

FT-IR Spectroscopic Analysis of Seasonal Impact of Mineral Assemblage in Coastal Soil Samples and Its Structural Study

Vinoth Kumar K C¹ and Jani Subha T²

¹Associate Professor, Department of Physics,
Udaya College of arts and Science, Vellamodi, Kanyakumari, India

²Associate Professor, Department of Chemistry,
Rohini College of Engineering and Technology, Kanyakumari, India

Abstract:

The mineral characterization of coastal sediment samples was analyzed using Fourier Transform Infrared (FTIR) spectroscopic technique. From this technique, several minerals are identified with the help of available literature. Among the various observed minerals, the minerals such as quartz, kaolinite and calcite are major and others are trace minerals. The performed analyses provided useful information about the mineralogical composition of the sediments. Altogether samples from five sampling locations of two seasons were studied, minerals identified and its structure too analyzed. Huge presence of clay, organic and silica minerals were identified.

Key Words: Coastal sediment, Mineral Analysis, FT-IR technique, Clay mineral, Quartz

1. Introduction

FT-IR is one of the widely used techniques normally used to study the molecular structure of the composition of new engineering material. An infrared spectrum gives a blueprint of the sample with its absorption peaks related to the frequencies of vibrations of the bonds of the atoms which make that material. This is because each of the composition elements in the material may be having its own absorption range producing different peaks in the spectrum. So that infrared spectroscopy can be used for qualitative analysis of different kind of material. The size of the peaks is the indication of amount of the material present in the sample. Since both qualitative and quantitative analyses are possible with this spectroscopic instrument it is found in wide variety of application. FT-IR spectroscopic peaks rely on the lattice vibrations

and/or molecular group vibrational modes. Mineral identification in a particular sample is feasible because minerals have the absorption bands in the mid-range of infrared (4000 to 400cm⁻¹). As an analytical tool it has its own advantage such as accurate, inexpensive and reliable, the required sample amount is in the sub milligram range and sampling procedure is simple. In infrared spectroscopy, when the sample is exposed to the IR radiation some of the energy is absorbed and some get transmitted. The obtained spectrum representing the molecular absorption and transmission gives the footage of the sample. In this technique no two different molecular structure produce same spectrum.

Thus Infrared spectroscopy is useful for various applications such as identifying minerals, its quantity and its quality in a given sample. When molecules or atoms exposed to IR radiation, it gets excited under vibrational and rotational modes. Two types of bond vibrational modes are in simple molecules, stretching and bending, stretching refers to periodic stretching of the bond along bond axis and bending refers to the displacement occurring at right angles to the bond axis. These vibrations produce periodic displacements of atoms with respect to one another by a change in dipole moment and they give rise to absorption of radiation in the infrared region. The frequencies of these periodic displacements are specific for particular atomic group. The versatility of FTIR spectroscopy makes it a foundational tool for soil scientists, despite several blockades in the acquisition and interpretation of soil spectra that arise from chemical heterogeneity. FT-IR spectroscopy is becoming one of the most suitable experimental methods for the analysis and characterization of components in the

field of material science and cultural heritage (Barone et al., 2011).

The changes in the crystalline and amorphous substances can be studied using this FT-IR spectroscopy technique. Fourier Transform Infrared spectroscopy (FT-IR) represents a powerful technique as it provides the molecular fingerprint of the substances (De Benedetto et al., 2005). Thus the advantages of FT-IR have made the measurements extremely accurate and reproducible. So, it is a very reliable technique for positive identification of any sample. The most important feature of Fourier Transform Infrared spectroscopic method are (i) Sample preparation in relatively fast and easy (ii) Very small amount of sample is required. (iii) Short time of experimentation. The great advantage of FTIR measurement is the high sensitivity that allows detection of many components. Thus, applying FT-IR technique for mineral analysis is more advantageous because of its rapid and non-destructive capabilities. The usage of FT-IR spectroscopy to the coastal soil in the study aimed to (i) To find the type of soil (ii) To identify the quantitative analysis of minerals present in the sample.

