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Investigation into a Novel Method for Fluoride Monitoring - The BIMI Method

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ABSTRACT

A novel analytical method for monitoring of fluorides in various media is proposed (BIMI Method). The developed method replaces 2-(4-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid, trisodium salt in the SPADNS – Zirconyl chloride method with 4,5-dihydroxy-1,3-benzenedisulfonic acid, disodium salt. Absorbance of the complex at its absorption maximum of 300 nm was found to decrease with increase in fluoride concentration in solution. The optimum pH for the required complex formation was determined to be between 4.25 and 4.75. The proposed BIMI method was applied to the analysis of fluorides in river water and T – test was used to compare concentrations of fluorides determined using the known method with those determined using the new BIMI method. At 95% confidence interval (p = 0.05) and 18 degrees of freedom, with critical value of 2.10, the $|t_{exp}|$ was 0.282. This shows there was no significant difference between the results obtained from the known method (SPADNS) and that obtained from the proposed method, since $|t_{exp}| < t_{critical}$. This implies that 4,5-dihydroxy-1,3-benzenedisulfonic acid, disodium salt can be used in place of 2-(4-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid, trisodium salt in the SPADNS – zirconyl chloride method.

Key words: Novel Analytical Method, Fluoride, Spectrometry, Tiron

INTRODUCTION

The goals of analytical chemistry are to improve established methods of analysis, to extend existing methods of analysis to new types of samples, and to develop new analytical methods. For once a method has been developed and tested; its application is best described as chemical analysis (Harvey, 2000). Such methods are recognized as standard methods. And this may be unique to the specific laboratory or it may be a widely accepted method used by many laboratories. It is therefore the duty of the analytical chemist to come up with new and improved ways of carrying out established procedures. The onus is on the analyst to continuously modify what has already been done in order to optimize or improve procedures to meet up with constantly evolving challenges of the real world.

The first few questions that must be answered are:

i) What constitutes a standard method?
ii) How much modification can one do to an established method in order to achieve a new method?

4,5-dihydroxy-1,3-benzenedisulfonic acid, disodium salt (Tiron) is a metal ligand and can be used in colorimetric metal assays for iron, manganese, titanium, molybdenum and zirconium (Merk Index, 11th Edition). Transition metal complexes tend to have their frontier orbitals separated by energy characteristics of photons of lights from the ultraviolet to the visible range. The interaction of such complexes with anions capable of replacing their ligands has been harnessed to quantitatively determine the concentration of such anions (Olga and Lyudmila, 2007; Chang-Qing *et al*., 2005; Breaux *et al*., 2003; Brossok *et al*., 1987; Paul *et al*., 2011).

Fluorine is the most chemically active of the non-metallic elements. It reacts directly with most elements and indirectly with nitrogen, chlorine and oxygen. Nearly all compounds are decomposed by fluorine to form fluorides that are among the most stable of all chemical compounds. But, in spite of its ready availability, fluorides are not found in enough deposits to make commercial exploitation viable.

Fluorine has a dual role in human and animal life. At lower concentration (less than 1.5 mg/L) it is an important element because it aids growth and prevents the enamel of the teeth from dissolving under high acidic conditions (WHO 1984). But at higher concentrations it is a toxic substance to the body (NIH, 1981; Campbell, 1987). In excess, fluoride ion results in dental, skeletal and non – skeletal fluorosis as well as renal, gastrointestinal and immunological toxicity. Various dietary components influence the absorption of fluorides from gastrointestinal tract and the absorbed fluorides are distributed throughout the body.

The source of fluoride pollution in the environment is from two channels; natural and anthropogenic (Cengeloglu *et al.* 2002). Fluoride is frequently encountered in minerals and in geochemical deposits and is generally released into subsoil water sources by slow natural degradation of fluorine contained in rocks. Fluoride is found naturally in water, foods, soil, and several minerals such as fluorite and fluorapatite. However, it is also synthesized in laboratories where it may be added to drinking water or used in a variety of chemical products.

Its occurrence in ground water is in different concentrations depending on the nature of rocks and natural minerals at certain depths. Other sources of fluorine include industries, well water and municipal water from which many people get drinking water.

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Sachet and bottled water may also contain some certain concentration of the element. Water and food are the major mediums of fluoride intake by humans. Fluoride can rapidly cross the cell membrane and get to the skeletal and cardiac muscles, liver and skin.

