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Estimation of fluoride ion in ground water of some areas of Theni district by spectrophotometric method

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ABSTRACT

Fluoride ion present in ground water of some areas in Theni District has been analysed using aluminium methyl orange complex by spectrophotometric determination. In this method the absorbance of methyl orange complex was measured and related to the concentration of fluoride ion in water. Present analysis of fluoride ion was compared with the values given by District Water Board. The method provides a reliable determination of fluoride in the range of 0.25-2 mg/L present in ground water. From the determination it was found that water samples contain permissible amount of fluoride ion as directed by World Health Organisation(WHO).

Keywords: Fluoride, ground water, spectrophotometric method, aluminium methyl orange complex.

1. Introduction

Ground water is one of the Nation's most important natural resources. It provides about 40 percent of the Nation's public water supply. In addition, more than 40 million people, including most of the rural population, supply their own drinking water from domestic wells. As a result, ground water is an important source of drinking water in every State. Fluoride occurs naturally in all types of water. Typically, surface waters and seawaters have low concentration of fluoride while groundwater may contain high levels of fluoride as it may be exposed to many inorganic fluoride-containing minerals. Fluoride salts are also frequently encountered in many industrial applications. Fluoride is known to contaminate groundwater reserves globally. The main source of fluoride in the water is fractured hard rock zone with pegmatite veins[1].

Major problems are being faced due to the presence of excess fluoride, arsenic and nitrate in groundwater in certain parts of country. Low levels of fluoride can help prevent dental cavities. However, higher levels of fluoride can induce dental fluorosis, which is the brown staining and/or pitting of permanent teeth. The fluoride level in drinking waters needs to be monitored and strictly controlled[2]. The World Health Organization (WHO) also sets a guideline value of 1.5 mg/L for fluoride in drinking waters[3].

There are many methods are available to determine the amount of fluoride ion in ground water such as alizarin method[4], colorimetric method[5], ion selective electrode method[6] and chromatographic method[7]. Recently Spectroscopic methods, which are widely used in the determination of fluoride, which are based on the reaction of fluoride with coloured metal chelate complexes, producing either a mixed ligand ternary complex or replacement of the

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ligand by fluoride to give a colourless metal fluoride complex and the free ligand[8]. Triphenylmethane[9] and Resorcin blue[10] dyes have been used to determine the fluoride ion concentration by forming complex with Aluminium Chloride. In this connection, we are interested to prepare aluminium methyl orange complex and to determine fluoride ion concentration in ground water by spectrophotometric method.

.2. Material and methods

2.1 Study area

Theni District is located in Tamil Nadu state in South India. The district is covered by hilly areas constituted by Periyakulam, Uthamapalayam and Aundipatty taluks with thick vegetation and perennial streams from the hills on the western side and Cumbum Valley which lies in Uthamapalayam taluk[11]. Periyakulam is located under the foot hills of Kodaikanal and it is surrounded by water sources such as Sothuparai dam and Kumbakarai Falls. Jayaraj Annapackiam College for Women is situated in a rock area called St. Anne's hillock, Thamaraikulam. The samples were collected in December 2014 from bore wells in six places namely Aundipatty, Karisalpatty, Pattiveeranpatty, Thamaraikulam, Periyakulam and Bodinayakkanur.

2.2 Apparatus

The UV–Visible spectra for absorbance studies were recorded using a Shimadzu 1800 UV Double beam spectrophotometer, BSR Lab, Jayaraj Annapackiam College for Women, Periyakulam. The IR spectra in KBr discs were recorded on a FTIR-Shima spectrophotometer BSR Lab, Jayaraj Annapackiam College for Women, Periyakulam.

2.3 Materials

Methyl Orange, Aluminum Chloride Hexahydrate and Sodium Fluoride were purchased from Sigma Aldrich and used without purification. The solvent ethanol was purified by the standard method described in the literature[12]. The analysis was carried out using double distilled water.

2.4 Preparation of metal complex

The complex for the spectrophotometric measurement was prepared by mixing aluminum and methyl orange in 1:2 ratio. 0.327 g (0.001mole) of methyl orange and 0.0665 g (0.0005 mole) of aluminum chloride were weighed and dissolved in 25 ml of ethanol solution taken in conical flask. The mixture was stirred in a magnetic stirrer for two hours. After two hours of constant stirring a brown precipitate was obtained. The completion of the reaction was confirmed by TLC. The precipitate was filtered by whattman filter paper and dried.

2.5 Reaction of sodium fluoride with the prepared complex Solution

2 mg of sodium fluoride was dissolved in one litre of double distilled water and the solution was diluted to 1, 0.5 and 0.25 mg/L concentrations. Various amount of fluoride were added in the range 0-2 mg/L to 25 ml volumetric flask containing 2 mg of aluminium methyl orange complex in ethanol ($2x10^{-4}$ M, 24.5 ml). The solution was completed to volume by double distilled water. The absorbance was measured at the wavelength 464 nm.