2. Materials and Methods

2.1 Sample Collection

Study area is situated along the south western side of the coastal stretch, in the southern part of Tamil Nadu, India. Ten soil samples of two different seasons (pre monsoon and post monsoon) were collected from 5 soil sampling stations. The samples are labeled as

- R1-Rajakamangalam (Pre monsoon)
- U1-Muttom (Pre monsoon)
- N1-Chinnavilai (Pre monsoon)
- K1-Kottilpadu (Pre monsoon)
- C1-Colachel (Pre monsoon)
- R2-Rajakamangalam (Post monsoon)
- U2-Muttom (Post monsoon)
- N2-Chinnavilai (Post monsoon)
- K2-Kottilpadu (Post monsoon)
- C2-Colachel (Post monsoon).

The distance between each sampling station falls around 5kms. The samples were placed in plastic pouches and transported to the STIC Laboratory, Cochin University Campus, Kerala. The location map is given in Figure 1.

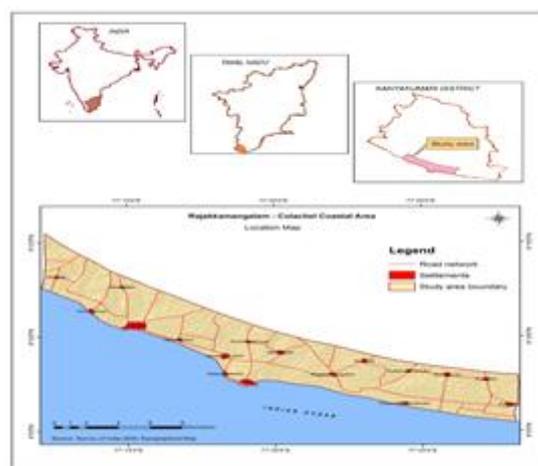


Figure 1: Location Map

2.2. Sample Preparation

Sample of 2 mg is mixed with 40 mg of spectroscopic KBr in the ratio 1:20 using a mortar and pestle. Before mixing, necessary amount of KBr powder is dried at 120 °C for six hours in an oven. The mineral sample was weighed in a microbalance and placed in a clean agate mortar along with the proper amount of dry KBr to prepare sample pellet. A pellet of 1mm in thickness and 13 mm in diameter is prepared. A small camel's hair brush is used to transfer the mixture to the die for pressing the pellet. The die is cleaned with water and acetone, and dried before another pellet is prepared. This procedure is followed for the preparation of every pellet. The prepared pellet is preserved in a moisture free glass container before it is placed in a suitable sample holder and introduced in the infrared beam for analysis.

3 Results and Discussion

Qualitative analyses with the collected soil samples are carried out to find out the major and minor constituent minerals present in the samples from the location of the peaks from the prominent FTIR absorption peaks. The minerals are identified with the available literature. In the typical FTIR spectroscopic diagram ranging from 400-4000 cm^{-1} given in the Figure 2 the observation band ranges are classified into clay minerals, organic matter and minerals.

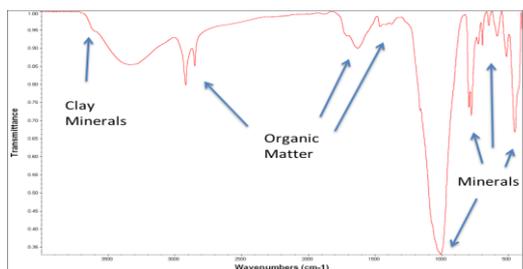


Figure 2: Typical FTIR spectroscopic diagram

The positions of the observed bands in wave number units are summarized in Table-1 and Table – 2 indicating the intensity of minerals in the study locations of two different pre and post monsoon season. In general weathering make changes in the accumulation of minerals because of the change in atmospheric pressure and temperature. The observed bands indicate the dominance of three major minerals such as clay mineral, carbonate mineral and quartz mineral irrespective of the change in station and season.

