



FTIR Spectroscopic Studies on Coastal Sediment Samples from Cuddalore District, Tamilnadu, India

S. Sivakumar¹, R.Ravisankar^{2*}, Y. Raghu³, A. Chandrasekaran⁴, J. Chandramohan⁵

¹Department of Physics, Arunai Engineering College, Tiruvannamalai-606603, Tamilnadu

²Post Graduate and Research Department of Physics, Government Arts College, Thiruvannamalai-606603, Tamilnadu, India

³Department of Physics, Aarupadaiveedu Institute of Technology, Paiyanoor-603 104, Chennai, Tamilnadu, India.

⁴Department of Physics, Global Institute of Engineering & Technology, Vellore-632509, Tamilnadu, India.

⁵Department of Physics, Mahabarathi Engineering College, Chinasalem-606201, Tamilnadu, India

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ABSTRACT

The coastal sediment collected in and around cuddalore district is subjected to mineral analysis. FTIR spectroscopic technique is applied to sediment samples to identify the constituent minerals. From the infra spectrum, the minerals are identified from the location or band position of peaks with the help of available literature. The minerals such as quartz, orthoclase, microcline, albite, kaolinite, montmorillonite, calcite, aragonite and organic carbon are identified. The performed analyses provided useful information about the mineralogical composition of the sediments. FT-IR spectroscopy seems to be useful method for the mineral analysis of coastal sediments.

Keywords: Coastal sediment, Mineral Analysis, FT-IR technique.

1. INTRODUCTION

Coastal sediments include beach, estuarine, aeolian and deltaic deposits. Sediment sources are from cliff erosion, platforms or submarine outcrops by wave action; biogenic sources such as shell and coral; and rivers, glaciers, waste disposal by man, and aeolian action. Coastal sediments are largely of marine origins at lower elevations, and of alluvial-colluvial-deltaic origin further inland. Coastal plains receive abundant rainfall and are therefore mostly acid, low in content of weather able minerals, and kaolinetic with some hydroxy interlayered vermiculite, except for the marine clays that are montmorillonitic. The sediments are low in content of iron having been subjected to reducing conditions at the time of deposition. Sediment, a naturally occurring material is broken down by processes of weathering and erosion, and is subsequently transported by the action of wind, water, or ice, and/or by the force of gravity acting on the particle itself. Sediments are most often transported by water (fluvial processes), wind (aeolian processes) and glaciers. Beach sands and river channel deposits are examples of fluvial transport and deposition, though sediment also changes in both crystalline and amorphous forms. Infrared spectroscopy utilization significantly in quantitative analysis of the minerals is less attempted. FTIR spectroscopy is a potential

often settles out of slow-moving or standing water in lakes and ocean dunes and loess are examples of aeolian transport and deposition. Glacial moraine deposits and till are ice-transported sediments.

The study area Cuddalore is most populated regions of Tamilnadu, India with intensive huge industrial activities and its effluents may be discharged for a long time into the river. Most of the industries and factories are situated on the banks of the river or very close to the river system. The study area presents a great interest because of the manufacturing unit, mini industries, chemical industries etc. Analysis of sediments provides environmentally significant information. Their chemical characterization is needed to understand the natural and anthropogenic influence on the bodies of water.

Infrared spectroscopy as an analytical tool presents a lot of advantages as it is accurate, inexpensive and reliable, the necessary sample amount is in the sub milligram range and sampling procedure is simple. As a major advantage, infrared spectroscopy permits the identification of the alternative method for acquiring quantitative mineralogy [1]. The main use is the identification of minerals and in structural studies. FTIR spectroscopy has recently been receiving attention

*Corresponding Author:

Email: ravisankarphysics@gmail.com

for its potential use in quantitative mineral analysis. In the present study, coastal sediments collected from cuddalore dist of Tamilnadu are subjected to mineral analysis using FTIR technique.