2.6 Determination of Fluoride ion in Real Water Samples

The ground water samples which had been collected and analysed by District level water testing laboratory belonging to Tamilnadu Water Supply and drainage board and the physico chemical parameters are given in Table 1.The UV-Vis spectrum of ground water samples with known weight of aluminium methyl complex was recorded and from the absorbance values the unknown concentration of fluoride ion was estimated.

Table 1: Analytical data of groundwater sample analysed by District Level Water Testing Laboratory

Factors	Aundipatti	Karisalpatti	Pattiveeranpatti	Thamarai kulam	Body	Periya kulam
pH	7.2	7.1	7	7	7	7.1
Total Alkalinity as $CaCO_3$(ppm)	170	340	170	440	320	170
Total hardness as $CaCO_3$(ppm)	220	400	210	500	200	205
Calcium	45	82	43	103	40	43
Magnesium	26	48	25	60	25	30
Iron	0.1	0.3	0.3	0.2	0.1	0.1
Manganese	0	0	0	0	0	0
Nitrate	8	7	8	3	7	7
Chloride	46	90	50	140	45	50
Fluoride	1	0.6	0.4	0.4	1	0.2
Sulphate	18	60	18	80	20	21
Phosphate	0.4	0.2	0.5	2	0.3	0.2

Concentration of fluoride ion was measured in the sample using aluminium methyl orange (1:2) complex and the obtained results were compared with that reported by the District level water testing laboratory in which fluoride ion was estimated using alizarin method

3. Result and discussion

3.1 Characterisation of Methyl Orange and its Aluminium Complex

Methyl orange is soluble in ethanol, methanol, acetic acid and acetone and slightly soluble in ether. Methyl orange exhibits orange colour in ethanol solution and display bands at 406 nm 261 nm and the concentration is 2×10^{-4} M. The complex shows absorption bands at 384 nm and 262 nm. Thus there is hypsochromic shift(decrease in the wave length) of about 22 nm after complexation with aluminium. This is resulting in a change in colour from that of the ligand, orange to the colour of the complex brown. The UV Visible spectra of methyl orange and its aluminium complex was given in Figure 1.

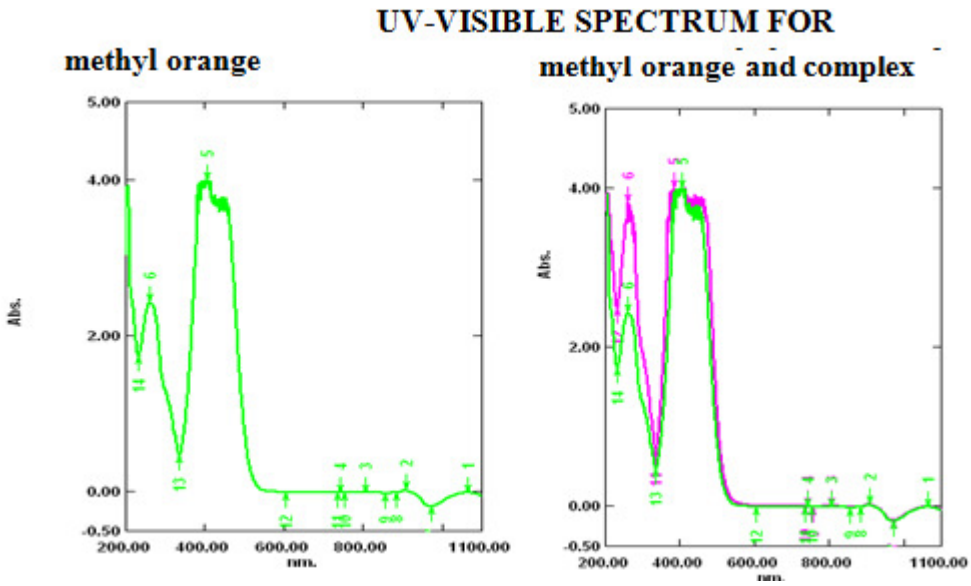

Figure1: UV- Vis spectrum

3.2 FT-IR Analysis

The IR spectrum of methyl orange and the aluminium complex exhibit the following absorption peaks. The IR stretching frequency of S=O in methyl orange is 1033 cm^{-1} and C-N frequency is 823 cm^{-1}. The stretching frequencies of S=O and C-N in aluminium complex has been shifted to 1024 cm^{-1} and 819 cm^{-1} and it indicates the coordination of metal through S=O group and C-N. The possible structure of the complex is shown in Figure 2.