3.1 Clay Minerals

From the Table 1 and Table 2 it is observed that the sampling location R1 and R2 of two different seasons shows some specific changes in the presence of minerals in between the pre and post monsoon season. The peak observed in 3440cm^{-1} shows the significant increase in accumulation of clay mineral Kaolinite in the samples. It is studied from the geomorphological knowledge that during the period of monsoon a huge discharge in the pariyar estuary is one of the reasons besides the man-made jetties in the sampling site for the increase in intensity of peak from weak band(WB) to medium band(MB). The jetties make the concentration of the minerals by obstructing the long shore current near to the shore line. Such climatically-related differences in clay mineral content are often used to infer changes in climates in the geological past. The bands in the region $3000\text{-}3800\text{ cm}^{-1}$ are all due to OH stretching and the weak peak obtained in the region 1621cm^{-1} in the samples U2,N2 and K2 are due to the OH bending modes of water or hydroxyls. No additional bands are observed in this region. The variations in the values of OH stretching and bending wave numbers from sample to sample are usually attributed to the varying strength of hydrogen bonding between the OH and H_2O molecules and some oxygen in the structure.

Kaolinite is the clay mineral with the chemical composition of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. It is layered silicate mineral, with one tetrahedral sheet linked through

oxygen molecules to one octahedral sheet of alumina octahedral as shown in the Figure 3. It is produced by the chemical weathering of feldspars. Because of its fine nature it is mixed with water and easily transported as liquid clay particle. The presence of an absorption band at or around 3400 and 1016 cm^{-1} indicate the presence of clay minerals such as kaolinite and montmorillonite from the available literature. IR absorption peaks in between the spectral range of $3420\text{-}3445\text{cm}^{-1}$ associated with the samples of pre monsoon season rather than post monsoon season indicates the presence of Kaolinite in considerable amount. This absorption peaks corresponds to stretching vibrations of inner surface of Hydroxyl group according to Russell (1987) and Ramasamy et al. (2005), and also their literature states that, if four peaks are observed in the region $3697\text{-}3620\text{ cm}^{-1}$, then the mineral is said to be in an ordered state. However, in the present study as no peak is observed at around 3690 cm^{-1} the presence of kaolinite mineral may be in disordered state. The FTIR peaks of kaolinite are reported by many workers as cited in the literature of the given reference [2-8,11,13-19,21-25].

Kaolinite is a 1:1-type minerals made up of one tetrahedral (silica) sheet combined with one octahedral (alumina) sheet. The tetrahedral and octahedral sheets in a layer of a kaolinite crystal are held together tightly by oxygen atoms, which are mutually shared by the silicon and aluminum cations in their respective sheets. These layers, in turn, are held together by hydrogen bonding.

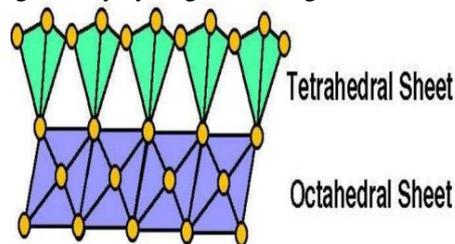


Figure 3: Kaolinite Structure

Kaolinite crystals usually are hexagonal in shape. In comparison with other clay particles, they are large in size. Because of strong binding force between their structural layers, kaolinite particles are not readily broken down into extremely thin plates. Kaolinite exhibits very little plasticity (capability of being molded), cohesion, shrinkage, and swelling [9].

2:1-Type Minerals (Montmorillonite) are characterized by an octahedral sheet sandwiched between two tetrahedral sheets as mentioned in the Figure 4.

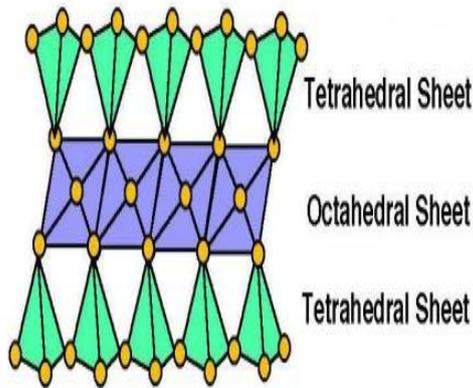


Figure 4: Montmorillonite Structure

Montmorillonite the smectite group of minerals is noted for their interlayer expansion and swelling when wetted. The water enters the interlayer space and forces the layers apart. Each layer is made up of an octahedral sheet sandwiched between two tetrahedral (silica) sheets. The FTIR absorption bands at 867-875, 1621 cm^{-1} show the presence of montmorillonite in the samples [5,13,14]. This group of mineral is almost visible in all the pre monsoon samples except K1. At the same time in post monsoon analysis it is understood that only R2 and C2 samples are having the peak values around 868 cm^{-1} corresponding to the montmorillonite mineral. The intensity of this mineral obtained in all the samples are nearer to a less value due to the change in weather.