2. MATERIALS AND METHODS:

2.1. Sample Collection

Sediment samples were collected using Peterson grab at all the designated locations during low tide. The stations were oriented to get the fresh samples in and around cuddalore district. The samples collected from different sites under study were labeled as CTK, CDM, COT, CAP, CSP, CPT and CPI. The distance between each station falls around 7kms. At each sample site, covering a sampling area of 1m², five wet samples were collected, each weighing about one kilogram. Among these five samples from a site, four were from the corners and one from the center. The other one of the sediment samples was also collected from a depth of 5 cm from the surface. The samples were placed in plastic pouches and transported to the laboratory. The location map is given in Figure 1.

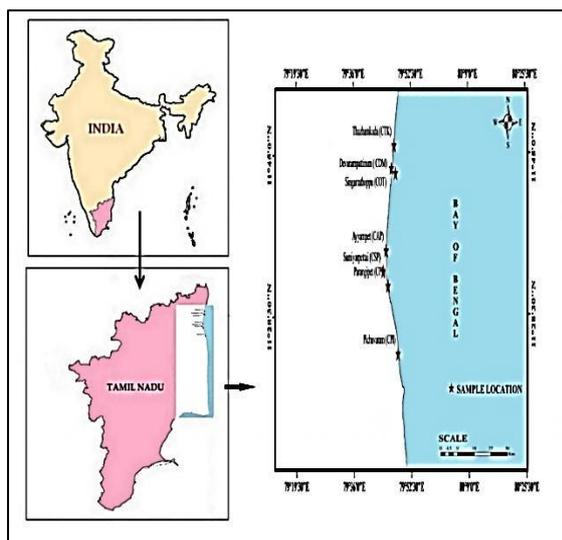


Figure1. Location Map.

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. Otherwise the broad spectral peak due to free OH will seriously affect the interpretation on the bound hydroxyls associated, with any of the minerals. 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. For each site, five to six samples were collected and for each sample five to six pellet specimens were prepared.

2.3. Sample analysis:

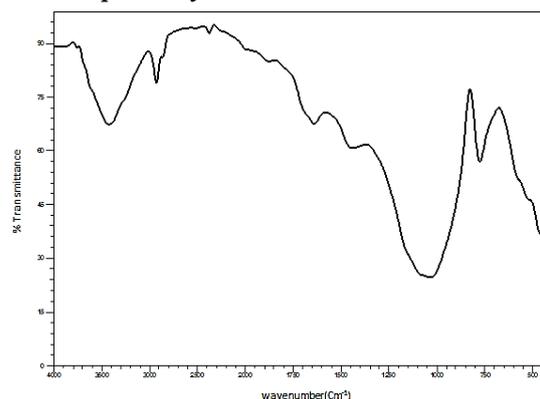


Figure 2. A typical FTIR spectrum of Coastal sediment samples of Cuddalore dist.

The Perkin Elmer FTIR spectrometer available in Department of Chemistry, Muthuramangam Government Arts College, Vellore; Tamilnadu, India is made use of in the present work for recording the FTIR spectra of the samples at room temperature. The KBr pellet technique (1:20) was followed for the mineral analysis. To provide a good characterization of a mineral by infrared spectroscopy, the spectrum should be recorded in the range of 4000-400 cm⁻¹. Such coverage of range ensures that most of the useful vibrations active in the infrared will be included. The instrument scans the spectra 16 times in 1 minute and the resolution is 5 cm⁻¹. This instrument is calibrated for its accuracy with the spectrum of a standard polystyrene film. Every time, before the spectrum of sample is obtained; the spectrum of the polystyrene film is taken and checked for the accuracy and transmittance. The best spectrum for each site was considered as a representative spectrum of the site. The typical FTIR spectrum is shown in Figure 2.

3. RESULTS AND DISCUSSION

Qualitative analyses are carried out to determine the major and minor constituent minerals present in the samples from the band position or location of the peaks from the prominent FTIR absorption peaks. The minerals are identified with the available literature. The positions of the observed

absorption bands in wave number units are summarized in Table-1 together with minerals.