MATERIALS AND METHODS

Materials:

A Jenway, 6405, UV/Vis Spectrophotometer and a 1.0 cm quartz cell were used for absorption studies; pH was measured with a Jenway3505 pH meter.

4,5-dihydroxy-1,3-benzenedisulfonic acid, disodium salt and 1,8-dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6-disulfonic acid trisodium salt ($C_{16}H_9N_2Na_3O_{11}S_3$) were obtained from Aldrich Chemicals; zirconyl chloride, sodium fluoride, sodium arsenate and other chemicals were purchased from Zayo-Sigma chemicals limited as analytical grade and used without further purification. Double distilled water was used for all dilutions. The reagent solutions were prepared as described in subsequent sections.

Methods:

Standard Fluoride Solution 10.00 mg L^{-1}:

0.5 g of sodium fluoride (NaF) was weighed and dried in an oven at 110 ^{0}C for a minimum of 120 minutes. 0.221 g of this was then dissolved in 1000 cm^3 of double distilled water. 100 cm^3 of this was further diluted to 1000 cm^3. The solution contains 0.010 mg F^- /cm^{-3}. 2.0, 4.0, 6.0 and 8.0 mg L^{-1} solutions were prepared by serial dilution.

SPADNS Solution:

1,8-dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6-disulfonic acid trisodium salt ($C_{16}H_9N_2Na_3O_{11}S_3$) (1.916 g), was weighed and dissolved in water and made up to 1000 cm^3 in a volumetric flask (3.36 x 10^{-3} M). This solution was stored in a brown bottle away from sunlight.

Tiron Solution:

Tiron (4,5-dihydroxy-1,3-benzenedisulfonic acid, disodium salt) (1.118 g), was dissolved in water and made up to the mark in a 1000 cm^3 volumetric flask (3.37 x 10^{-3} M).

Zirconyl Acid Solution:

Zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$) (0.135 g), was weighed and dissolved in about 25 cm^3 water. 200.0 cm^3 of concentrated HCl was then slowly added and stirred, followed by an additional 150.0 cm^3 HCl. The solution was stirred thoroughly and made up to 500 cm^3 with water (1.29 x 10^{-3} M of $ZrOCl_2.8H_20$).

Zirconyl - SPADNS Mixed Reagent:

Equal volumes of the SPADNS solution and the zirconyl acid solution were mixed to form a single reagent. This zirconyl – SPADNS solution was kept in a brown bottle away from sunlight, ready for further work.

Procedure

A

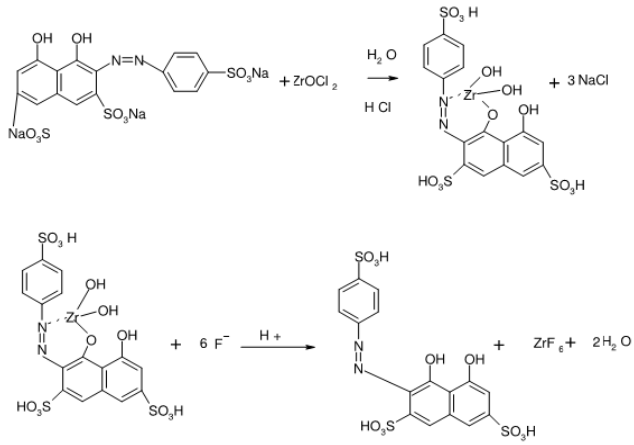
Into a 100.0 cm^3 volumetric flask was transferred 10.0 cm^3 of NaAc - HAc buffer solution (pH 4.60, 0.20 M), the fluoride solution and 10.0 cm^3 of the zirconyl acid solution. The mixture was diluted to 100 cm^3 with distilled water and thoroughly mixed. 10.0 cm^3 of the SPADNS solution was then added and mixed again. It was allowed to stand for 30 minutes on a water bath at 85 ^{0}C and the absorbance of the sample, A, and that of the blank, A_0 (that is without the fluoride solution) were measured at 570 nm. These measurements were carried out at the same time to minimize errors.

B

The procedure in A above was repeated, using another 100.0 cm^3 volumetric flask. Instead of the SPADNS solution, 10.0 cm^3 (1.0 x 10^{-3} mol L^{-1}) of the Tiron solution was added and mixed again. It was then allowed to stand for 10 minutes on a water bath at 85 ^{0}C and the absorbance of the sample, A^T, and that of the blank, A^T_0 were measured at 300 nm.

