1. INTRODUCTION

1.1 General introduction

Fluorine is the lightest member of the halogen group and is one of the most reactive of all chemical elements. It is not, therefore, found as fluorine in the environment. It is the most electronegative of all the elements which means that it has a strong tendency to acquire a negative charge, and in solution forms F^- ions. Other oxidation states are not found in natural system, although uncharged complex may be. Fluoride ions have the same charge and nearly the same radius as hydroxide ion and may replace each other in mineral structures. Fluoride thus forms mineral complexes with a number of cation and some fairly common mineral species of low solubility contain fluoride.

Fluorine in the environment is therefore found as fluoride which together represent about 0.06-0.09 percent of the earth's crust. The average crustal abundance is 300mg kg^{-1}. Fluoride are found at significant levels in a wide variety of minerals, including fluorspar(CaF_2), rock phosphate, cryolite (Na_3AlF_6), fluoroapatite [$Ca_3(PO)_2Ca(FCl)_2$], chiolite($Na_5Al_3F_{14}$), mineral of low solubility occurring in both igneous and sedimentary rock(1,2).

Fluoride is found in all natural waters at some concentration. Seawater typically contains about 1mg L^{-1}while Rivers and lakes generally exhibit concentration of less than 0.5 mg L^{-1}. In ground waters, however, low or high concentration of fluoride can occur, depending on the nature of the rocks and the occurrence of fluoride bearing minerals. Concentrations in water are limited by fluoride solubility, so that in the presence of 40mg L^{-1} calcium it should be limited to 3.1mg L^{-1}. It is the absence of calcium in solution which allows higher concentrations to

be stable. High fluoride concentrations may also increase in ground water in which cation exchange of sodium for calcium occurs.

Due to dust, industrial production of phosphate fertilizers, coal ash from the burning of coal and volcanic activity, fluorides are widely distributed in the atmosphere. However air is typically responsible for only a small fraction of total fluoride exposure. In non-industrial areas, the fluoride concentration in air is typically quite low (0.05-1.90µg m^{-3} fluoride). In areas where fluoride containing coal is burned or phosphate fertilizers are produced and used, the fluoride concentration in air is elevated leading to increased exposure by the inhalation.

A number of products administered to, or used by, children to reduce dental decay contain fluoride. This includes toothpaste (1.0-1.5g kg^{-1}fluoride), fluoride solution and gels for topical treatment (0.25-24.0g kg^{-1}fluoride) and fluoride tablets (0.25, 0.50 or 1.00mg fluoride per tablet), among others. These products contribute to total fluoride exposure, albeit to different degrees. Vegetables and fruits normally have low levels of fluoride and thus typically contribute little to exposure (1, 3). However, higher levels of fluoride have been found in barley and rice taro, yams and cassava been found to contain relatively high fluoride levels. In general, the levels of fluoride in meat (0.2-1.0mg kg^{-1}) and fish (2-5mg kg^{-1}) are relatively low.

Drinking-water is typically the largest single contributor to daily fluoride intake. However, this is not necessarily true in every case. For a given individual, fluoride exposure (mg $kg^{-1}$of body weight per day) via drinking-water is determined by the fluoride level in the water and the daily water consumption (liters per day).

American dietetic association (4) reaffirms that fluoride is an important eluent for all mineralized tissues in the body; appropriate fluoride consumption is beneficial to bone and teeth integrity and as such has an important positive impact on oral health and overall health. Fluoride has beneficial effects on teeth at low concentration in drinking water, but excessive exposure to fluoride in drinking water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects. These range from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases. Crippling skeletal fluorosis is a significant cause of morbidity in a number of regions of the world. Crippling skeletal fluorosis, which is associated with the higher level of exposure, can result from osteosclerosis, ligamentous and tendinous calcification and extreme bone deformity. High level of fluoride present in concentrations up to 10mg L^{-1}, are associated with dental fluorosis (yellowish or brownish striations or mottling of the enamel) while low levels of fluoride, less than 0.1mg L^{-1}, are associated with high levels of dental decay, although poor nutritional status is also an important contributory factor(1,4,5). The margin between the beneficial effects of fluoride and the occurrence of dental fluorosis is small and public health programmes seek to retain a suitable balance between the two.

WHO noted that mottling of teeth (i.e. dental fluorosis) is sometimes associated with fluoride level in drinking water above 1.5mg L^{-1} and crippling skeletal fluorosis can ensue when fluoride levels exceeds 10mg L^{-1}. A guideline value of 1.5mg L^{-1} was therefore recommended by WHO (2006) as a level at which dental fluorosis should be minimal. The 1.5mg L^{-1} fluoride guideline value of WHO is not a “fixed” value but is intended to be adapted to take account of local conditions (e.g. diet, water consumption etc.).

Due to narrow range between beneficial effect and adverse effect of fluoride in drinking water accurate and simple method of quantitative determination of fluoride is very important in quality control laboratory. Several methods have been developed for the determination of fluoride in various samples; some important and widely used methods for the determination of fluoride in water are discussed below.

1.2 Methods of determination of fluoride in drinking water

Among the different methods used to determine fluoride ions in water, following are the some well known methods.

1.2.1 Ion selective electrode method

Fluoride is determined potentiometrically using a fluoride electrode in conjunction with a standard single-junction, sleeve-type reference electrode and a pH meter having an expanded millivolt scale or a selective ion meter having a direct concentration scale for fluoride. Fluoride ion activity depends on the solution total ionic strength and pH, and on fluoride complex species. Adding an appropriate buffer provides a nearly uniform ionic strength background, adjusts the pH, and breaks up complexes so that the electrode measures concentration. The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by Ag/AgCl-(0.3),F-(0.001) LaF_3 | test solution | reference electrode. In general, the quantification range of fluoride by this method is 0.1–100 mg L^{-1}. Reproducibility, expressed as relative standard deviation, in proficiency tests to be 3.6–4.8 per cent with a range of synthetic samples of concentration 0.750–0.900 mg F^- L^{-1}. Extremes of pH interfere; the sample pH should be between 5 and 9. Fluoride forms complexes with several polyvalent cations such as Si^{4+}, Fe^{3+} and Al^{3+}. The degree of

interference depends on the concentration of complexing cations, the concentration of fluoride and complex species. The addition of pH 5.0 buffer containing a strong chelating agent preferentially complexes aluminium (the most common interference), silicon and iron, and eliminates the pH problem (1, 6, 7).

Although the fluoride selective electrode is used for the determination of fluorides in drinking water, in industrial effluents, sea water, air and aerosols, flue gases soils and minerals, urine, serum, plasma, plants and other biological materials within wide range, it cannot be afforded by all laboratories due to the high cost of fluoride- ion selective electrode. Moreover fluoride- ion selective electrode does not have prolonged life due to its storage problem. A proper TISAB (Total Ionic Strength Adjustment Buffer) must be used for different samples. Though it is a standard method of determination of fluoride, it cannot be used by all laboratories.

1.2.2 Ion-chromatography method

This technique of Ion Chromatography (IC) uses non-hazardous reagents and it effectively distinguishes between halides and oxy-anions. This method is applicable, after filtration to remove particles larger than 0.2 μm, to surface waters, ground waters, wastewaters, and drinking-water. A small volume of sample is introduced into an ion chromatograph. The anions are separated on the basis of their relative affinities for a low capacity, strongly basic anion exchanger (guard and separator columns). The separated anions, in their acid forms after the suppressor, are measured by conductivity. They are identified on the basis of retention time as compared to standards. Reproducibility, expressed as relative standard deviations, is found in reagent tests (0.26–8.49 mg L^{-1}) to be 0–15 per cent (1).

This method has low determination range and the price for an ion chromatograph system is approximately US$ 30,000–60,000 which cannot be afforded by all laboratories, so this cannot be an appropriate method for determination of fluoride to all laboratories.

1.2.3 Spectrophotometric methods

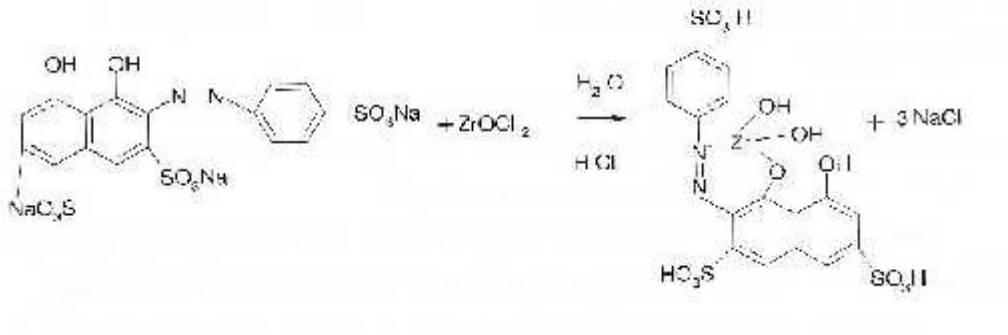
Spectrophotometric methods of determination of fluoride in water and in different samples is widely used since the running cost of this method is very low and the spectrophotometer required for this method is usually available in most of the analytical laboratories. When fluoride is added to certain coloured complexes of multivalent cations, it forms colourless complexes like $(AlF_6)^{3-}$, $(ZrF_6)^{3-}$, $(FeF_6)^{3-}$, $(ThF_6)^{3-}$etc with ligand exchange reaction. The decrease in absorbance is proportional to the concentration of fluoride. This gives rise to the technique of quantitative estimation of fluoride in the sample. The calibration curve can be constructed using standard solution of fluoride for quantitative determination of fluoride in unknown sample.

One of the reagents used in spectrophotometric methods is the complexone, alizarin fluorine blue-lanthanum reagent which forms a blue complex with fluoride. It can determine fluoride ranging concentration from 0.1mg /L to 2.0mg/L, so it can be used for the determination of fluoride in water samples if water is free from interfering ions. If water samples contain interfering ions then water first needs to be distilled prior to the determination of fluoride (1).

