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A NOVEL CURCUMIN–BASED METHOD OF FLUORIDE DETERMINATION – THE PAGIKAND METHOD

ELAOYI DAVID PAUL, CASIMIR EMMANUEL GIMBA, JAMES ADAGADZU KAGBU AND GEORGE ILOEGBULAM NDUKWE

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ABSTRACT

Fluoride concentrations above and below certain limits are deleterious to human health, having been implicated in diseases such as fluorosis, arthritis, caries, cancers etc. Better methods of its qualitative and quantitative determination are therefore necessary. A novel, less toxic and more environmentally friendly analytical method for determination of fluorides, named the PAGIKAND method, is proposed, based on the complex formation capability of diferuloylmethane with zirconium. Absorbance of the complex at its absorption maximum of 465 nm was found to decrease (up to 94.69%) with increase in fluoride concentration in solution (up to 10 mg $F^- L^{-1}$). The optimum pH for the required complex formation was determined to be 8.5, and the Detection Limit (LOD) for the proposed method was calculated to be 1.3 x 10^{-6} mol L^{-1}. The proposed method was applied to the analysis of fluorides in river water and T – test was used to compare contents of fluorides determined using a known method (SPADNS) with those determined using the new method. The mean fluoride concentration for the new method was found to be 0.1232±0.030 mg L^{-1} while that of the SPADNS method was 0.1257±0.289 mg L^{-1}. At 95% confidence interval (p = 0.05) and 18 degrees of freedom, with critical value of 2.10, the $|t_{exp}|$ was 1.987. This indicates there is no significant difference between the results obtained from the known method (SPADNS) and that obtained from the proposed method, since $|t_{exp}| < t_{critical}$.

KEYWORDS: Novel Method, Fluoride, Spectrometry, Curcumin, Diferuloylmethane

INTRODUCTION

Fluorides are gaseous, dissolved, or solid compounds which contain fluorine. They are mostly generated by industrial processes, but can be found in some geological deposits. An excess of fluorides in food or water above 1.5 mg L^{-1} can cause fluorosis in humans and animals, while concentration lower than 0.5 mg L^{-1} can result in improper formation of the teeth, a condition known as caries, especially in the formative years of human life. Concentrations as low as 0.005 mg L^{-1} have been known to blight maize, a condition where the maize plant withers without rotting, while concentrations as low as 0.001 mg L^{-1} has also been known to lower citrus production (Weinstein, 1983; Paul *et al.*, 2011; Businessdictionary.com, 2012). It is therefore very important to be able to quickly, cheaply and accurately determine the presence and quantity of fluorides in any medium of interest.

Curcumin, 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione, is a metal ligand with an available diketone bonding site that can be used to form complexes with many transition metals. The strong chelating ability of diketones towards a great number of metal ions has been investigated and curcumin has been known for its ability to form such complexes (Rattanapirun, 2007; Sundaryono *et al.,* 2003; Jayaprakasha *et al.,* 2005; Warunyoupalin, 2007). This propensity for complex formation is greatly aided by the keto – enol tautomerism of curcumin. The interaction of such complexes with anions capable of replacing their ligands has been harnessed to quantitatively determine the concentration of such anions (Paul *et al.,* 2011; Olga and Lyudmila, 2007; Chang-Qing and Jin-Long, 2005; Breaux *et al.,* 2003; Brossok *et al.,* 1987).

It has also been shown that β – diketone is one of the preferred functional groups needed in a reagent for colorimetry and fluorimetry. This functional group permits the formation of stable ring structures with zirconium and other transition metals (Peng-Joung and Chuen-Ying, 1971). This work utilizes the complex forming capability of Curcumin to quantitatively determine the amount of fluorides in a medium by reacting the resultant complex with fluoride ions. This new method has been named the PAGIKAND method.

MATERIALS AND METHOD

Materials:

A Jenway 6405, UV/Vis Spectrophotometer and a 1.0 cm quartz cell were used for absorption studies; pH was measured with a Jenway 3505 pH meter.

Curcumin, 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione was obtained from BDH Chemicals, London; zirconyl chloride, sodium fluoride, sodium arsenate, methanol, ethanol and other chemicals were purchased from Zayo-Sigma chemicals

Elaoyi David Paul, Department of Chemistry, Ahmadu Bello University, Zaria, 810006, Nigeria
Casimir Emmanuel Gimba, Department of Chemistry, Ahmadu Bello University, Zaria, 810006, Nigeria
James Adagadzu Kagbu, Department of Chemistry, Ahmadu Bello University, Zaria, 810006, Nigeria
George Iloegbulam Ndukwe, Department of Chemistry, Ahmadu Bello University, Zaria, 810006, Nigeria

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 and 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.