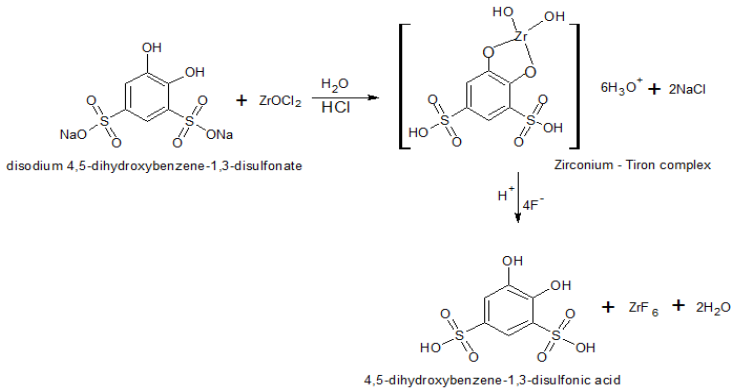
RESULTS AND DISCUSSION

2-(4-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid, trisodium salt (SPADNS) has been in use for the quantitative determination of fluorides in various media over the years. The basic concept lies in the fact that 2-(4-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid, trisodium salt forms a low dissociation constant complex with zirconium, as shown in scheme 1. This complex, in the presence of a strong anion like fluoride, regenerates the 2-(4-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid moiety, leading to a shift in the absorption maximum of the Zr – SPADNS complex.



Scheme 1: SPADNS – $ZrOCl_2$ Reaction and subsequent bleaching with F^- ion.

Since 4,5-dihydroxy-1,3-benzenedisulfonic acid, disodium salt has a catechol type bidentate chelating group, we have attempted to use it as a substitute indicator to make a novel process for the quantitative determination of fluorides. The proposed reaction between 4,5-dihydroxy-1,3-benzenedisulfonic acid, disodium salt and zirconyl chloride, and the subsequent reaction with fluoride ions is given in scheme 2:



Scheme 2: Tiron – $ZrOCl_2$ Reaction and subsequent reaction with F^- ions

The pKa value for the 4,5-dihydroxy-1,3-benzenedisulfonic acid, disodium salt was calculated to be 6.727 from the pH of its solution.

The absorption spectra of tiron - zirconyl chloride at a pH of 4.6 is given in Figure 1. It can be seen that the complex has an absorption maximum at 300 nm.

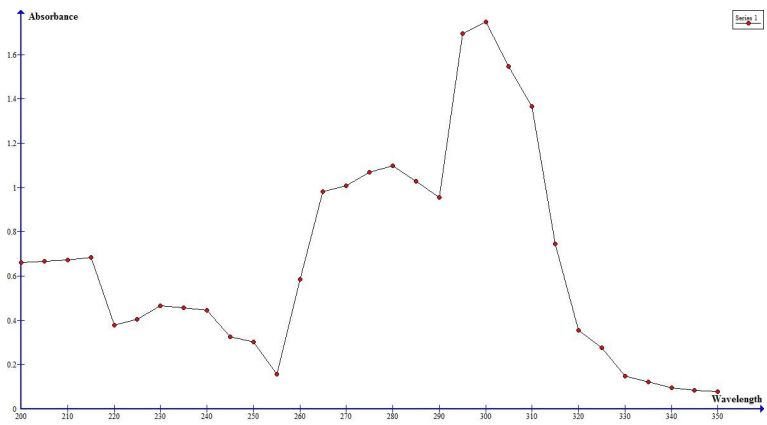


Fig. 1: Plot showing absorption maximum of Tiron – Zirconyl chloride complex at 300 nm

The absorption maximum of a solution of tiron is at 280 nm. Introduction of the zirconyl chloride to the solution at a controlled pH of 4.6 gave the shift in wave length of maximum absorption to 300 nm as observed.

Figure 2 gives the effect of pH on the detection of fluoride ions. From the results, it can be seen that the best pH at which there was observable change in the absorbance (Ao – A, where Ao = absorbance in the absence of F^- ions and A = absorbance in the presence of F^- ions) was between 4.25 and 4.75. There was no significant difference in the absorbance of the tiron – zirconyl chloride complex in the presence of the fluoride ions and in the absence thereof at pH values lower than 4.25 and higher than 4.75. The best pH for the interaction of the complex with fluoride ions is therefore between 4.25 and 4.75. the pH of 4.6 was chosen as optimum for the purpose of this work.