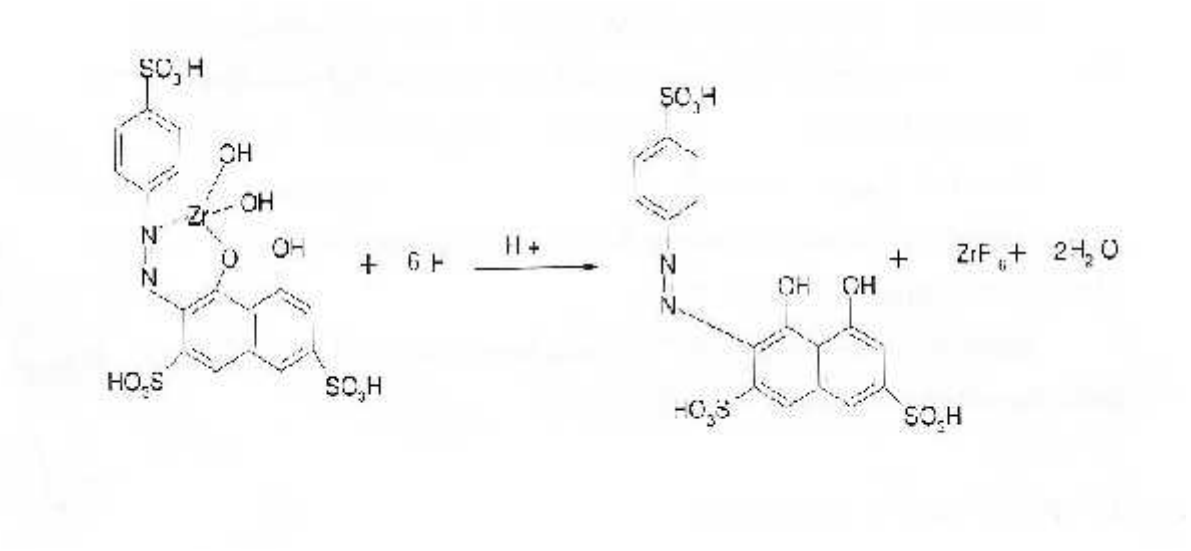
SPADNS [sodium 2-(parasulfophenylazo)-1, 8-dihydroxy-3, 6-napthalene disulfonate] method is the standard method of determination of fluoride in water and is widely used method. It is based on the reaction between fluoride and a

Zirconium-dye lake. Fluoride react with the dye lake dissociating a portion of it into a colourless complex anion $(ZrF_6)^3$; and the dye. As the amount of fluoride increases, the colour produced becomes progressively lighter (8, 9). This method has the detection range of 0 to 1.4 mg F^-/L. So this method is applicable for the determination at lower concentration range of fluoride, but for determination of higher fluoride concentration proper dilution is necessary. SPADNS- Zirconyl chloride reagent is quite costly and not readily available in laboratories. Moreover the reaction rate between fluoride and SPADNS- Zirconyl chloride reagent is influenced greatly by the acidity of water.

The reaction between SPADNS reagent and Zirconyl chloride and between SPADNS- Zirconyl reagents can be shown as:



(SPADNS reagent (red)) (SPADNS-Zirconyl acid reagent)



(Blood red colour) SPADNS - (Red colour)

Fluoride in the absence of interfering anions such as phosphate, citrate tartarate and interfering cations such as cadmium, tin, strontium, iron may be determined with thorium chloroanilite in aqueous 2-methoxyethanal. The main reaction (10) is,

$$Th(C_6Cl_2O_4)_2 + 2F^- + H^+ \longrightarrow ThF_2C_6O_4 + HC_6Cl_2O_4^-$$

The bleaching action of fluoride on the purple coloured thorium-chromotrope 2B dye complex is used for the fluoride determination of fluoride. This is rapid and sensitive method but the reagent is somewhat costly and has the detection range of 2.5 to 20mg F^-/L and cannot be used for the determination of fluoride in lower concentration range.

Iron (III)-methyl salicylate complex had been investigated for the determination of fluoride in pharmaceutical preparation. In this method the bleaching action of fluoride on the red violet complex of iron–methyl salicylate was explained for the determination of fluoride. Methyl salicylate being insoluble in water possesses some difficulty in using this method. So those authors used ethyl alcohol as a

solvent for the preparation of the reagent. This reagent cannot be used for the determination of fluoride in potable water.

With the growth of the practice of fluoridation of water, accurate, simple and low cost methods for the determination of fluoride are constantly investigated.

1.3 Theoretical Basis of Spectrophotometric Analysis

When radiation is passed through a layer of a solution containing an absorbing substance, the intensity of the radiation emerging from the solution is less than the intensity of radiation entering it; it is because the part of radiation is absorbed. The extent of absorption depends upon the wavelength of the radiation, thickness of the medium and concentration of the solution used. Thus by measuring the intensity of radiations absorbed or transmitted one can estimate the concentration of the species present in the solution. Quantitative analysis of the species present in the solution is based on Lambert's and Beer's law.

1.3.1 Lambert-Beer's law

Lambert's law states that when a monochromatic light is passed through an absorbing medium perpendicularly, the rate of decrease in intensity with the thickness of the medium is proportional to the intensity of the light.

Mathematically;

$-dI/dB \alpha I$

Or, $- dI/dB = k I$

On integration and simplification, we get,

$$I = I_o 10^{-ab} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where I is the intensity of the transmitted light.

I_o is the intensity of the incident light of wavelength λ.

b is the thickness of the absorbing homogenous medium.

a is constant.

Beer's law states that when a monochromatic light is passed through an absorbing medium perpendicularly the rate of decrease in intensity with the concentration at constant path of the medium is proportional to the intensity of the light.

Mathematically,

$$-dI/dC \alpha \quad I$$

$$\text{Or,} \quad -dI/dC = k\, I$$

On integration and simplification, we get,

$$I = I_o\, 10^{-ac} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Combining (1) and (2). We get,

$$I = I_o 10^{-abc}$$

$$\log(I_o/I) = abc\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where 'a' is called absorptivity in which concentration 'c' of the solution is expressed in gram per litre and thickness in cm.

The equation (3) is the fundamental equation of colorimetry and spectrophotometry which is known as Lambert-Beer's law.

If the concentration of the solution 'c' is expressed in molarity and thickness in cm the constant 'a' is replaced by 'ε' which is known as Molar extinction coefficient or Molar absorptivity. The sensitivity of the spectrophotometric methods depend upon the value of 'ε'. The higher is its value, the more sensitive is the method. The quantity log (I_o/I) is known as absorbance or optical density and designated by the symbol 'A'. With this abbreviation equation (3) becomes;

$$A = \varepsilon bc \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

The equation (4) is the most useful form of the Beer-Lambert's law. Many commercial spectrophotometers are directly calibrated in absorbance.

The absorbance due to given solution depends upon the wavelength of incident radiation. For a particular absorbing species there is a particular wavelength for which the absorbance is maximum called λ_{max} . λ_{max} is the characteristics of the coloured absorbing species(10).

1.3.2 Calibration curve

The Lambert-Beer's law is applicable only when its component relations are valid. Since, there are no known exceptions to Lambert-Beer's law; all apparent deviations from the combined law are due to the concentration factor, c. The applicability of Lambert-Beer's law may be tested for any particular system by measuring the absorbance of series of solutions of known concentration of absorbing species. A plot of the experimental data in terms of absorbance 'A' versus concentration 'C' should yield a straight line passing through the origin if the Lambert-Beer's law is obeyed. More often a plot of data over a wide range of concentrations will give a graph as shown in the figure below indicating that the Lambert-Beer's law is applicable only upto the concentration 'C'. If a suitable calibration curve plot is prepared from a series of solutions of known concentrations of absorbing species, it is possible to determine the concentration of the absorbing substance in an unknown sample from this calibration curve. Beyond concentration C, deviations from Lambert-Beer's law occur which are due to the intermolecular interactions, concentration dependent dissociations or associations, reactions with solvent or with hydrogen ions or formation of complex ions with varying number of ligands (10, 11).

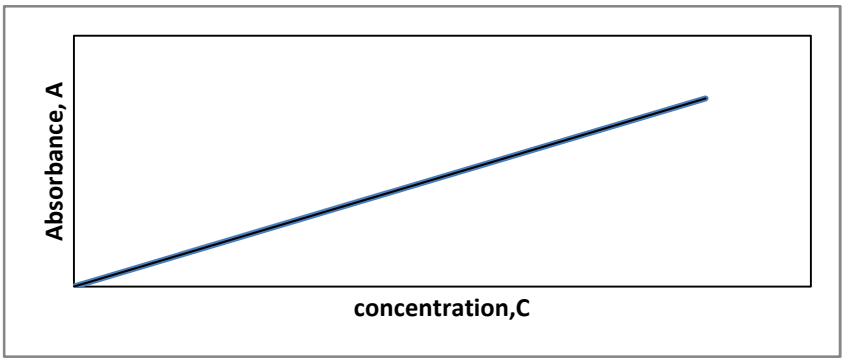


Fig: Plot of absorbance vs concentration of coloured complex for adherence to Lambert's-Beer's Law.

In indirect spectrophotometric determination of a species a calibration curve will have a different nature. In indirect method, a coloured species of particular concentration is prepared which will have a reasonable absorbance and increasing amount of determinant species is added which will bleach the coloured species thereby the absorbance will be decreased . If absorbance is plotted against the concentration of determinant species a straight line will be obtained if Lambert-Beer's law is followed, with negative slope as shown in figure below.