Curcumin Solution:

1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione (36.84 g), was dissolved in 500 cm^3 absolute methanol. The solution was then diluted with distilled water to obtain a 50% Methanol: distilled water solution in a 1000 cm^3 volumetric flask. The concentration of the solution was then adjusted to obtain a 1.0 x 10^{-4} M solution of the curcumin.

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.

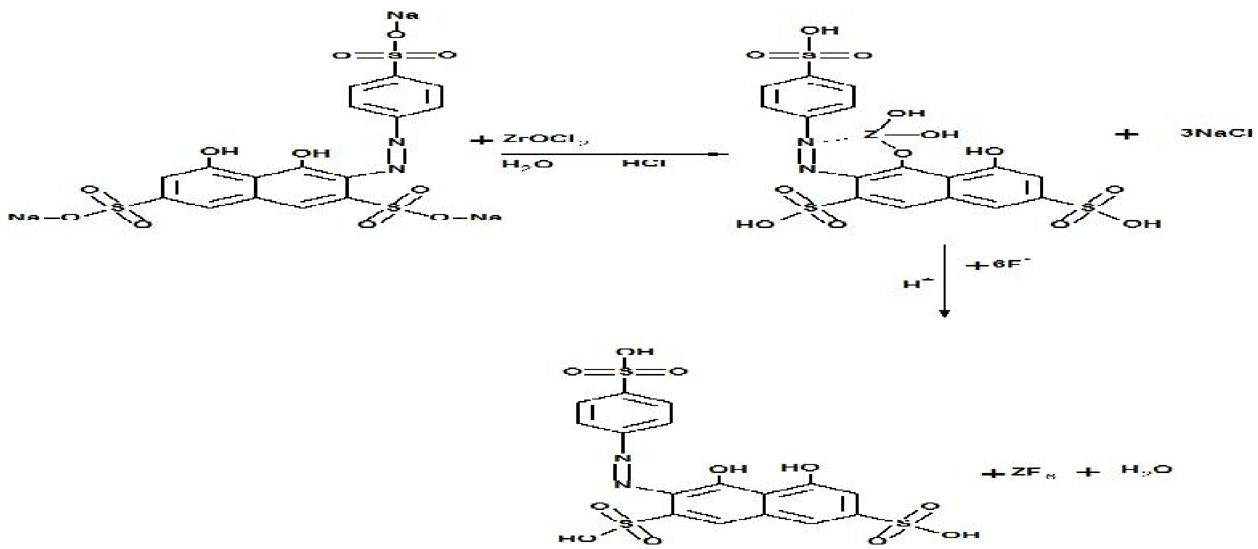
Procedure

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.

This procedure in was repeated, using another 100.0 cm^3 volumetric flask. In place of the SPADNS solution, 10.0 cm^3 (1.0 x 10^{-4} mol L^{-1}) of the Curcumin 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^C, and that of the blank, A^C_0 were measured at 465 nm.

RESULTS AND DISCUSSION

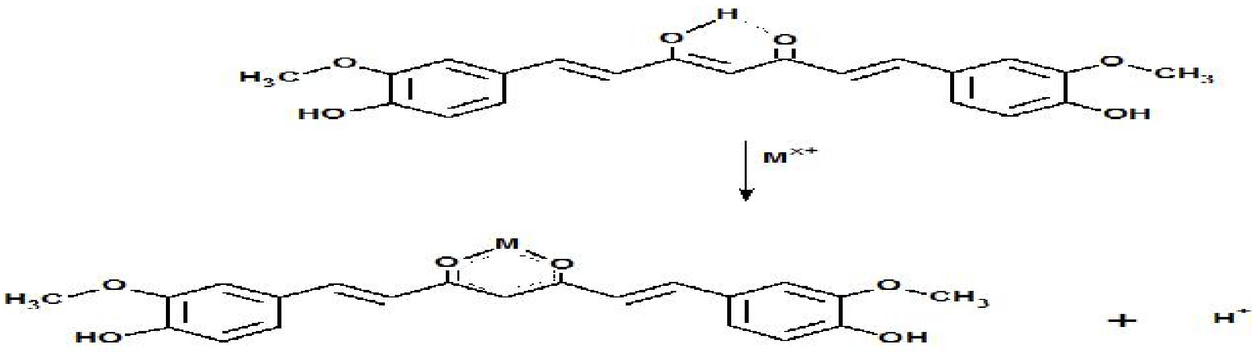
2-(4-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid, trisodium salt (SPADNS) has been in use for the quantitative determination of fluorides in various media over the years. The basic concept lies in the fact that 2-(4-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid, trisodium 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.