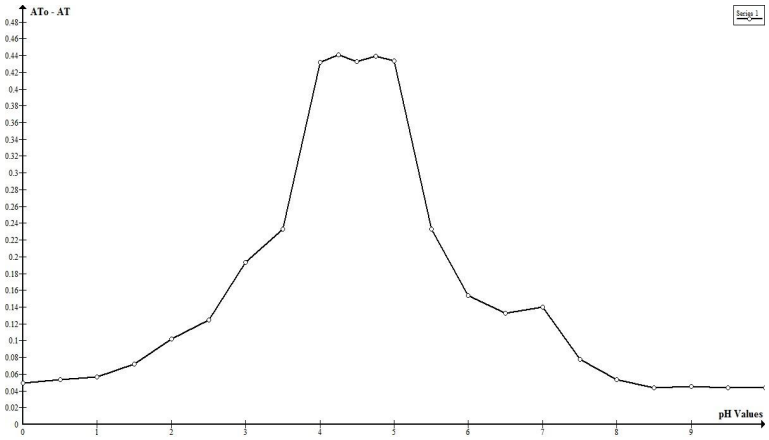


Fig. 2: Effect of pH on detection of fluoride ions

The effect of incubation time was also investigated in order to select the optimum time required to allow for complete reaction between the complex and the fluoride ligand. It was observed that at incubation time less than ten minutes, the reaction appeared not to have taken place. At incubation time above twenty minutes, there was no further difference in the absorbance of the fluoride reacted tiron – zirconyl chloride complex and the free complex that has not been subjected to reaction with fluoride. The reaction appeared to have reached equilibrium. The best incubation time was therefore taken to be fifteen (15) minutes (Figure 3)

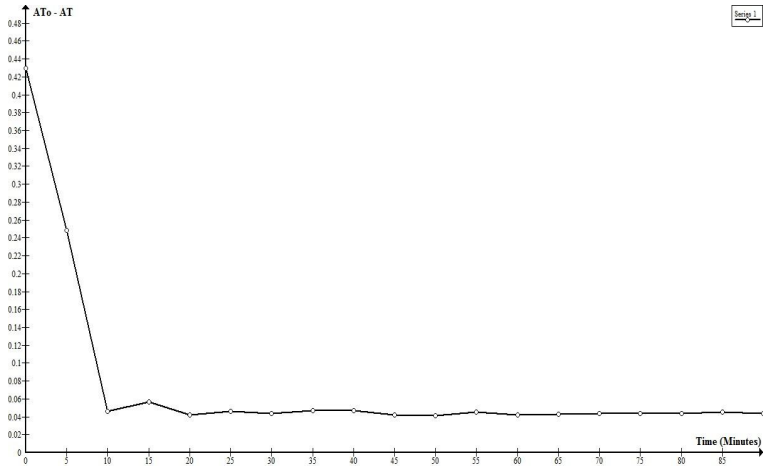


Fig. 3: Effect of incubation time on change in absorption of Tiron – zirconyl chloride complex before and after the introduction of fluoride ions ($A^To - A^T$).

Using the optimized conditions, a calibration curve for the absorbance of the complex at different concentrations of fluoride was prepared as shown in Figure 4. There was a change in the absorbance of the Tiron – zirconyl chloride complex at 300 nm from 0.425 in the absence of fluoride ions to 0.041 after the addition of 10.0 mg L^{-1}. This means only about 9.65% of the complex still show some absorbance at the wavelength of 300 nm. This shows a very good decrease of absorbance of about 90.35%