(i). Quartz

Quartz is one of the commonest of all rock forming minerals and also most important constituent of the earth's crust. It is the second most abundant mineral in the earth's crust. Chemically it is silicon dioxide, SiO_2 . It occurs in crystals of the hexagonal shape commonly having the form of a six-sided prism terminating in a six-sided pyramid; the crystals are often distorted and twins are common. Quartz is a common constituent of granite, sandstone, limestone and many other igneous, sedimentary and metamorphic rocks.

The FTIR absorption peaks of quartz were reported by many workers [1-17]. It could be observed from the Table-1, the FTIR. absorption bands appearing at 455-460, 515-520, 695-700, 775-780, 795-800, 1080-1085, 1615-1620, & 1870-1875 cm^{-1} may suggested the presence of quartz in the samples.

The bending vibration at 700 cm^{-1} , symmetrical stretching vibration at 775 cm^{-1} and symmetrical stretching vibration 800 cm^{-1} are assigned. The pattern of absorption in quartz can be explained by ascribing the 455 cm^{-1} region (Si-O asymmetrical bending vibrations), the bands in the region 695 cm^{-1} (Si-O symmetrical bending vibrations), the bands in the region 775 cm^{-1} (Si-O symmetrical stretching vibrations) and 795 cm^{-1} (Si-O symmetrical stretching vibrations).

There is maximum of six to eight peaks are observed in any samples. The characteristic feature of quartz is doublet appearing at or around 800 cm^{-1} and 780 cm^{-1} . Such a clear observation of doublet was noticed in the samples (CTK, CDM & CPI) and any of these peaks was noticed in the samples (COT, CAP, CSP & CPT). The peak appearing at 695 cm^{-1} is most useful to determine nature of the mineral with regard to the structural stability. Many workers have calculated the crystallinity index of quartz using the symmetrical bending vibration of Si-O group obtained at 695 cm^{-1} . As 695 cm^{-1} is present in the spectra of all the samples indicate the quartz mineral in these samples are well in crystalline form. Band assignments for different minerals of coastal sediment samples of cuddalore district are given in Table 2.

(ii) Feldspar

Feldspar an abundant group of rock forming minerals, which constitute 60% of the earth's crust. Chemically the feldspar is silicates of aluminum contain sodium, potassium, iron, calcium or barium or combinations of these elements. Feldspar is found in association with all rock types including granite, gneiss, basalt and other crystalline rocks

and is essential constituents of the most igneous rocks.

From the table 1, the FTIR absorption peaks appearing at 405-410, 420-425, 425-430, 430-435, 460-465, 465-470, 535-540, 580-585, 585-590, 640-645, 645-650, 720-725, 740-745, 765-770, 785-790, 990-995, 1040-1045, 1050-1055 cm^{-1} was assigned to feldspar mineral. The peak pertaining to the range 535 cm^{-1} is due to Si-O. The feldspar group of minerals was analyzed by FTIR. technique and reported by many workers [1- 3, 6, 11, 14, 16-23]. The different types of feldspar minerals are given below.

(a) Microcline

The peaks at 425-430, 460-465, 535-540, 585-590, 640-645, 740-745, & 1050-1055 cm^{-1} indicate the presence of microcline.

(b) Orthoclase

Orthoclase was observed in the samples by the presence of peaks at 430-435, 465-470, 535-540, 580-585, 645-650, 765-770 & 1040-1045 cm^{-1} .

(c) Albite

The peaks at 405-410, 420-425, 720-725, 785-790, & 990-995 cm^{-1} are observed for albite.

(iii) Clay minerals

The presence of kaolinite, illite and montmorillonite indicate clay minerals in samples. Kaolinite is clay mineral crystallizing in the monoclinic system and forming the chief constituent of china clay and Kaolin. It is a hydrous aluminum silicate commonly formed by weathering and decomposition of rocks containing aluminum silicate compounds; feldspar is a chief source. Kaolinite is the basic raw material for ceramics and large quantities are also used in the manufacture of coated paper.