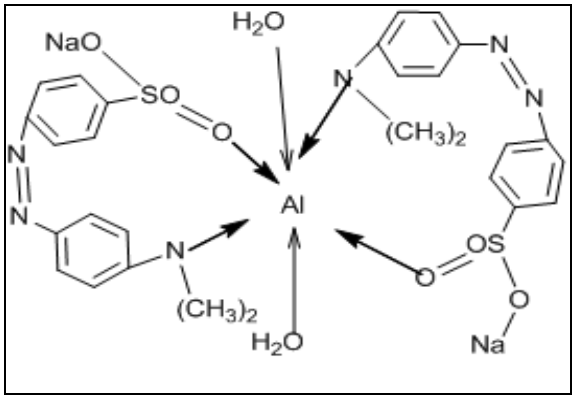

Figure 2: Possible structure for aluminium methyl orange 1:2 complex

3.3 Calibration curve for standard sodium fluoride solution

Fluoride reacts with the aluminium methyl orange complex to produces aluminium fluoride complex by replacement of the methyl orange by fluoride and liberating of the free ligand. Aluminium react with fluoride to give compounds of the nature of (AlF_6^{-3}).

$$Al\ (\text{methyl orange})_2 + 6F^{-1} \longrightarrow AlF_6^{-3} + 2(\text{methyl orange})$$

Fluoride interacts with complex under investigation and results in increase in absorbance at 462 nm due to the releasing of the free ligand. Calibration curve was plotted by taking known concentration of sodium fluoride ion and the absorbance of the methyl orange which was

measured by UV-Vis spectroscopy method. The absorbance was related to the concentration of fluoride ion. In the curve the absorbance varies linearily with the concentration of sodium fluoride[9]. The calibration curve was given in Figure 3.

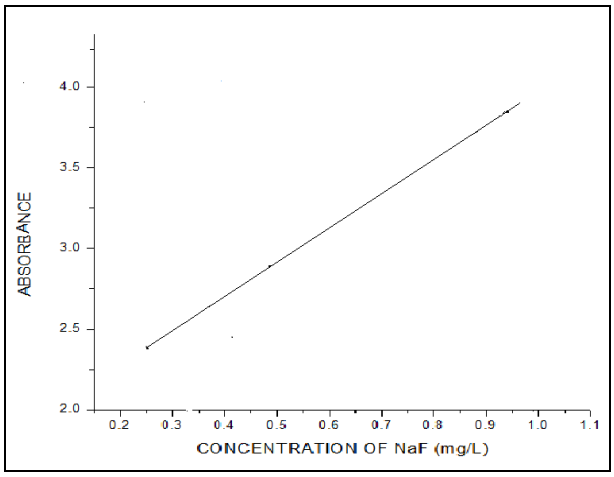

Figure 3: Calibration curve for determination of fluoride ion in the range (0.0 - 1.1) mg·L^{-1} at 464 nm by aluminum methyl orange complex of 2.0×10^{-4} M**.**

3.4 UV- Vis Spectrum for water samples with complex

Ground water samples are collected at different areas such as Aundipatty, Karisalpatty, Pattiveeranpatti, Thamaraikulam, Bodinayakkanur and Periyakulam in Theni district. The UV-Vis spectra of all the samples were given in Figure 5. The concentration of fluoride ion in different samples are represented graphically and the graph is depicted in Figure 4. The absorbance values of different water samples at 462 nm and fluoride ion concentration are given in Table 2.

Table 2: Absorbance values and fluoride concentration of different water samples

Places	Wavelength(nm)	Absorbance	Fluoride ion concentration(mg/L)
Aundipatti	461	3.99	0.99
Bodinayakkanur	462	3.77	0.90
Karisalpatti	462	3.40	0.72
Pattiveeranpatti	464	2.54	0.33
Thamaraikulam	461	2.47	0.26
Periyakulam	464	2.06	0.15

Fluoride ion is measured using the proposed spectroscopic method in 6 water samples and low fluoride content is present in the Periyakulam sample.The observed concentrations are compared with the reported values by the District level water testing laboratory and found to be that the fluoride ion can be estimated in ground water.

Prevoius study report[10] that sulphate upto 100 mg/L does not interfere with the determination of fluoride. The water samples in this study contain sulphate ion less than 100 mg/L. If sulphate present more than 100 mg/L in water it can be removed by precipitating sulphate in the cold by the addition of aqueous barium chloride solution and aqueous agar-agar solution, then to separate the precipitate by filltration.