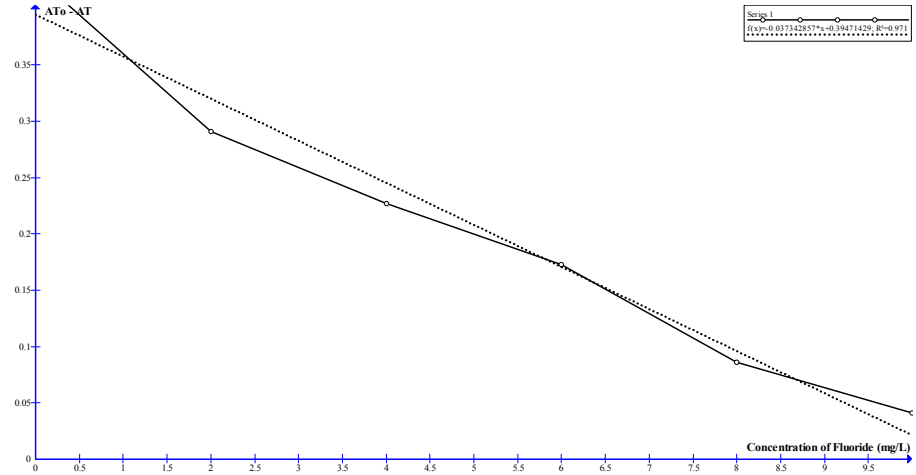


Fig. 4: Callibration curve for Tiron – Zirconyl chloride complex absorption at 300 nm with addition of standard fluoride solution

The developed BIMI method was compared to the known SPADNS method, in real life situation, by comparing results from the analysis of some river water samples from both methods. Results for fluoride ion concentrations using both methods show little differences.

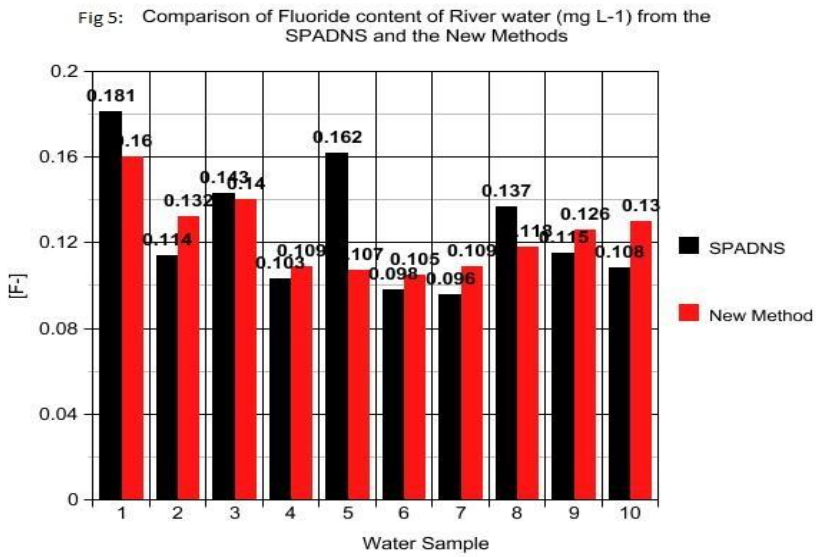


Table 1: Statistical Data Analysis of Data in Figure 5

	N	Minimum	Maximum	Mean	Std. Deviation	Variance	Std. Error Mean
SPADNS METHOD	10	.096	.181	.12570	.028929	.001	.00915
BIMI METHOD	10	.105	.160	.12360	.017608	.000	.00557
Valid N (listwise)	10						

Table 2: Comparison of means of means of River water fluoride content (t – test)

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	SPADNS METHOD – BIMI METHOD	.002100	.023511	.007435	-.014719	.018919	.282	9	.784

Statistical analysis of the results from the two methods showed that the measured concentration of fluoride ranged between 0.096 and 0.181 mg L^{-1} in the SPADNS method, and 0.105 and 0.160 mg L^{-1} in the proposed BIMI method. The mean concentration of fluorides in the river waters were 0.126±0.029 mg L^{-1} and 0.124±0.018 mgL^{-1} with standard error means of 0.009 and 0.006 for the SPADNS and the BIMI methods respectively. The proposed BIMI method showed less variance (0.00) than the SPADNS method (0.001). These errors are however more likely to be systematic δ_{sys} than random δ_{ran}.

Table 5 shows a comparison of the mean fluoride concentrations of the two methods using t – test at 95% confidence level (p = 0.05) for 18 degrees of freedom, and critical value, $t_{critical}$ = 2.10. There was no significant difference between the results from the two methods, since $|t_{exp}|$, (0.282), was less than the critical value.

CONCLUSION

In conclusion, a novel colorimetric method, the BIMI Method, for the assessment of fluorides was developed. This method is based on the selective ligand exchange reaction between fluoride and 4,5-dihydroxy-1,3-benzenedisulfonic acid moiety. Given that the value of the variance of determinations using the new BIMI method is in the range one – half (1/2) to twice the estimated value, the proposed method performed acceptably well in comparison to the known SPADNS method.

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