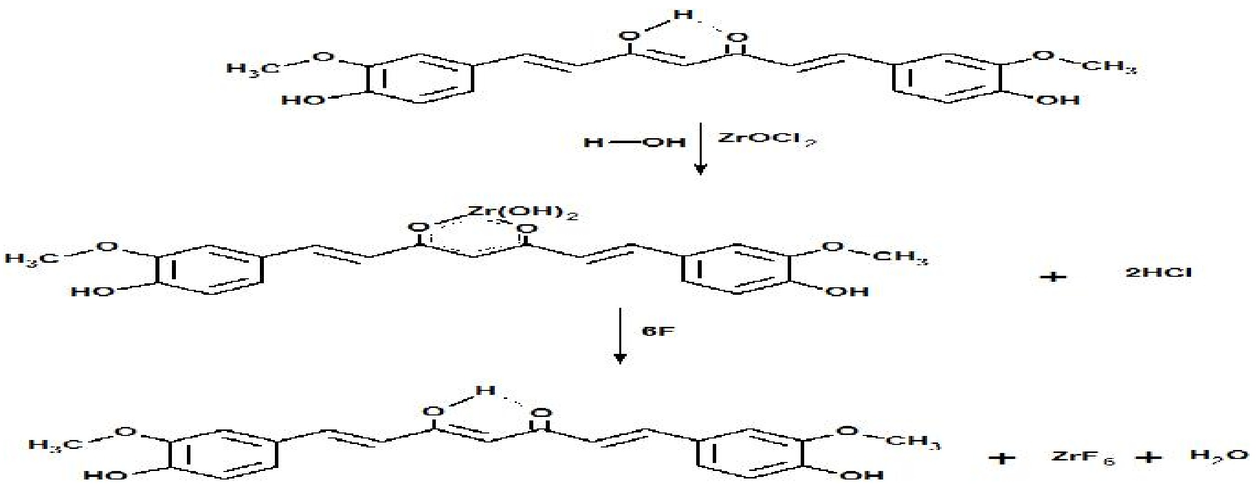
Scheme 1: SPADNS – $ZrOCl_2$ Reaction and subsequent bleaching with F^- ion

Since 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione has a bidentate chelating group, we have attempted to use it as a substitute indicator to make a novel process for the quantitative determination of fluorides.

Scheme 2 gives the reaction between metal ion and 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione (Warunyoupalin, 2007), while the proposed reaction between 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione and zirconium ion, and the subsequent substitution with fluoride ions is given in scheme 3.



Scheme 2: Metal – Curcumin Reaction Scheme



Scheme 3: The proposed reaction between Curcumin and zirconyl chloride, and the subsequent substitution with fluoride ions

The pK_b value for the 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione was calculated to be 5.201 from the pH of its 50% methanolic solution (pH = 9.4).

The absorption spectrum of curcumin - zirconyl chloride complex at a pH of 8.5 is given in Figure 1. It can be seen that the complex has an absorption maximum at 465 nm. Also, a slight drop in the value of the pH was observed, from 9.4 to 8.5, upon addition of the zirconyl chloride solution. This can be attributed to the release of H^+ ions as a result of the formation of the curcumin – zirconium complex as shown in scheme 2 (Warunyoupalin, 2007).