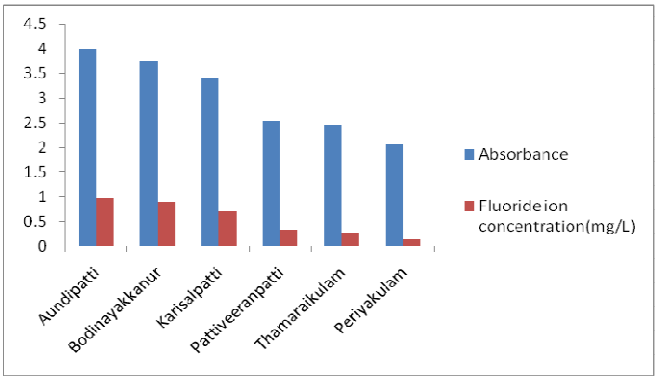

Figure 4: Concentration of fluoride ion in water samples

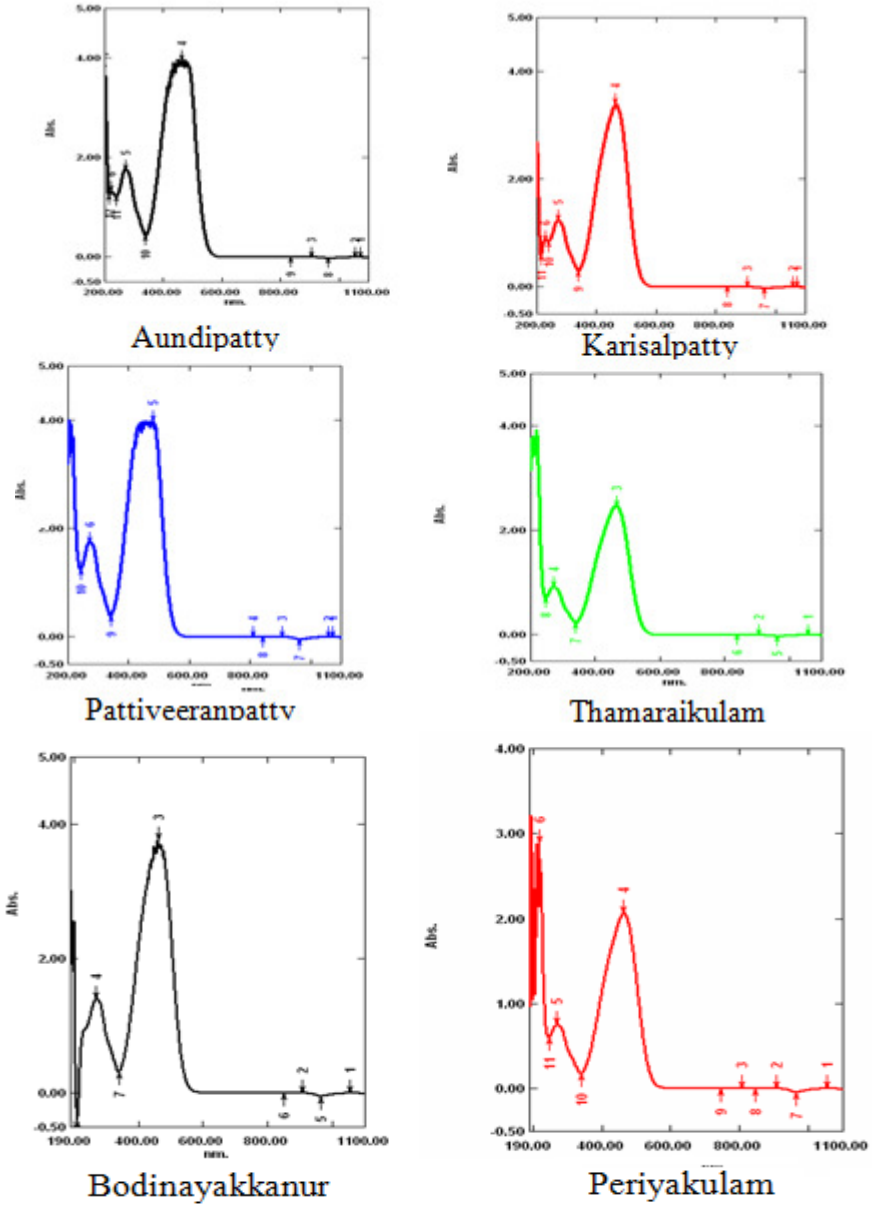

Figure 5: UV-Vis spectra of various water samples with complex

4. Conclusion

Aluminium methyl orange complex can be used in the examination of water samples that naturally contain fluorides in ground water in the concentration range 0.0 – 2.5 mg/L. The relationship of the reaction of fluoride with aluminium methyl orange complex is found to be linear. The fluoride ion concentrations determined by this present study are compared with the results from the certified laboratory from District Water Board and it was found that the results match with the certified lab values. All the water samples contain fluoride ion less than 1 mg/L. Due to its simplicity and sensitivity, the method can be used as new spectrophotometric reagent for determination of fluoride in ground water at low concentration.

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