3.2 Carbonate mineral

Calcite is the most common carbonate mineral in the sediments. Carbonates are commonly deposited due to the accumulation of dead planktonic life on the sea floor. The mid infrared region (1400-1500 cm^{-1}) of the spectra is dominated by the vibrational modes of carbonate ions (Ramasamy et al., 2011). From the Table 1 and 2, it can be observed that the absorption peak in the range 1470-1475 cm^{-1} is presented in all the samples. This helps to recognize the presence of calcite in all the samples invariably. Also, presence of some other peaks in 2517 - 2521 cm^{-1} certain sample sites such as R1,R2 and U1 as shown in the Fig.7 and Fig.8 signifies the existence of calcite. The variation of some peaks from sample to sample may be due to the interference of silicate minerals or due to the particle size of the minerals (Ramasamy et al., 2009a). The observed band intensity from the Table 1 and 2 indicates that there are strong and sharp intensities of calcite presence in most of the premonsoon season samples rather than post monsoon season. Therefore the monsoon weather

makes a great role in the settlement of this calcite minerals in the samples U1,U2,N1,N2 and K1,K2 except R1,R2 and C1,C2 samples. The molecular structure of the carbonate mineral is as shown in the Figure 5.

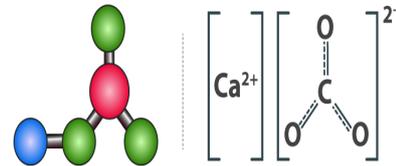


Figure 5: Carbonate Structure

The solubility of carbonate mineral is high compared to the aluminosilicates and are more prevalent in arid and semi-arid regions. The major carbonate minerals are calcite (CaCO₃). From Table 1 and 2 the I.R absorption bands at 2516, 1750-1800, 1470-1475 cm^{-1} are found to be calcite [1, 4, 5, 13, 16-18, 20].

3.3 Quartz

Quartz is the mineral that contains silicon dioxide (SiO₂) mainly with the molecular structure as shown in the Figure 6. Quartz is the widely spread mineral in the earth's crust. It can be seen in all the three rocks such as igneous, metamorphic and sedimentary. It is particularly dominant in sedimentary rocks since it is extremely resistant to physical and chemical breakdown by the weathering process. Generally, white sand beaches are typically formed due to quartz-rich sediments. In our study since all the 5 study locations are coastal region, the samples are dominant with white sand. In our seasonal study, quartz is the only mineral which does not show any significant changes due to the weather. It is because of its hardness and chemical structure. Therefore, quartz is often the most common mineral found in beach sediments. In the present study all minerals other than quartz has shown a variation in the concentration at various sampling sites with respect to pre and post monsoon season. The presence of quartz is explained by Si-O asymmetrical bending vibration at around 462 cm^{-1} and Si-O symmetrical stretching vibrations around 694 cm^{-1} . The 1082 and 1162 cm^{-1} absorption region arises from Si-O asymmetrical stretching vibration due to low Al for Si substitution are also indicates the presence of quartz. These assessments are in good correlation with the observation on the quartz obtained by Ramasamy et al., (2004a, 2005, 2006b, 2009a and 2011) and Hlavay et al., (1978).