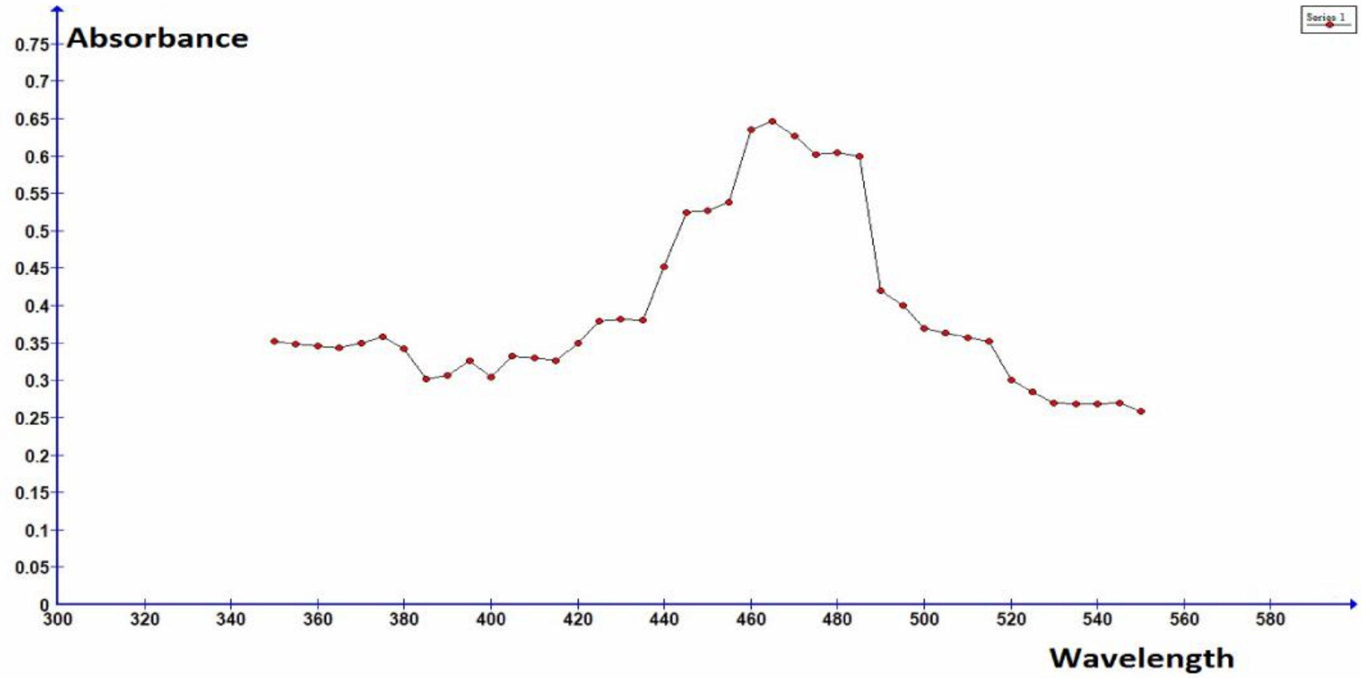


Figure 1: Absorption of Zirconium – Curcumin complex over a range of wavelengths. Absorption maximum is at 465 nm

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 of complex in the absence of F^- ions and A = absorbance in the presence of F^- ions) was at 8.5. The absorbance sharply increased from pH = 6.0 and peaked at 8.5. There was a steady drop in the absorbance of the curcumin – zirconyl chloride complex in the presence of the fluoride ions as the pH value was increased above 8.5. The best pH for the interaction of the complex with fluoride ions is therefore 8.5.