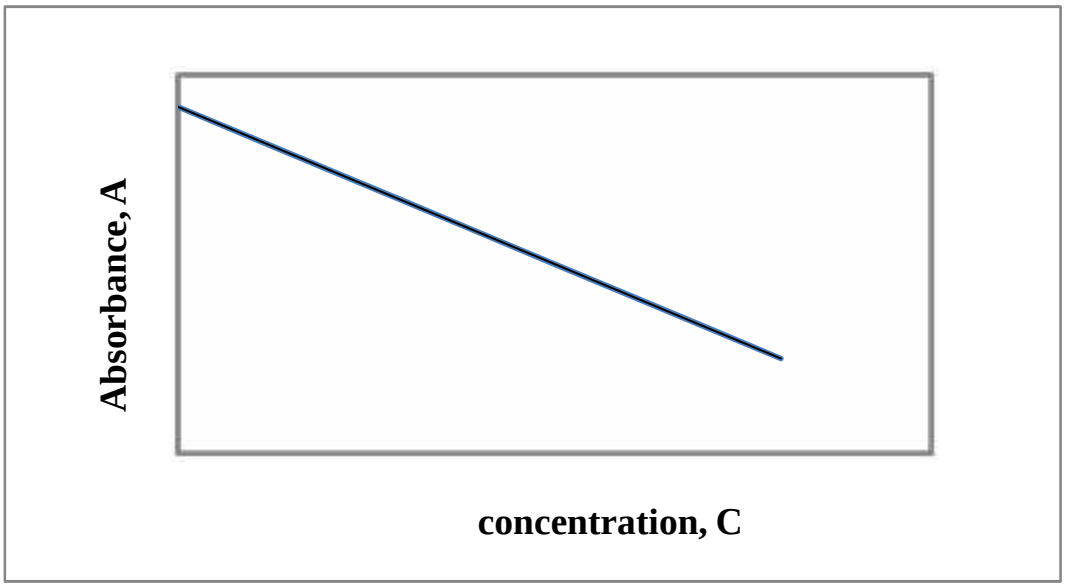


Fig: Calibration curve for the determination of coloured bleaching species.

1.4 Sensitivity and Detection Limit

One of the important parameter of any spectrophotometric method of determination is the sensitivity and detection limit. Different types of sensitivity and detection limit are used in analytical chemistry. The more widely used sensitivity is discussed below;

1.4.1. Calibration sensitivity

Calibration sensitivity is the change in response signal per unit change in analyte concentration. The calibration sensitivity is thus the slope of the calibration curve (12).

Detection limit (DL) is the smallest concentration that can be reported with a certain level of confidence. For methods that employ a calibration curve, the detection limit is defined as the analytical concentration yielding a response of a confidence factor *k* higher than the standard deviations of the blank, s_b, as,

$$DL = k\, s_b/m$$

Where *m* is the calibration sensitivity. Usually the factor *k* is chosen to be 2 or 3. A *k* value of 2 corresponds to confidence level of 92.1%, while a *k* value of 3 corresponds to 98.3% confidence level (12).

1.4.2 **Sandell's sensitivity**

It is defined as the smallest weight of substance that can be determined in a column of solution having unit cross section. Weight is expressed in µg and area in sq.cms. This is valid only if system adheres to Lambert Beer's law indefinitely at low concentration. Two factors are involved in the sensitivity. Intrinsic sensitivity is directly proportional to the molar absorptivity of the solution of colored product and ability of observer directly or indirectly to detect small difference in light transmission or absorption of solution. In spectrophotometry the minimum amount of colored substance that can be determined depend upon the reproducibility of measurement of transmittance of faintly colored solution. About 0.001 differences in absorbance can be detected in a good instrument (0.2T). Thus if 0.001 absorbance is given by 0.025µg of the metal ion, the Sandell's sensitivity is

0.025µg ml^{-1} cm^{-2}. If molar absorptivity of colored compounds is known then we can readily calculate the Sandell's sensitivity as;

Sandell's Sensitivity= M/ε = molecular weight/molar absorptivity of colored Species.

Thus, sensitivity is the number of microgram of element converted to colored product which are in a column of solution having cross section of $1cm^2$, shows an extinction of 0.001absorbance and expressed as µg ml^{-1} cm^{-2}. Organic reagents with high molecular weight furnish maximum sensitivity, if used as chromogenic agent(13).

1.5 Literature survey

For determination of fluoride in water a number of methods had been developed and the choice of method depends upon the nature, type and composition of sample and required precision and accuracy. Around 1960's many spectrophotometric method were developed (14-15) based upon the formation of fluoride complexes.

Some chromatographic techniques, flow injection methods were also developed. But due to less sensitivity these methods are less commonly used these days. In 1966 Frant and Ross developed (16) Fluoride ion selective electrode for the determination of fluoride in variety of samples. It was used for varieties samples but this method needs an expensive fluoride ion selective electrode and to prevent interference with various ions, it demands the use of judiciously adjusted total ionic strength adjustment buffer (TISAB). Ion selective electrode had been a standard method for determination of water and waste water (9).

Gaunghan et al (17) used traditional polarography with dropping mercury electrode to determine the trace amount of fluoride in foods, detection limit being $5x10^{-8}$ M.

Some other methods like gas chromatography, ion chromatography, capillary zone electrophoresis have been approved (9). Although these methods are capable of providing reliable, precise and accurate results requirement of sophisticated instruments and specialization make them expensive and hence are not affordable by all laboratories.

A multielectron proton induced gamma emission method has been developed by AKM Fazlul Hoque, M. Khaliquazzman et. al to analyze fluoride in water residues obtained by evaporation(18). It was very accurate but the instrument for this method is very expensive and unaffordable by all laboratories.

Since spectrophotometric methods are simple, rapid and cheaper than other methods, these methods and their refined version are still in use (19).

Sen (1956) develop a method (20) for the determination of fluoride using the demasking principle; using the method of bleaching, ferric sulfosalicylate, ferric tiferronate, titanium-chromotropic acid and Zirconium- alizarin coloured systems had been thoroughly investigated and ferric sulfosalicylate system had been proved to be the best. The method gave reproducible result when the fluoride concentrations in the range of 0.8 ppm to 4.0 ppm

Belcher et al. (1959) used alizarin fluoride blue method for direct spectrophotometric determination of fluoride (21). The basic reaction was that a red cerium complex with alizarin complexone turns blue on the addition of fluoride ions.

Weinstein, et al (1963), applied direct spectrophotometric method by using alizarin fluorine blue – lanthanum reagent to form a blue complex that was measured colorimetrically at 620 nm (9). This method was applicable to potable, surface, and

saline waters as well as domestic and industrial waste waters. The range of the method, which can be modified by using the adjustable colorimeter, is 0.1 to 2.0 mg F^-/L.

Yasuaki Shimoishi and Tadashi Hayami (1966) studied spectrophotometric determination of fluorine with the PAC-Th complex (22). This method of determining micro amounts of fluorine was based on the bleaching of the thorium complex of 2- (1, 8- dihydroxy- 3, 6-disulfo-2-naphthylazo)-phenoxyacetic acid (PAC) by fluoride ions, which are strongly co-ordinated to the thorium in the complex and with thus liberate the free PAC. The optimum pH range was from 2.5 to 3.5.

Bellack and Schouboe (1968) developed a rapid spectrophotometric determination of fluoride with SPADNS – Zirconium lake. It was based on the reaction between fluoride and a Zirconium-dye lake. Fluoride reacts with dye lake dissociating a portion of it into a colourless complex anion ZrF_6^{2-} and the dye. This method was sensitive from 0 to 2 mg F^-/L by using linear calibration curve and sensitive up to 4.0 mgF^-/L by using non-linear calibration curve (12).

Kaur and Gupta (1987) also studied spectrophotometric determination of fluoride in water. The method was based on the bleaching action of fluoride on the purple coloured thorium chromotrope2B dye complex (λ_{max}-550nm) and the measurement of the decrease in colour intensity at 579 nm (the wavelength of maximum difference; the pure dye has λ_{max} at 510nm) (23).

Okazaki, et al (1992) studied spectrophotometric determination of fluoride ion with Zirconium (iv) salt of tetraphenyl porphine trisulfonate. A Zirconium salt of water soluble porphine TPPSZr, was found to be applicable to determination of fluoride

ion in water. This result was regarded on expanding analytical applications of porphines (24).

Sandulescu, et al (1995) studied spectrophotometric determination of fluoride in dosage forms and dental preparations. This method was based on the reaction between fluoride ions and the coloured complex of Fe (III) with methyl salicylate to form stable, colourless hexafluoride complex. The ligand exchange was greatest at pH 1-3 and the range for fluoride determination was found to be 10 – 80 mg/L at 525nm (25).

Shimad, et al (2004) developed an automatic flow injection system on-line separation by micro distillation and spectrophotometric detection for the determination of trace amounts of fluoride. This ion was separated from sample matrix by distillation in the presence of sulphuric and phosphoric acids and was subsequently determined with spectrophotometry based on the mixed-ligand complex of lanthanum (III) - fluoride-alizarin complexone. The FI system has high sampling frequency (20 samples h^{-1}), small sample size (600µl) and the dynamic range of 0.05- 15 mgL^{-1} with relative standard deviations of below 1.2% (20).

Adelantado et al studied the spectrophotometric determination of fluoride in fluoride bearing minerals after decomposition by fusion with sodium hydroxide. The fusion was done in a silver crucible with a Bunsen burner. The cooled melt easily soluble, giving solutions was suitable for spectrophotometric determinations of fluoride by the Zr (IV) – fluoride –Erichrome cyanine- R method (26).

Lucja Lenarczyk, Zygmunt Marczenko and Maciej Jarosz studied indirect spectrophotometric determination of fluoride using the ternary system; Thorium-chrome azurol S-Cetyltrimethylammonium (27).

Thus the methods of determination of fluoride in different samples containing fluoride are constantly investigated.

1.6 Objectives of the present work

Accurate determination of fluoride has increased its importance owing to its health impact and a number of methods for determination of fluoride are available but the cost of analysis, equipment required and complicities of method limit the utility of each method. Spectrophotometric method is a simple, accurate and easily adoptable method, however the reagents required for the determination of fluoride is costly and not readily available in the laboratory. So the objective of the present work is to investigate a simple and low cost spectrophotometric method of determination of fluoride using reagent that are readily available in the laboratory.

The specific objectives of the present work are:

1. To investigate the bleaching action of fluoride on different coloured complex of iron (III) for the determination of fluoride.
2. To study the effect of ratio of Fe^{3+} and ligand, pH, stability of coloured complex for the determination of fluoride in water.
3. To study the interfering ions in the determination of fluoride by using ferric complex.
4. To construct the calibration curve for the determination of fluoride in water and evaluate the calibration sensitivity, Sandell's sensitivity and detection limit of the method.
5. To compare the present method with standard spectrophotometric method using SPADNS – Zirconyl chloride reagent.

