0.20	1.85 ± 0.12	1.85 ± 0.11
2	0.88 ± 0.10	1.00 ± 0.23	1.05 ± 0.16	0.99 ± 0.20	0.96 ± 0.09
3	4.22 ± 0.14	4.41 ± 0.20	4.41 ± 0.16	4.40 ± 0.19	4.32 ± 0.26
4	0.90 ± 0.10	0.96 ± 0.09	1.01 ± 0.16	0.99 ± 0.21	0.94 ± 0.15
5	3.06 ± 0.14	3.29 ± 0.15	3.33 ± 0.08	3.20 ± 0.12	3.13 ± 0.16
6	2.21 ± 0.09	2.42 ± 0.14	3.08 ± 0.08	2.46 ± 0.11	2.29 ± 0.09
7	0.28 ± 0.14	0.45 ± 0.13	0.40 ± 0.10	0.40 ± 0.10	0.36 ± 0.02
8	0.13 ± 0.10	0.16 ± 0.05	0.21 ± 0.07	0.17 ± 0.06	0.18 ± 0.04
9	1.02 ± 0.24	1.14 ± 0.12	1.27 ± 0.15	1.08 ± 0.15	1.04 ± 0.06

Table 1: The calibration parameters obtained for the different treatments.

Treatment	Equation	Linearity (R2)
CDTA	-59.1 × +120.8	0.9999
EDTA	-59.0 × +120.6	0.9996
Citrate	-56.6 × +118.4	0.9991
Acetate	-56.3 × +117.9	0.996
No Buffer	-53.7 × +114.2	0.9955

Table 2: Fluoride content in water samples with different treatments (TISABS).

	Percent Recovery				
SAMPLE ID	No Buffer	EDTA Buffer	CDTA Buffer	Citrate Buffer	Acetate Buffer
1	92.5	97	98	94.5	94.5
2	89	95	101	92	92
3	93.3	99.1	98	97.8	97.6
4	91	101	101	92	94
5	96.3	101	99.3	96.3	98
6	96.4	100	100	98.4	96
7	96	94	94	90	90
8	75	95	100	95	90
9	90	101	98	95	94

Table 3: Fluoride recovery with different treatments (methods).

The percentage recovery was found to be in the acceptable range for all treatments. Again CDTA produced recovery close to the true value as compared to the rest and in 7 of the 9 samples non-treated samples resulted in the lowest recovery. It was found that seven of the nine water samples produced fluoride concentration above the threshold recommendation limit by World Health Organisation (WHO), which is 1.0mg /L. Sample numbers 1, 3, 5 and 6 recorded above 1.8mg /L, 4.2mg /L, 3.1mg /L and 202mg /L fluoride in that order.

Conclusion

EDTA and CDTA buffers proved comparably the best TISABs between the compared buffers with CDTA slightly bettering EDTA with respect to linearity, slope and higher fluoride content. The linearity for the calibration graph was 0.9999, the slope -59.1mV/decade and recovery ranging between 94.0% and 101%. The percentage recovery is on par for EDTA and CDTA. Citrate has the third recovery which was better than acetate.

Conflict of Interest

The authors declare there is no conflict of interest.

Data Protection

All data generated or analyzed during this study are included in this published article.

Authors' Contribution

All authors contributed to the study conception and design. T Forsido and P. Ndibewu performed material preparation, data collection and analysis.

T. Forsido wrote the first draft of the manuscript and P. Ndibewu commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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