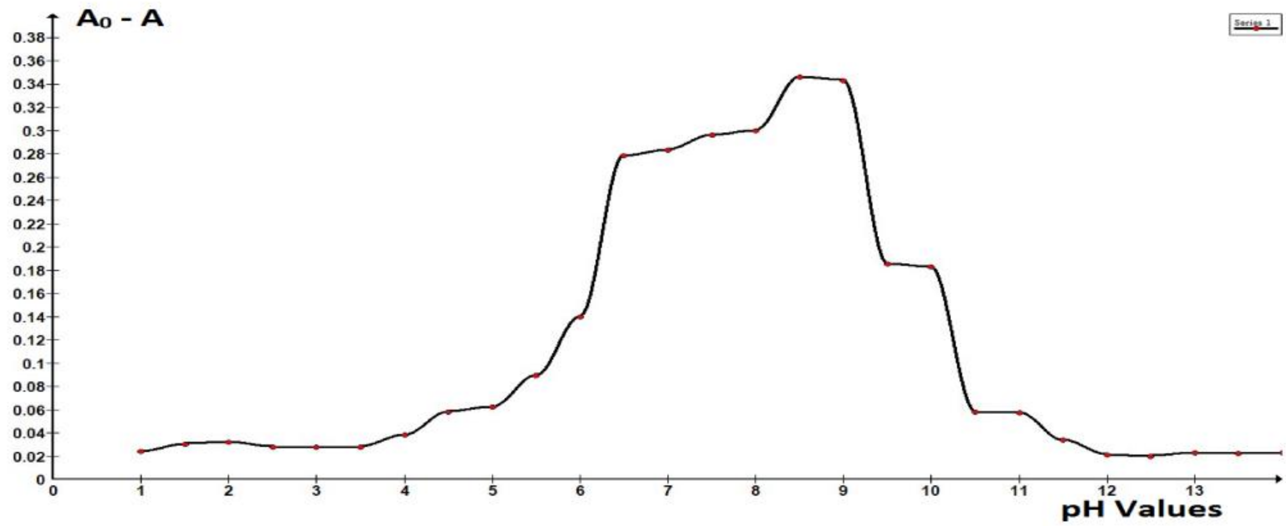


Fig 2: Effect of varying pH on Curcumin – Zirconium complex absorption upon addition of F^- ions.

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 fluoride ions. At incubation time less than five minutes, only a diminutive amount of reaction appeared to have taken place. However, above ten minutes, there was no further difference in the absorbance of the fluoride reacted curcumin – zirconyl chloride complex and the unreacted complex. The reaction appeared to have reached equilibrium. The best incubation time was therefore taken to be ten (10) minutes (Figure 3)

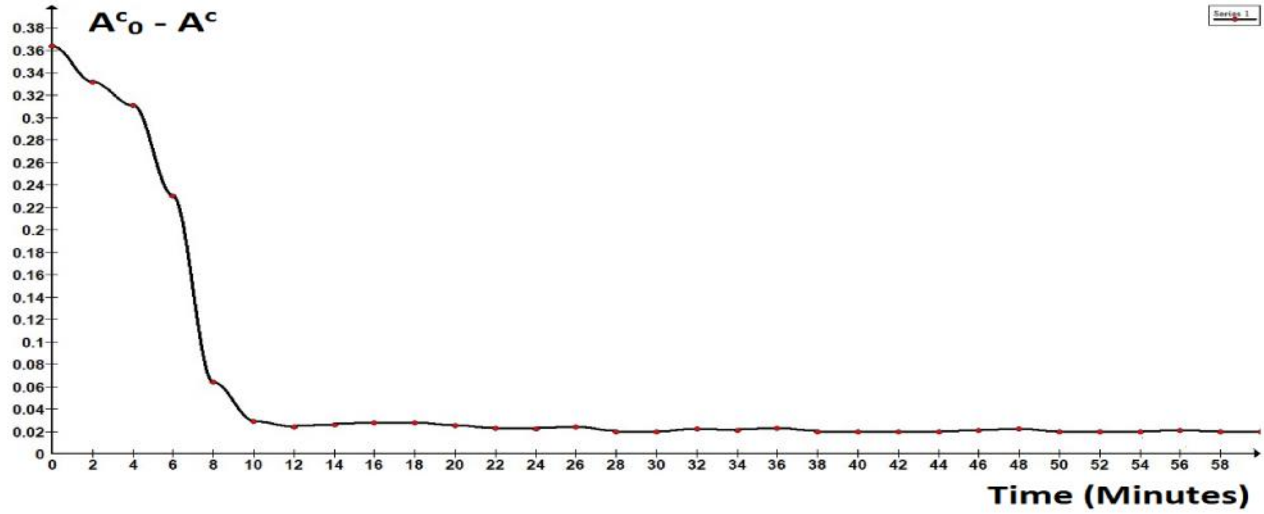


Figure 3: Effect of incubation time on change in absorption of Curcumin – zirconyl chloride complex before and after the introduction of fluoride ions ($A^C o – A^C$).

The effects of foreign ions on the determination of 1.09 x 10^{-6} mol L^{-1} of fluoride ions in solution were studied. The foreign ions that gave relative percentage errors between -10 and +10 % are listed in Table 1.