2. EXPERIMENTAL

2.1 Instrumentation

2.1.1 Spectrophotometer

All spectral measurements were done by using WPA Spectrophotometer and Perkin Elmer Lamda 40 UV/VIS Spectrophotometer using 1 cm glass cuvette.

2.1.2 Potentiometer

Osaw digital potentiometer was used for the measurement of potential to maintain pH of the solution by using Antimony electrode.

2.2 Preparation of reagents

2.2.1 Stock Fe (III) solution (10^{-2}M)

4.82gm of $FeNH_4(SO_4)_2.12H_2O$ was dissolved in ≈ 300ml of distilled water and 50 ml of 1M HNO_3 and the solution was diluted to 1000 ml with distilled water.

2.2.2 Stock salicylic acid (0.1M)

6.906 gm of salicylic acid was dissolved in 0.2 M NaOH in 500ml volumetric flask upto the mark.

2.2.3 Stock Fe (III)- salicylate reagent:

100 ml of $2.25x10^{-2}$M Fe (III) solution and 400 ml of $5.6x10^{-3}$M salicylic acid was mixed in 500 ml V.F., which is stable for at least two months.

2.2.4 Stock Fluoride solution (100μg F^-/ml)

221.0 mg anhydrous sodium fluoride, NaF, was dissolved with distilled water in 1000 ml volumetric flask upto the mark.

2.2.5 SPADNS solution (0.839M)

479mg SPADNS; Sodium 2-(parasulfophenyl azo) - 1, 8-dihydroxy-3, 6 naphthalene disulfonate, also called 4, 5 dihydroxy -3(parasulfophenyl azo)-2,6 naphthalene disulfonic acid trisodium salt, was dissolved in distilled water and diluted upto the mark.

2.2.6 Zirconyl-acid reagent (0.2062M)

66.5 mg Zirconyl chloride octahydrate, $ZrOCl_2.8H_2O$ was dissolved in about 25 ml distilled water and 175 ml conc. HCl was added and diluted upto 250 ml.

2.2.7 Acid Zirconyl-SPADNS reagent

Equal volume of SPADNS solution and Zirconyl acid reagent was mixed. The combined reagent is stable for at least two years.

2.2.8 Reference solution

10 ml of SPADNS solution was added to 100ml distilled water. 7ml of conc. HCl diluted to 10ml and added to the diluted SPADNS solution. The resulting solution was used for setting the instrument reference point (zero), is stable for at least one year.

2.2.9 $Na_2S_2O_3$.$5H_2O$ solution (1000μg/ml)

0.25 gm of $Na_2S_2O_3$ was dissolved in250 ml volumetric flask with distilled water and diluted upto the mark.

2.2.10 $NaHCO_3$ solution (1000µg/ml)

0.25 gm of $NaHCO_3$ was dissolved in250 ml volumetric flask with distilled water and diluted upto the mark.

2.2.11 KNO_3 solution (1000µg/ml)

0.25 gm of KNO_3 was dissolved in250 ml volumetric flask with distilled water and diluted upto the mark.

2.2.12 KCl solution (1000µg/ml)

0.25 gm of KCl was dissolved in250 ml volumetric flask with distilled water and diluted upto the mark.

2.2.13 Na_2CO_3 solution (1000µg/ml)

0.25 gm of Na_2CO_3 was dissolved in250 ml volumetric flask with distilled water and diluted upto the mark.

2.2.14 Na_2HPO_4 solution (1000µg/ml)

0.25 gm of Na_2HPO_4 was dissolved in250 ml volumetric flask with distilled water and diluted upto the mark.

2.2.15 $CaCl_2$ solution (1000µg/ml)

0.25 gm of $CaCl_2$ was dissolved in250 ml volumetric flask with distilled water and diluted upto the mark.

2.2.16 $MgCl_2$ solution (1000µg/ml)

0.25 gm of $MgCl_2$ was dissolved in250 ml volumetric flask with distilled water and diluted upto the mark.

2.2.17 $AlCl_3$ solution (1000µg/ml)

0.25 gm of $AlCl_3$ was dissolved in250 ml volumetric flask with distilled water and diluted upto the mark.

2.2.18 Buffer Solution of pH 4.0, pH 7.0 and pH 9.2

Buffer tablets of pH 4.0, pH 7.0 and pH 9.2 were dissolved separately in 100 ml of distilled water in a 100ml glass bottle.

2.3 Procedure

2.3.1 Investigation of bleaching action of fluoride on coloured complex of iron (III) for the determination of fluoride.

Iron (III) form colour complexes with certain ligands. When fluoride is added to these complexes the colour of the solution decreases with the formation of stable, colourless $(FeF_6)^{3-}$ complex. This bleaching action of fluoride can thus be used for the spectrophotometric determination of fluoride. For this purpose complex of iron (III) with salicylic acid, methyl salicylate and acetyl salicylic acid was studied briefly. Iron (III)-methyl salicylate complex was investigated by Sandelescu et al (1995) for the determination of fluoride and used for the determination of fluoride within range 10-80mg/L. Iron (III) also formed violet coloured complex with salicylic acid and wine red coloured complex with acetyl salicylic acid. Also when fluoride was added to those complexes the colour was bleached with the decrease in absorbance. Hence these complexes can also be used for the spectrophotometric determination of fluoride as like Iron (III)-methyl salicylate complex. From that concept Iron (III)-salicylic acid complex was taken for the further study of determination of fluoride as the reagents are easily available in the laboratory and easily soluble in water.

2.3.2 Determination of λ_{max} for ferric salicylate complex

Ferric salt form violet coloured complex with salicylic acid. The absorbance for the ferric salicylate complex was measured from 400 to 600 nm and the maximum absorbance was found at 525 nm as shown in figure (1). The concentration of ferric salt and salicylic acid to make ferric salicylate complex was adjusted so as to give measurable absorbance value.

2.3.3 Adherence of ferric salicylate complex to Lambert – Beer's law

Different sets of complexes were prepared, with concentration of ferric salt varying from 0 to $10x10^{-4}$ M and the concentration of salicylic acid was fixed to be $3x10^{-3}$ M so as to give the absorbance with in measurable range. The absorbance of the complexes formed in different set was measured. And the absorbance so measured and the concentration of Fe^{3+} was plotted to observe that the ferric salicylate complex follows Lambert-Beer's law or not which is shown in figure (2).

2.3.4 Optimization of conditions (concentration ratio, pH and stability)

2.3.4.1 Concentration ratio of ferric salt and salicylic acid

The concentration of ferric salt was taken such that it lies with in the range within which it follows Lambert- Beer's law. The concentration of ferric salt was therefore taken to be $7.5x10^{-3}$ M. By taking 1 ml $7.5x10^{-3}$ M Fe(iii) solution in different sets, different volume of $7.5x10^{-3}$ M salicylic acid was added and the final volume was made to be 10 ml which is shown in table (1) and absorbance for all the sets was measured. The ratio of Fe (III)- solution and salicylic acid in which maximum absorbance was found (i.e. 1:4) was taken for the further study. Thus in the final solution concentration of Fe (III) salt and salicylic acid becomes $7.5x10^{-4}$ M and $4x7.5x10^{-4}$ M respectively.

2.3.4.2 Stability of ferric salicylate complex

The complex made as above by mixing ferric salt and salicylic acid was stable at least for 2 months. The absorbance of the complex was studied at different time intervals at 525nm and pH 3.0.The absorbance of the complex was found to be same for at least two months of research time.

2.3.4.3 Effect of pH on determination of fluoride

The determination of fluoride ion spectrophotometrically by using ferric salicylate complex is based on the ligand exchange reaction between complex and the fluoride ions, where fluoride ions exchange with the salicylate ion forming colourless $[FeF_6]^{3-}$ complex. So the ligand exchange reaction may be dependent on pH. For determination of fluoride, effect of pH on ligand exchange reaction was studied. The pH was maintained for the mixture of complex and different increasing concentration of fluoride at different pH values (1, 2, 3, 4, 5, 6, 7, 8, 9, and 10) was added. The pH of the solution was measured potentiometrically using Antimony electrode since ordinary glass electrode cannot be used to determine pH in a solution containing fluoride ions. First of all, antimony electrode was standardised using different buffer solutions. The standard curve obtained is as shown in figure (3). Then the pH of the complex was maintained by maintaining the corresponding potential for that pH. Then the absorbance changes were studied for different concentration of fluoride at different pH at 525 nm. The pH at which higher absorbance and higher ligand exchange was seen was noted and was found in the range of pH 2-4.

2.3.5 Calibration curve for the determination of fluoride ion by using ferric salicylate complex

Fluoride standards in the range of 0 to 20 mg/L were prepared by diluting appropriate quantities of standard fluoride solution to 50 ml with distilled water. 10

ml of ferric-salicylate reagent (with composition $4.5x10^{-3}$M of Fe(III) solution and 1.8 $x10^{-3}$M salicylic acid so that composition of Fe(III) and salicylate in the final solution becomes 7.5 $x10^{-4}$M and 3.0 $x10^{-4}$M respectively) was added to each set. Spectrophotometer was set to zero absorbance with reference solution at 525 nm and absorbance was measured for each set. A curve for the milligram fluoride per litre versus absorbance was plotted. This study was done by maintaining the pH of all the solutions at 3.0. The calibration curve thus obtained is as shown in figure (4).

2.3.6 Interference study for different ion with ferric salicylate complex

First of all, in 50 ml of 5 mg/L fluoride solution 10 ml of ferric salicylate complex was added and absorbance was measured for it. Then 50 ml of sample containing 5mg/L of fluoride and 500 mg/L of each of ions that may interfere in the fluoride determination was taken in different sets. Then 10 ml of ferric salicylate complex was added in all the sets and absorbance was measured for those sets. Those ions which didn't bring any change in absorbance from the absorbance measured in their absence do not interfere in the fluoride determination where as others which bring changes interfere. For those interfering ions similar procedure was repeated with their decreasing concentration up to which they don't interfere the absorbance in the fluoride determination. All the measurements were done at pH 3.0. The common ions measured were Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, $S_2O_3^{--}$, HCO_3^-, NO_3^-, Cl^-, CO_3^{--}, HPO_4^{--}, SO_4^{--} which is shown in table (5).