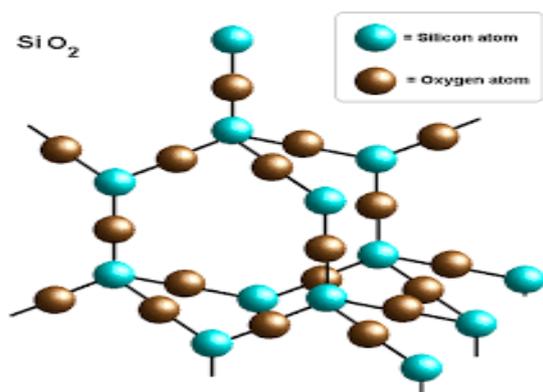
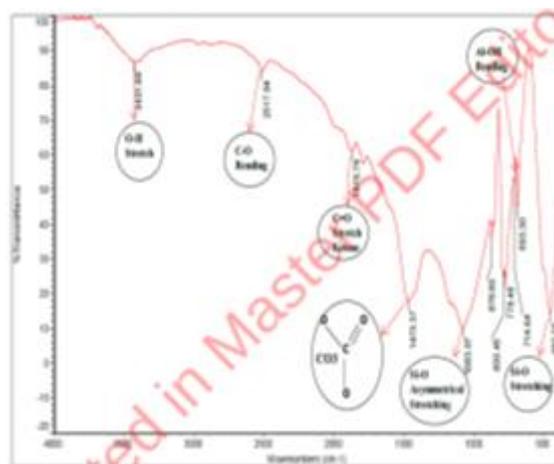


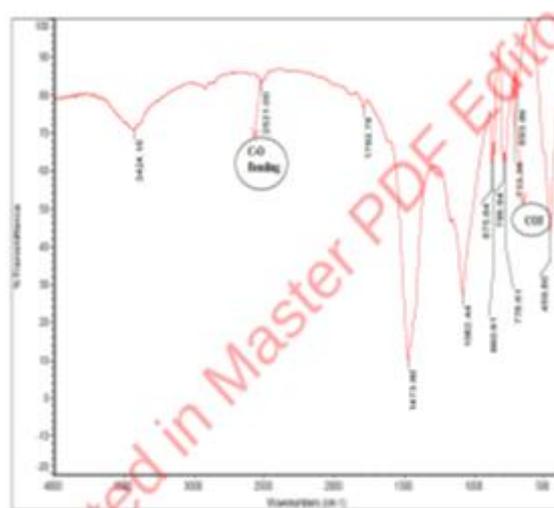
Figure 6: Quartz Structure

The mid infrared spectra of silicate in between the range 1200–400 cm^{-1} are classified into four characteristic bands around 1000, 780, 695 and 450 cm^{-1} with reference to the standard quartz spectra. Among these four characteristic peak regions shown in the Table1 and Table 2, the peak at 695 cm^{-1} is unique with quite weak bands during both pre monsoon and post monsoon seasons indicating a short fall in the crystallinity of the quartz mineral while comparing to rest of the three bands.

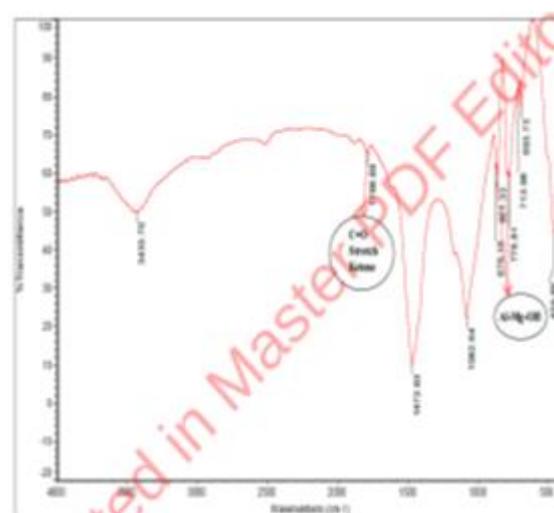
The absorption band at 780 cm^{-1} and 462 cm^{-1} arises due to the tetrahedral site symmetry for silicate, the tetrahedral dimensions are generally considered to be little affected by pressure and temperature. The absorption band at 695 cm^{-1} arises due to the octahedral site symmetry. The tetrahedral site symmetry is stronger to that of octahedral site symmetry. Therefore, for any structural change, the damage occurs first in octahedral site symmetry then in tetrahedral site symmetry. The intensity of the bands due to the vibrations of these two symmetries will provide direct information on the crystallinity. The absorption bands located at $\sim 780 \text{ cm}^{-1}$ and $\sim 462 \text{ cm}^{-1}$ involve atomic motions within the SiO_4 tetrahedra. The frequencies of all the ten studied samples during both pre-monsoon and post monsoon as shown in the Table1 and Table2 is assigned with reference to Fig.6 and Fig.7[3].