Table 1: Effect of foreign substances on the determination of 1.09 x 10^{-6} mol L^{-1} F^-

Foreign Ions	Concentration (mol L^{-1})	Relative Error Caused (%)
None		0
Cl^-	1.0 x 10^{-1}	-10.60
Cl^-	1.0 x 10^{-2}	-4.20
Cl^-	1.0 x 10^{-2}	-1.90
Cl^-	1.0 x 10^{-3}	0.20
Br^-	1.0 x 10^{-3}	-1.60
I^-	1.0 x 10^{-3}	-1.20
SCN^-	1.0 x 10^{-3}	7.60
NO_3^-	1.0 x 10^{-3}	3.40
HCO_3^-	1.0 x 10^{-3}	1.80
SO_4^{2-}	1.0 x 10^{-3}	1.30
HSO_3^-	1.0 x 10^{-3}	1.10
$H_2PO_4^-$	1.0 x 10^{-3}	0.80

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 Curcumin – zirconyl chloride complex at 465 nm from 0.320 in the absence of fluoride ions to 0.017 after the addition of 10.0 mg L^{-1}. This means only about 5.31% of the complex still show some absorbance at the wavelength of 465 nm. This shows a very good decrease of absorbance of 94.69%

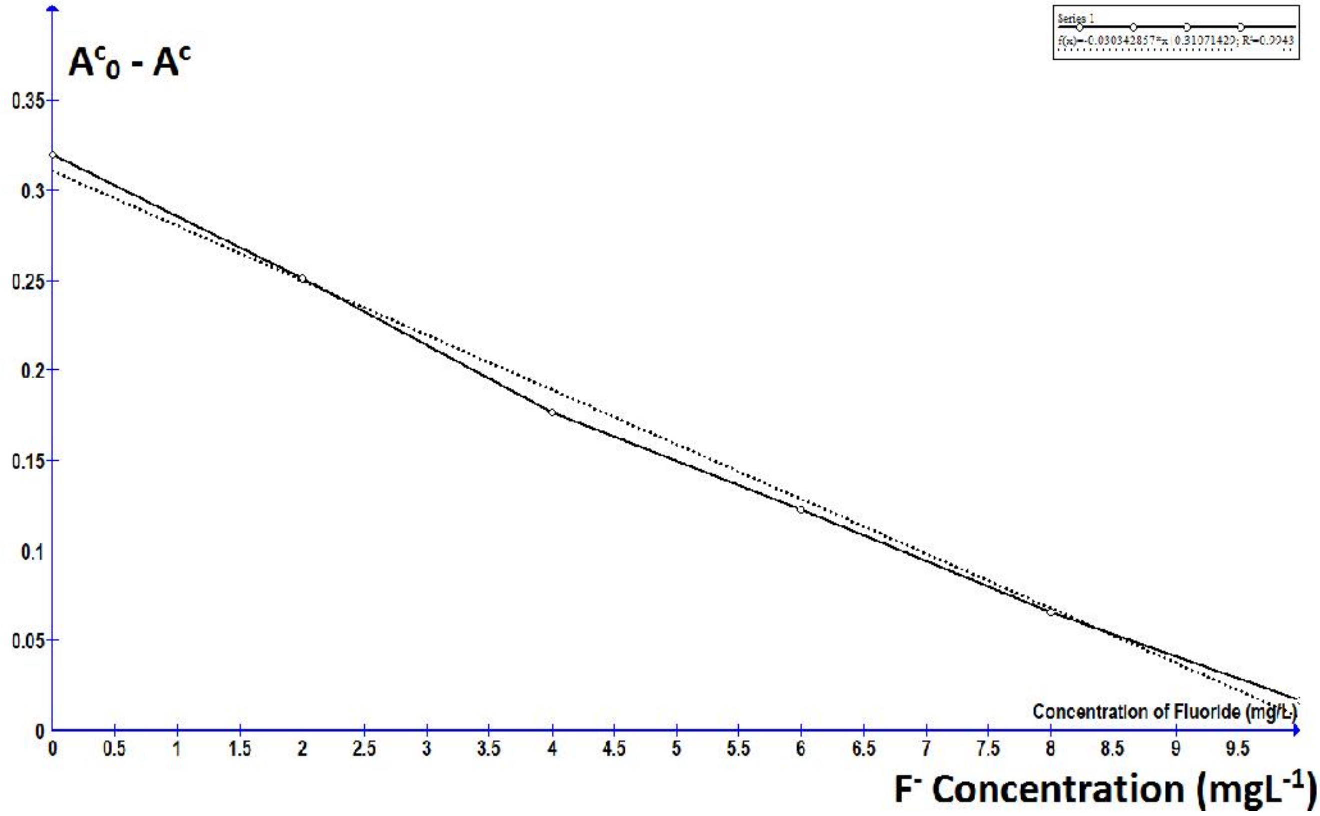


Figure 4: Callibration curve for Curcumin – Zirconyl chloride complex absorption at 465 nm with addition of standard fluoride solution ($A^C - A^C_0$ = f(x)=-0.030342857*x+0.31071429; R^2=0.9943)

The regression calibration equation obtained under the optimum conditions was $A^C - A^C_0$ = f(x)=-0.030342857*x+0.31071429, where x is the concentration of the fluoride ions [F^-].