2.3.7 Preparation of standard curve by using SPADNS- Zirconyl acid reagent

The λ_{max} for the SPADNS- Zirconyl acid reagent was found to be 570 nm (9) as shown in figure (6). Fluoride standards of concentrations 0, 0.4, 0.8, 1.2 and 1.6µg/ml were prepared by diluting appropriate quantities of standard fluoride solution to 50 ml with distilled water. Then, 10ml of mixed acid – Zirconyl –

SPADNS reagent was added to each standard and mixed well. Spectrophotometer was set to zero absorbance with the reference solution and absorbance was obtained for each standards.

A curve of concentration of F^- ions versus absorbance was plotted, which is the calibration curve for determination of fluoride by using SPADNS method as shown in figure (7).

2.3.8 Comparison between the determination of fluoride ions by using ferric salicylate complex method and SPADNS method

Calibration curve was drawn for the determination of fluoride by using ferric salicylate complex as mentioned in 2.3.5 and by SPADNS method as mentioned in 2.3.6 from which the concentration of fluoride in unknown samples can be determined. Two different fluoride samples of known concentrations were taken and the fluoride concentration in these two sets was measured by using both methods at same lab conditions. The agreement between these two methods was studied by studying the statistical parameters which is shown in table (7).

3. RESULTS AND DISCUSSION

3.1 Complex of ferric salt with Salicylic Acid

Ferric salt when treated with salicylic acid in acidic medium violet coloured ferric salicylate complex was formed with maximum absorbance at 525nm i.e. in the visible region. The reaction was instantaneous and the complex formed was stable

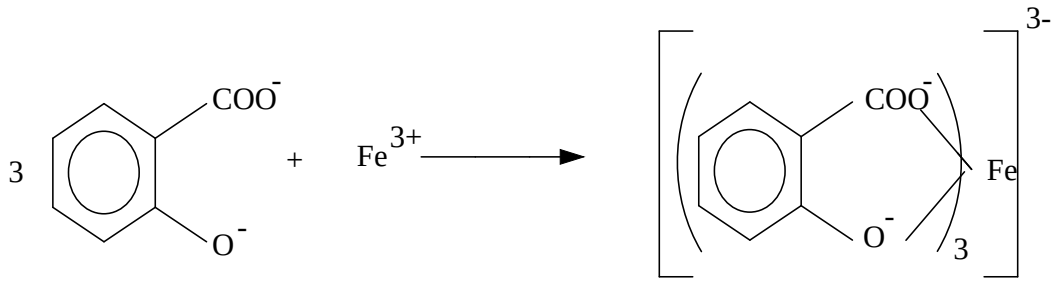
for long duration. When fluoride solution was added the absorbance was decreased due to the replacement of salicylate ligand by fluoride forming more stable colourless complex; $(FeF_6)^{3-}$. Hence ferric salicylate complex was studied for quantitative determination of fluoride in water by spectrophotometric technique. The validity of the present method was tested by comparing the resultswith the standard method using SPADNS Zirconyl reagent.

3.2 λ_{max} determination and adherence to Lambert- Beer's law of ferric salicylate complex

The maximum absorbance for the ferric salicylate complex was found at 525 nm. When the absorbance obtained for the different sets, containing Fe^{3+} concentration 0 to $10x10^{-4}$ M and salicylic acid concentration $3x\ 10^{-3}$M, was plotted against the corresponding concentration of Fe^{3+} , a straight line passing through the origin was obtained as shown in figure (2). This plot concludes that the ferric salicylate complex follows Lambert- Beer's law. The slope of this line gives the Molar extinction coefficient (ε) for this system which is found to be 1569. Above $10x10^{-4}$M concentration of Fe^{3+}, it does not give straight line when plotted against corresponding absorbance for the same concentration of salicylic acid. So, also from above observation it is concluded that the ferric salicylate complex follows Lambert-Beer's law within the range of 0 to $10x\ 10^{-4}$M concentration of Fe^{3+}. Therefore for the study of determination of fluoride by using ferric salicylate complex, the concentration of Fe^{3+} is chosen within this range.

3.3 Study of the ferric salicylate complex for the determination of fluoride

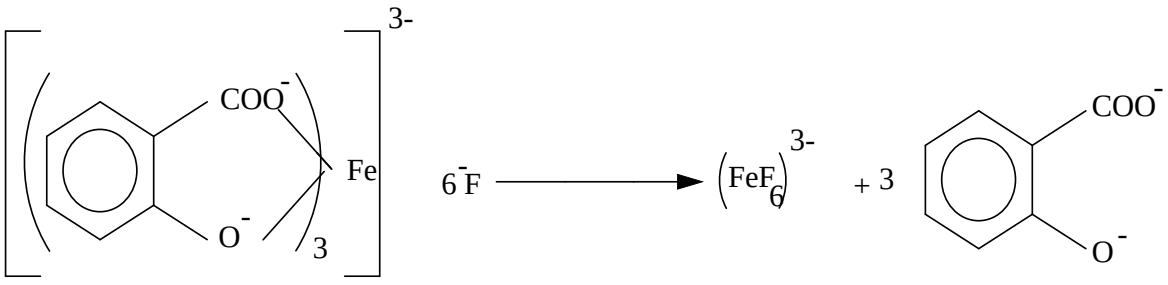
The ferric ammonium sulphate formed violet coloured complex with salicylic acid. It is due to the fact that salicylic acid gets co-ordinated with Fe^{3+} ion and form complex which absorbs in the visible region.



(Colourless) (Violet Colour)

λ_{max} = 525 nm

When F^- ions are added to this complex F^- ion displaces salicylate ions with the formation of colourless fluoride complex $[FeF_6]^{3-}$ i.e. ligand exchange reaction occurs between ferric salicylate complex and fluoride ions.



(Violet Colour) (Colourless)

Hence, the ferric salicylate complex may be used for the determination of fluoride ion spectrophotometrically, as we add F^- ions on the complex, the absorbance of the mixture decreases gradually with the increase in the concentration of F^- ions. It is due to the formation of colourless $[FeF_6]^{3-}$ complex which is found to be more stable than ferric salicylate complex.

3.4 Study of conditions for determination of fluoride

3.4.1 Concentration ratio of Fe^{3+} and salicylic acid

The concentration of Fe^{3+} was chosen so that it lies within the range it follows Lambert- Beer's law. For suitable absorbance after studying for many

concentration of Fe^{3+} was chosen to be 7.5x 10^{-4} M in the final solution .Then taking 7.5x 10^{-3}M of salicylic acid and different ratio of Fe^{3+} and salicylic acid, the absorbance was studied which showed that the absorbance was maximum and within suitable range for 1:4 ratio of Fe^{3+} and salicylic acid. So that the concentration of salicylic acid becomes 3.0x 10^{-4}M in the final solution as shown in table (1).

Table 1: Variation of absorbance with concentration ratio of Fe(III) and salicylic acid.

S.N.	Fe^{3+}(7.5x10^{-3}M)ml	SA(7.5x10^{-3}M)ml	H_2O, ml	Total volume,ml	Absorbance
1	1	1	8	10	0.90
2	1	2	7	10	1.06
3	1	3	6	10	1.10
4	1	4	5	10	1.16
5	1	5	4	10	1.12
6	1	6	3	10	1.10

3.4.2 Stability of the ferric salicylate complex

The absorbance was measured for the ferric salicylate complex at different duration of time. The absorbance was found to be constant during the research interval (2 months). Therefore it can be concluded that the complex is stable for at least 2- months and it can be used for the determination of fluoride up to at least 2-month as shown in table (2).

Table 2: Variation of absorbance with time.

Time	0	1hr	2hr	3hr	6hr	1 day	2 day	1 month	2 month

absorbance	1.16	1.16	1.16	1.16	1.16	1.16	1.16	1.16	1.16

3.4.3 Effect of pH on the determination of fluoride by using ferric salicylate complex

As we know the spectrophotometric determination of fluoride by using ferric salicylate depends on the ligand exchange between ferric salicylate and the fluoride ions, this ligand exchange depends upon the pH of the solution. The absorbance of the complex also depends upon the pH (28). When the absorbance of the ferric salicylate complex (Fe^{3+}: SA=1:4) was studied at different pH values, it was found that at pH 2-4 the absorbance for the complex was found to be maximum. The pH was maintained potentiometrically by using antimony electrode standardised with different buffer solutions.

The ligand exchange reaction also found dependent upon the pH of the solution. As we add fluoride solution to the complex, the absorbance of the solution decreases due to the formation of colourless $[FeF_6]^{3-}$ complex. On studying this ligand exchange between ferric salicylate and fluoride ion with series of fluoride concentration at different pH values it was found that absorbance decrease for the addition of increasing fluoride concentration was maximum at the pH range 2-4. Therefore the ligand exchange was found to be maximum at pH 2-4 i.e. in acidic medium as shown in table (3) and figure(4). So this pH range is regarded suitable for the study of determination of fluoride by using ferric salicylate complex and all the measurements are done at 525 nm and at pH 3.0 as calibration curve gives linearity at this pH.

Table 3: Variation of absorbance of ferric salicylate complex with pH of the solution.

S.N.	pH of the complex	Absorbance of the complex
1	1.0	1.14
2	2.0	1.16
3	3.0	1.16
4	4.0	1.16
5	5.0	1.12
6	6.0	1.12
7	7.0	1.10
8	8.0	0.62(colour changed-reddish colour; λ_{max}-450
9	9.0	0.24(colour changed-red colour ; λ_{max}-430)
10	10.0	0.24(colour changed-red colour ; λ_{max}-430)

3.5 Determination of fluoride by using ferric salicylate complex

The decrease in absorbance of ferric salicylate by the addition of different concentration of fluoride solution was measured by maintaining all the solutions to pH 3.0 approximately. The absorbance obtained for the addition of different concentration of fluoride is as shown table below;

Table 4: Calibration of the complex for the determination of fluoride by using ferric salicylate complex.