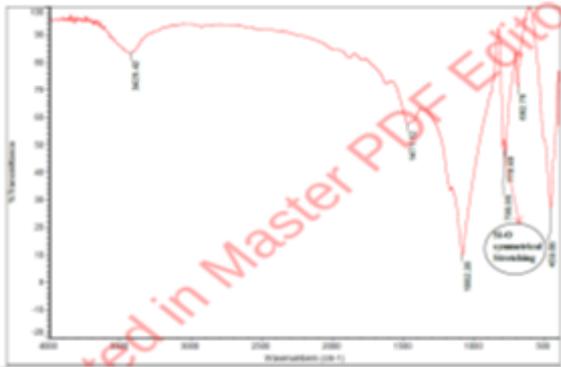
(a) R1



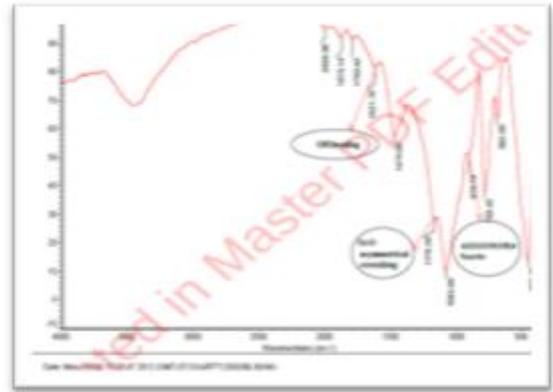
(b) U1



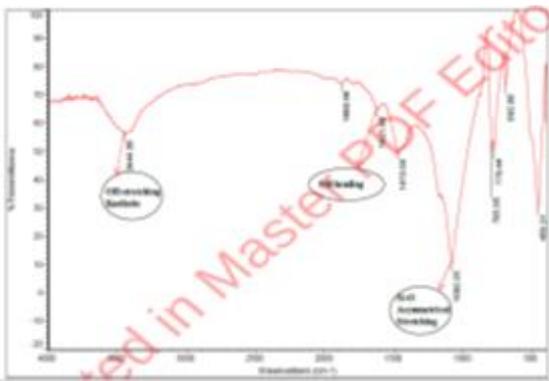
(c) N1



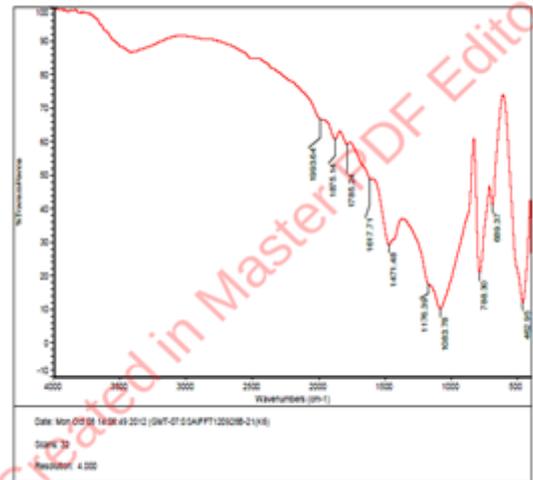
(d) K1



(b) U2

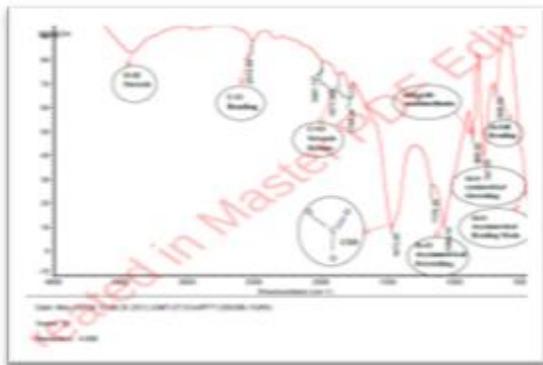


(e) C1

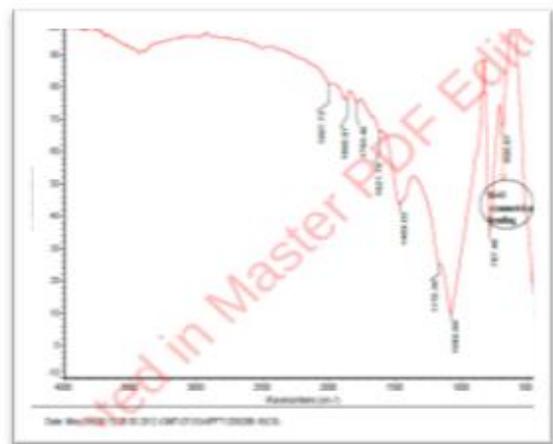


(c) N2

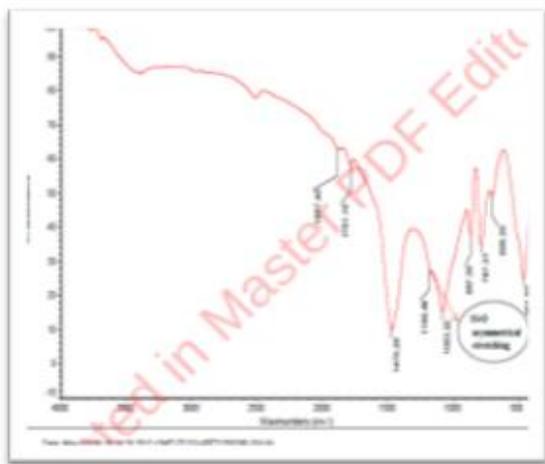
Figure 7: FT-IR graph showing the mineral distribution during pre-monsoon season at (a) Rajakkamangalam-R1 (b) Muttom-U1 (c) Chinnivilai -N1 (d) Kottilapdu-K1 (e) Colachel-C1.



(a) R2



(d) K2



(e) C2

Figure 8:FT-IR graph showing the mineral distribution during post monsoon season at (a) Rajakkamangalam – R2 (b) Muttom – U2 (c) Chinnavilai – N2 (d) Kottilapdu – K2 (e) Colachel-C2

Table 1: Characteristic peak intensities including assignments at sampling location during pre-monsoon

Sl.No	Frequencies	Intensities (pre Monsoon)					Assignments
		R1	U1	N1	K1	C1	
1.	3425-3445	WB	WB	WB	WB	MB	O-H Stretching
2.	2517-2520	W	W	W	-	-	C-O bending
3.	1750-1900	W	W	W	-	W	C=O Stretch