The correlation coefficient was R = 0.9943.

The Detection Limit (LOD) for the proposed method was calculated to be 1.3×10^{-6} using the formula LOD = KS_O / S

Where K is a numerical value chosen according to the desired confidence level (here, chosen to be 3), S_O is the standard deviation of the blank absorbance (0.03003), and S is the sensitivity of the calibration graph (Slope of the standard curve) (Harvey, 2000; Parejiya *et al.*, 2011).

The new 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 levels using both methods show no significant differences.

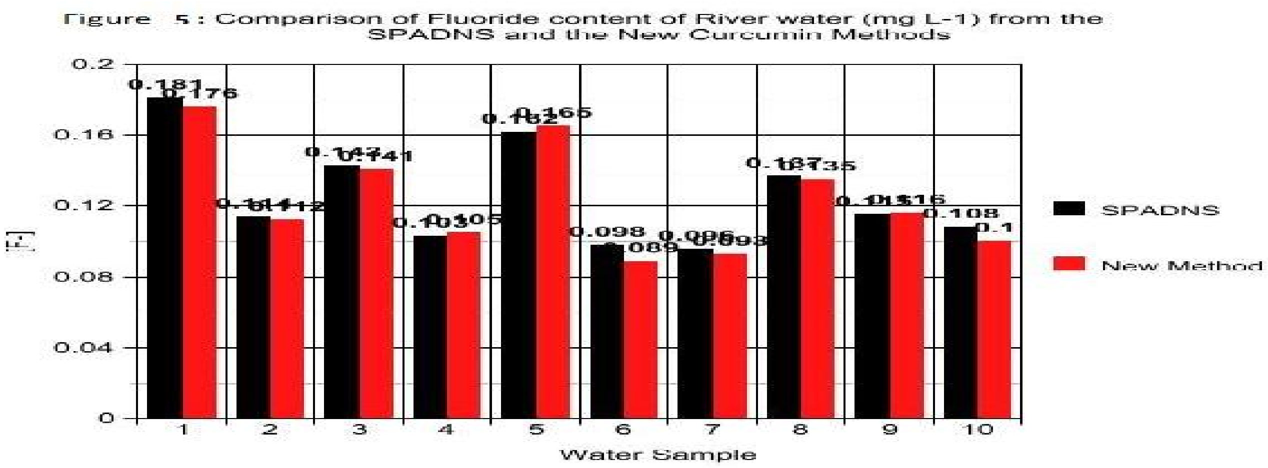


Table 2: Statistical Analysis of Data in Figure 5

	N	Minimum	Maximum	Mean	Std. Deviation	Variance	Std. Error Mean
SPADNS METHOD	10	0.096	0.181	0.12570	0.028929	0.001	0.009148
NEW METHOD	10	0.089	0.176	0.12320	0.030036	0.001	0.009498
Valid N (listwise)	10						

Table 3: Paired Sample Test (T- test) of river water fluoride content

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	SPADNSMETHOD - NEWMETHOD	0.0025	0.003979	0.001258	-0.000346	0.005346	1.987	9	0.078

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 0.089 and 0.176 mg L^{-1} in the proposed PAGIKAND method. The mean concentration of fluorides in the river waters were 0.126±0.029 mg L^{-1} and 0.123±0.030 mgL^{-1} with standard error means of 0.009 and 0.009 for the SPADNS and the PAGIKAND methods respectively. The proposed PAGIKAND method showed a variance of 0.001 same as the variance for the SPADNS method.

Table 3 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 $|t_{exp}|$, (1.987), was less than the critical value.

CONCLUSION:

In conclusion, a novel colorimetric method, named the PAGIKAND Method, for the assessment of fluorides was developed. This method is based on the selective ligand exchange reaction between fluoride and 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione (curcumin or diferuloylmethane). Curcumin is a less toxic, more environmentally friendly and thus greener alternative to the traditional 1,8-dihydroxy-2-(4-sulfophenylazo)naphthalene-3,6-isulfonic acid trisodium salt. It is thus suggested as an alternative chromogenic agent for the spectrometric determination of fluorides in the method described.

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