S.N.	Concentration of fluoride (mg/L)	Absorbance
1	0	1.16
2	2	1.08

3	4	1.00
4	6	0.94
5	8	0.86
6	10	0.78
7	12	0.72
8	14	0.62
9	16	0.54
10	18	0.40
11	20	0.28

A plot is drawn between concentrations of F^- ion versus absorbance measured. Thus the standard linear calibration curve is obtained which consists of straight line with negative slope as shown in figure (5). From this standard calibration curve we can determine the concentration of fluoride in unknown sample by using the following relation.

mg F^-/L = A/mL sample x B/C

Where, A = µg F^- determined from plotted curve

B = final volume of diluted sample, mL and

C = volume of diluted sample used for colour development.

The detection limit of this method is calculated to be 0.756 mg/L with confidence level of 92.1% while 1.13 mg/L for 98.3% confidence level. The sandell's sensitivity is calculated to be 0.02 µg $mL^{-1}cm^{-2}$.

3.6 Interfering ions in the determination of fluoride by using ferric salicylate complex

Different ions may interfere in the ligand exchange reaction between ferric salicylate complex and fluoride ions and may give erroneous results. Some cations and anions which may be present in water are studied for their interference in the determination of fluoride ions. The ions which interfere the ligand exchange between ferric salicylate complex and fluoride ions is due to the formation of more stable complexes with the Fe^{3+} ion or fluoride ions. Thus, when these ions are present in water the absorbance decrease in the ferric salicylate complex may also due to these ions along with the fluoride ions. Hence a greater decrease in absorbance is found for the sample containing these ions giving a negative error. Hence the critical concentrations of these ions are also determined above which they interfere in the determination of fluoride and were determined.

The effect of some important ions and the type of interference shown by them is shown in the table (5).

Table 5: List of some interfering ions in the determination of fluoride by using ferric salicylate complex.

S.N.	Ions that may be present in water	Interference
1	Na^{+}	No effect up to 500 mg/L
2	K^{+}	No effect up to 500 mg/L
3	Ca^{2+}	No effect up to 500 mg/L
4	Mg^{2+}	No effect up to 500 mg/L
5	Al^{3+}	Affect above 8 mg/L(-ve effect)
6	$S_2O_3^{--}$	No effect up to 500 mg/L
7	NO_3^{-}	No effect up to 500 mg/L

8	Cl^-	No effect up to 500 mg/L
9	SO_4^{--}	No effect up to 100 mg/L
10	HCO_3^-	Affect above 10 mg/L(-ve effect)
11	CO^-_3	Affect above 2.5 mg/L(-ve effect)
12	PO_4^{--}	Affect above 0.5 mg/L(-ve effect)

Thus from above observation it is found that cations like Na^+, K^+, Ca^{2+}, Mg^{2+}, and anions $S_2O_3^{--}$, NO_3^-, Cl^-, SO_4^{--} ions does not interfere in the determination of fluoride by using ferric salicylate complex where as some anions like HCO_3^-, CO^-_3, PO_4^{--} and cations Al^{3+} interfere in the determination of fluoride by using ferric salicylate complex. So these give negative error. HCO_3^- ions interfere in some extent , its critical concentration is 10 µg /ml above which only it interfere and below this concentration it have no effect with the complex. Similarly critical concentration of CO_3^{--}, HPO_4^{--} and Al^{3+} ions are 2.5, 0.5 and 8µg/ml respectively above which they

form complexes with Fe^{3+} and F^- and interfere in the fluoride determination but below this concentration they have no effect. So these ions (HCO_3^-, CO_3^{--}, PO_4^{--} and Al^{3+}) are said to have negative error whereas others have no effect.

3.7 Determination of fluoride by using SPADNS method

As similar as the determination of calibration curve for the fluoride determination by using ferric salicylate, calibration curve for SPADNS reagent can be drawn. Different concentrations of fluoride were added to the SPADNS-Zirconyl reagent as described in the experimental section. The decrease in the absorbance of this reagent with the addition of increasing concentration of fluoride ions is observed and the absorbance obtained on addition of different concentration of fluoride on the SPADNS- acid Zirconyl reagent is plotted against the corresponding

concentration of fluoride. A linear curve is obtained up to the 1.6µg F^-/ml concentration which is the standard calibration curve for the determination of fluoride.

Table 6: Calibration curve determination for the determination of fluoride by SPADNS method.

S.N.	Concentration of F^-(µg/ml)	Absorbance
1	0	0.58
2	0.4	0.52
3	0.8	0.42
4	1.2	0.36
5	1.6	0.26

The plot of concentration of F^- versus absorbance for this method gives almost linear calibration plot up to 1.6µg/ml concentration of F^- with negative slope which is as shown in figure (7). But above the concentration 1.6µg/ml of F^-, a non –linear plot is obtained. The concentration of fluoride in unknown sample by using SPADNS method can be determined by using the following relation.

mg F^-/L = A/mL sample x B/C

Where, A = µg F^- determined from plotted curve

B = final volume of diluted sample, mL and

C = volume of diluted sample used for colour development.

So, the concentration of unknown sample concentration lying up to the above range (0 to 1.6µg/ml) can be easily determined by this method.

The interference study was also made for SPADNS method. For SPADNS-acid Zirconyl reagent Aluminium (Al^{3+}), Iron, Phosphate showed negative effect with the critical concentration 0.1µg/ml, 10µg/ml, 16µg/ml respectively.

3.8 Comparison between ferric salicylate complex- method and SPADNS-method for the determination of fluoride

It is seen that SPADNS method has a linear analytical range of 0 to 1.6 mgF^-/L. But use of nonlinear calibration can extend the range to 4.0 mgF^-/L.

By the use of ferric salicylate complex from the concentration mentioned in the experimental section fluoride concentration up to the concentration 20mg/L can be determined. Here in this research work, in order to compare between these two methods we have calibrate the fluoride concentration from 0 to1.6mg/L by SPADNS method and from 0 to 20 mg/L by ferric salicylate complex. To compare these methods the following samples of fluoride were measured for it's concentration by using both method. All these measurements were done at the same lab conditions and by using the procedure above mentioned. And for ferric salicylate method pH of the solution was maintained approximately to 3.0.

Table 7: Comparison between ferric salicylate method and SPADNS-method in the determination of fluoride.

Sample no.	NaF taken (µg/ml)	Ferric Salicylate complex method		Statistical parameter		SPADNS method		Statistical parameter	
		NaF found(µg/ml)	% recovery	Mean (%) recovery	Standard deviation	NaF found (µg/ml)	% recovery	Mean (%) recovery	Standard deviation
1	0.80	0.74	92.5	95	2.50 %	0.82	102.5	102.33	2.84 %
	0.80	0.78	97.5			0.80	100		

	0.80	0.76	95.0			0.82	102.5		
2	1.50	1.45	96.6	96.2	0.34 %	1.48	98.6	98.17	0.73 3%
	1.50	1.44	96			1.46	97.33		
	1.50	1.44	96			1.48	98.6		

Hence it is found that mean percentage recovery of fluoride by using present method is 95.6, whereas by using SPADNS method is 100.23. Also the average standard deviation for ferric salicylate complex is 1.42%, and that for SPADNS method is 1.78%. The calibration sensitivity of the present method and SPADNS- zirconyl chloride method is found to be 0.042 μg^{-1} $mLcm^{-1}$ and 0.2 μg^{-1} $mLcm^{-1}$ respectively.

4. CONCLUSION

From the present work it can be concluded that fluoride in water can be determined by bleaching action of fluoride on the violet red coloured ferric salicylate complex. The ferric salicylate complex has λ_{max} at 525 nm and follows Lambert-Beer's law upto the concentration of $10x10^{-4}$ M of iron (III). The present method of fluoride determination can be used to determine fluoride upto 20 mg/L. Most of the ions usually present in ground water do not interfere but if phosphate and aluminium are present then they need to be removed prior to the determination of fluoride. Similar is the case with standard method of determination of fluoride by SPADNS-zirconyl chloride reagent.

The method is comparable with a standard spectrophotometric method for the determination of fluoride by using SPADNS- zirconyl chloride reagent. However the sensitivity of the present method is less than that of SPADNS- zirconyl chloride method but the detection range of present method is high. The calibration

sensitivity of the present method and SPADNS- zirconyl chloride method are found to be 0.042 μg^{-1} $mLcm^{-1}$ and 0.2 μg^{-1} $mLcm^{-1}$ respectively. Similarly the detection limit of this method is calculated to be 1.1 mg/L for 98.3% confidence level. The sandell's sensitivity is found to be 0.02 $\mu g\ mL^{-1}cm^{-2}$.

The basic principle of determination of fluoride by the present and that of SPADNS- zirconyl chloride method is identical. Hence for training purpose and for the determination of fluoride in water containing higher concentration of fluoride the present ferric-salicylate complex reagent is useful since the reagents are inexpensive, readily available in the laboratory and technique is simple and rapid.

Due to time constrain the applicability of the present method for the determination of fluoride in toothpaste and pharmaceutical product is left for further study.