4.	1621	-	-	-	-	-	-
5.	1470-1475	SB	SS	SS	WB	MB	CO3
6.	1081-1085	S	SS	SS	SS	-	Si-O Asymmetrical Stretching
7.	800	S	MS	SS	SS	SS	Si-O symmetrical Stretching
8.	693	M	MS	w	W	W	Si-O symmetrical Bending
9.	459-463	SS	SS	SS	SS	SS	Si-O asymmetrical Bending

W=Weak; WB=Weak Broad; MB=Medium Broad; S=Strong; SS= Strong Sharp,MS=Medium Sharp

Table 2: Characteristic peak intensities including assignments at sampling location during post monsoon

Sl.No	Frequencies	Intensities (post Monsoon)					Assignments
		R2	U2	N2	K2	C2	
1.	3425-3445	MB	MB	W	W	W	O-H Stretching
2.	2517-2520	W	W	W	W	W	C-O bending
3.	1750-1900	W	W	W	W	W	C=O Stretch
4.	1621	-	W	W	W	-	O-H bending
5.	1470-1475	SS	W	W	MB	SS	CO3
6.	1081-1085	SS	SS	SB	SS	MB	Si-O Asymmetrical Stretching
7.	800	MS	SS	SS	SS	MS	Si-O symmetrical Stretching
8.	693	W	W	w	W	W	Si-O symmetrical Bending
9.	459-463	SS	SS	SS	SS	MS	Si-O asymmetrical Bending

W=Weak; WB=Weak Broad; MB=Medium Broad; S=Strong; SS= Strong Sharp,MS=Medium Sharp

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