APPENDIX

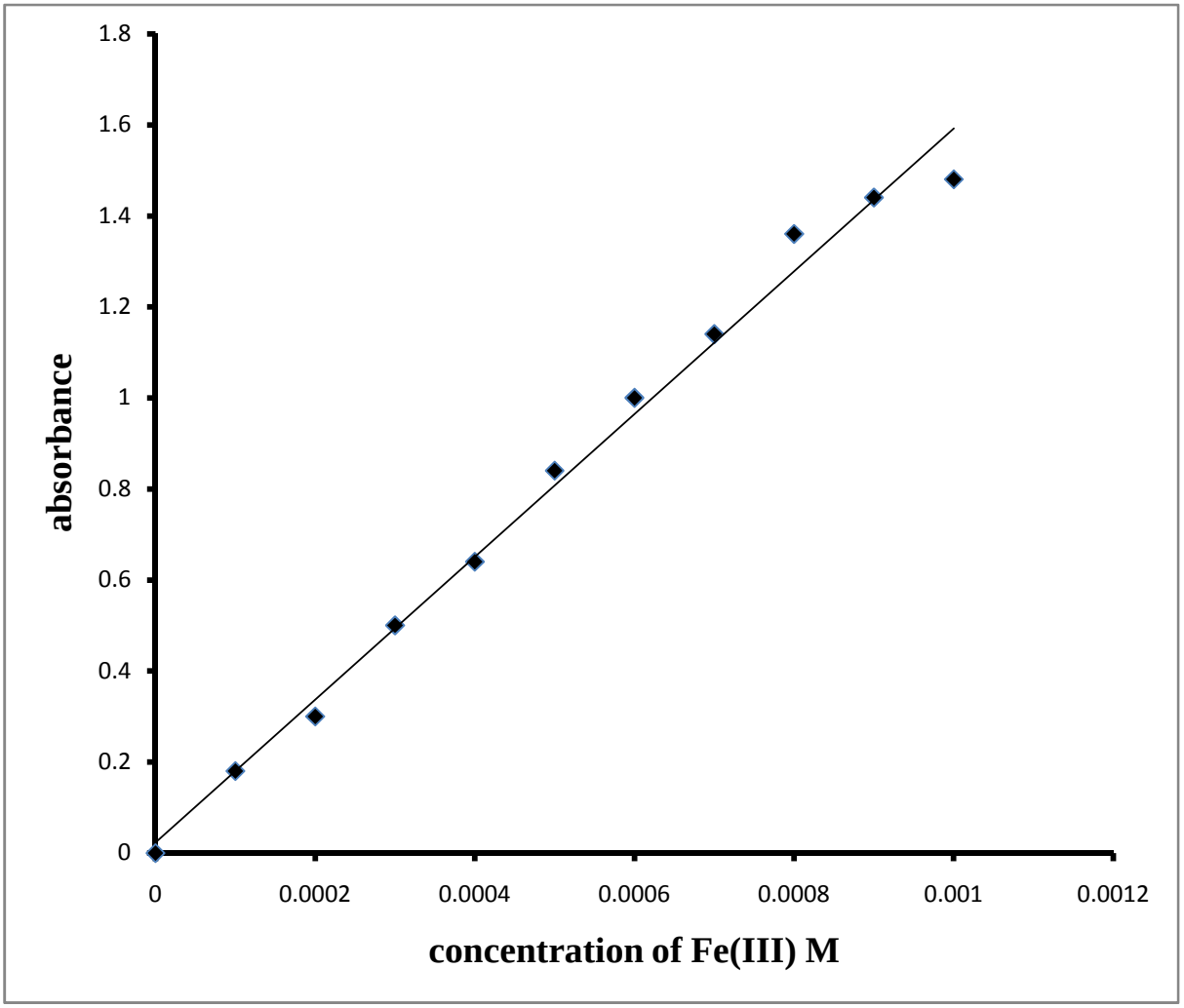


Fig. 2: Adherence of ferric salicylate complex to Lambert-Beer's law.

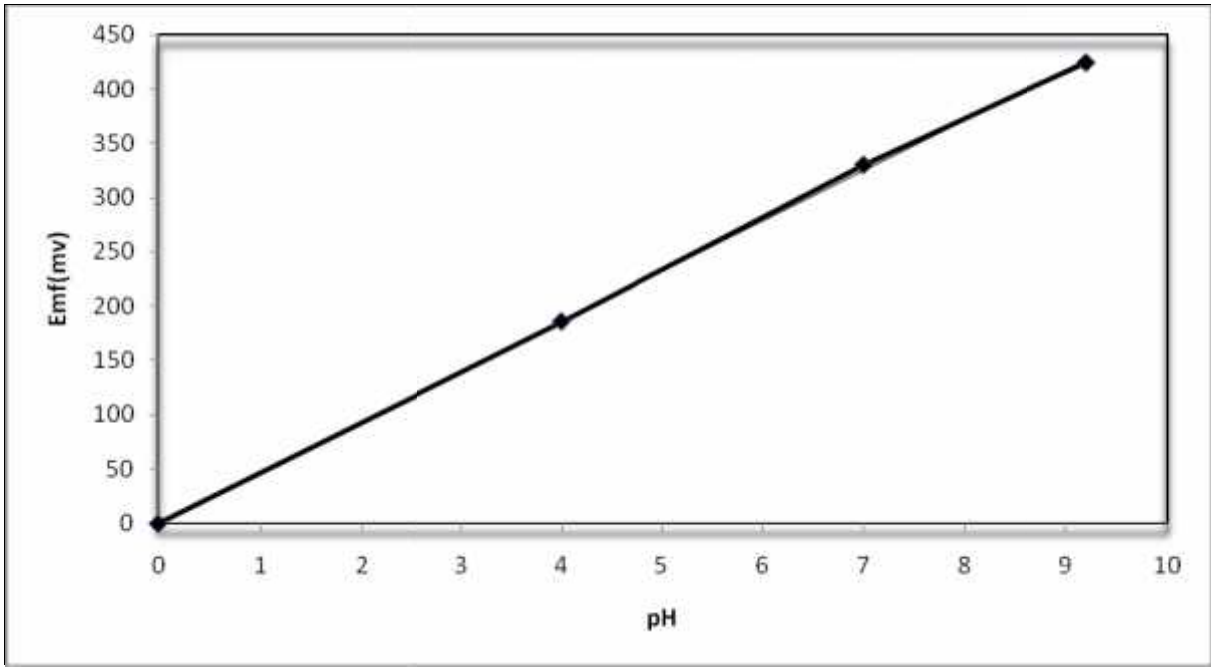


Fig.3: Calibration of buffer solution for the determination of pH of the complex by using Antimony electrode.

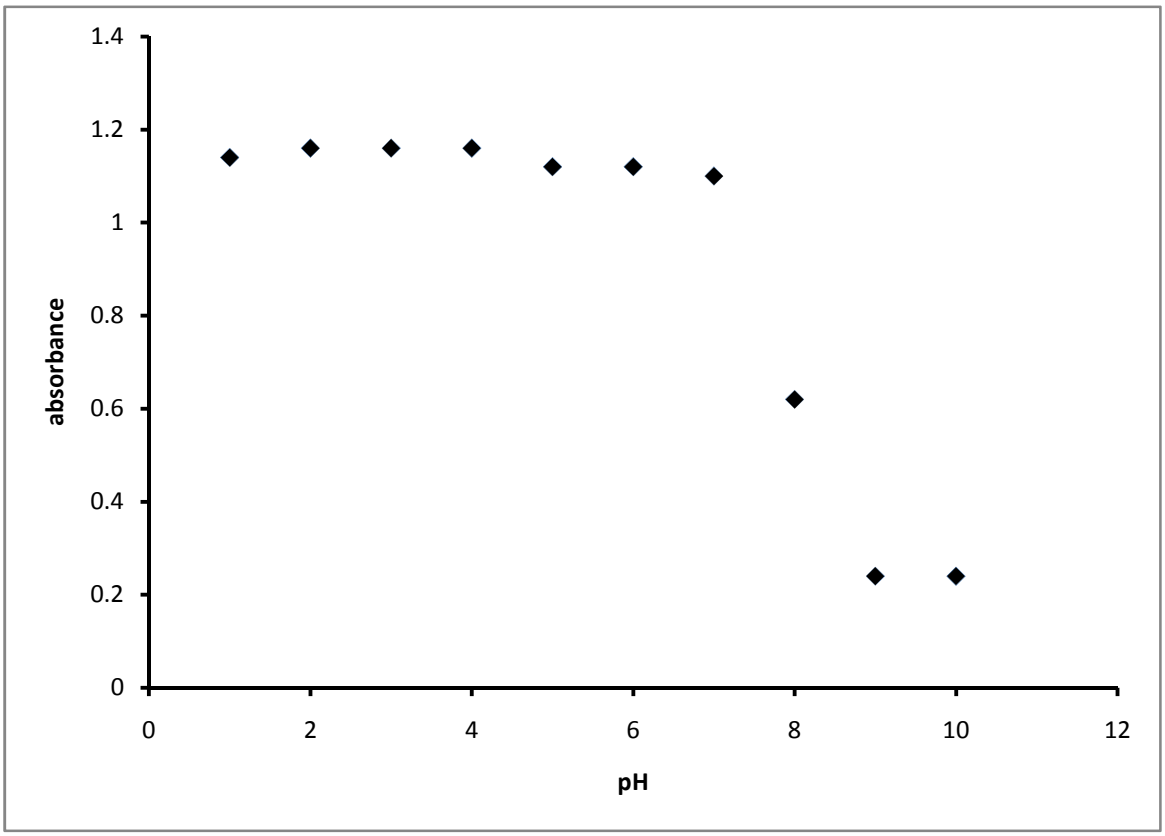


Fig.4: Effect of pH on the absorbance of ferric salicylate complex.

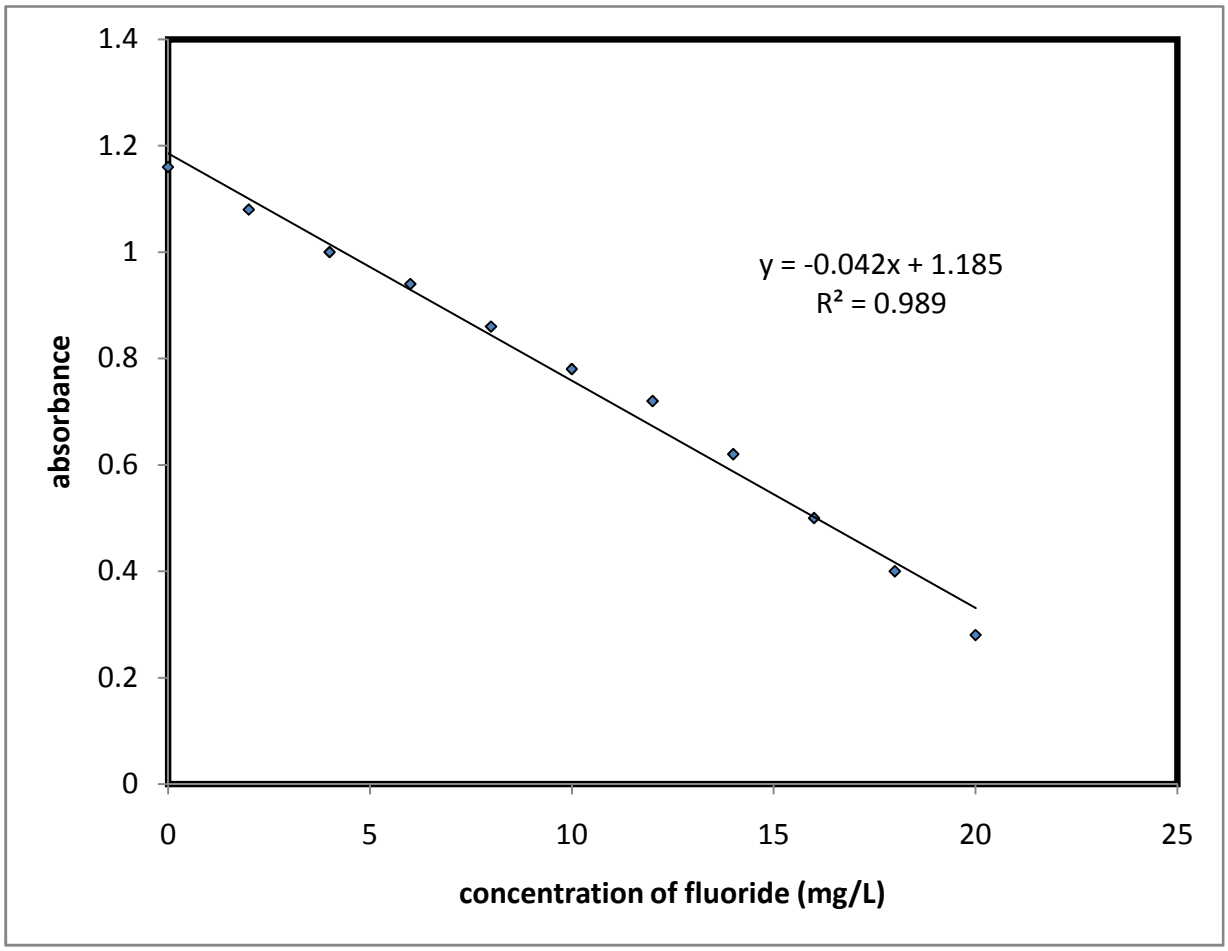


Fig. 5: Calibration curve for the determination of fluoride by using ferric salicylate complex.

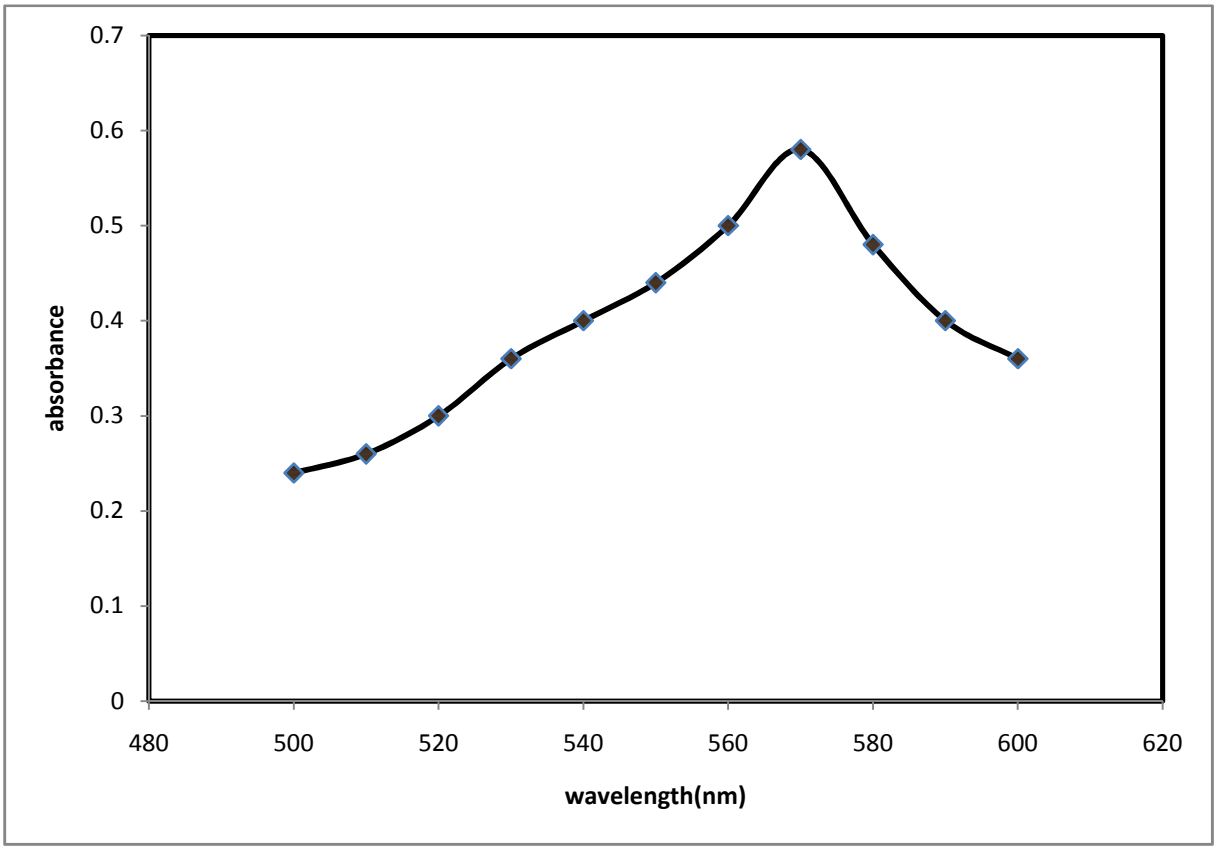


Fig.6: λ_{max} for SPADNS-acid Zirconyl reagent

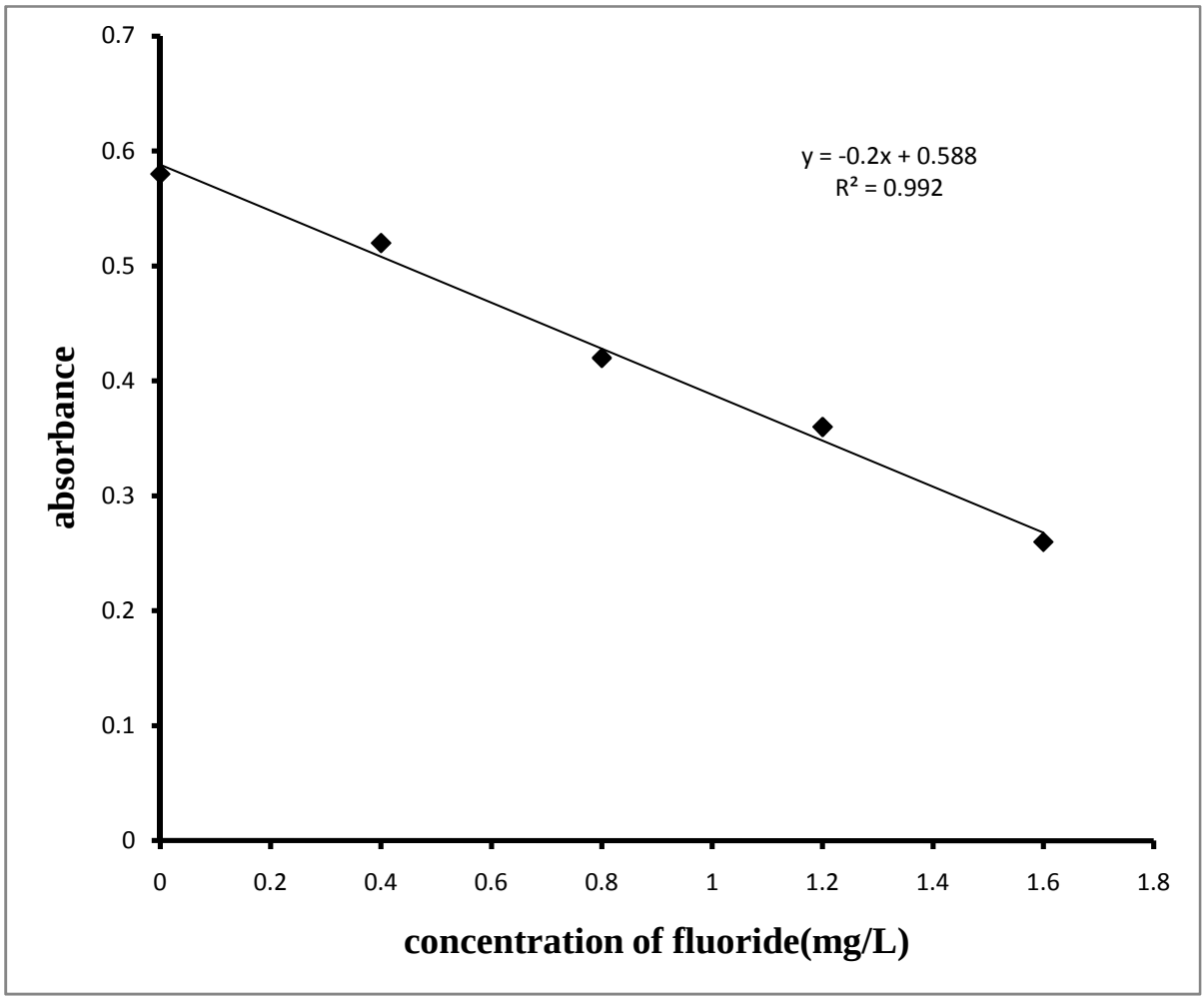


Fig. 7: Calibration curve for the determination of fluoride by SPADNS-method

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