It could be observed from table-1, the FTIR absorption peaks appearing at 470-475, 915-920, 935-940, 1015-1020, 1030-1035, 1115-1120 & 3420-3425 cm^{-1} in the samples indicate kaolinite. Absorbance at 1030 cm^{-1} is attributed to Si-O stretching of clay minerals, The i.r. absorption peaks of kaolinite are reported by many workers [1,3,6,11-14,16-18,22,24-30].

Montmorillonite is a very soft phyllosilicate mineral that typically forms in microscopic crystals, forming clay. Montmorillonite, a member of the smectite family is 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. It is the main constituent of the volcanic ash weathering product, bentonite.

The FTIR absorption bands at 875-880, 1640-1645 and 3440-3445 cm^{-1} show the presence of montmorillonite in the samples [1,3,14]

Table 1. FTIR observed Frequencies (cm^{-1}) of Coastal sediment samples of Cuddalore District with mineral densifications.

S. No.	Location	Sample ID	Silicate Minerals	Feldspar			Clay Mineral		Organic carbon	Carbonate Minerals	
			Quartz	Microcline	Orthoclase	Albite	Kaolinite	Montmorillinite		Calcite	Aragonite
1	Thazhankuda	CTK	519,695,776, 797,1090, 1619,1875	427, 461, 535, 642	432, 580	405,420, 785,990	915,935, 1016,1030, 1116,3422	880, 1640	2850, 2925	1420	1790
2	Devanam pattinam	CDM	459,515,695,778,795, 1080,1616, 1875	1050	435, 470, 538, 583, 650, 765	720	935,3425	-	2850, 2920, 2930	875, 880, 1795	855
3	Singarathoppu	COT	457,515,695,780,1080, 1622,1875	462, 645, 742	-	787,990	3425	-	2855, 2925, 2930	1795	-
4	Ayyampet	CAP	455,695,779, 1080,1615, 1874	428, 462, 590, 640	-	785	471,3425	-	2855, 2925	-	1790
5	Samiyarpet	CSP	459,695,779, 1080,1620, 1875	460, 640	-	785	3425	-	2850, 2925	1795	1790
6	Parangipet	CPT	455,515, 695,778, 1080,1618, 1875	461, 640	467, 1040	422,785, 991	3425	3440	2855, 2915, 2926	-	1786
7	Pichavaram	CPI	457,515,695,777,795, 1080,1615, 1875	642	435, 467, 540, 581	420,785,993	-	3440	2850, 2925	1795	1785

Table 2. Band assignments for different minerals of coastal sediment samples of cuddalore district.

Minerals	Frequency (cm^{-1})	Tentative assignments	References
Quartz	459	Si - O asymmetrical bending vibration	[4. 15, 20]
	695	Si - O symmetrical bending vibration	
	780	Si - O symmetrical stretching vibration	
	797	Si - O symmetrical stretching vibration	
Feldspar	535	Si - O asymmetrical bending vibration	[4.15, 18. 20]
	642	Al - O - Co-ordination vibration	
Kaolinite	1030	Si-O Stretching O-H deformation	[6.16, 16]
	935		
Montmorillinite	3440	O-H Stretching of absorbed water molecule	[6. 16]
Calcite	875	Fe^{3+} (Al-OH)	[16]

17,19,25,31,32]. The band typically centred at 3400cm^{-1} is due to O-H stretching of water molecule present in the interlayer region of montmorillinite.

(iv) Carbonate Minerals

The carbonates consist of those minerals containing the anion $(\text{CO}_3)^{2-}$ and include calcite and aragonite (born calcium carbonate), dolomite (magnesium/calcium carbonate) and siderite (iron carbonate). Carbonates are commonly deposited in

marine settings when the shells of dead planktonic life settle and accumulate on the sea floor.

Carbonates are also found in evaporitic settings and also in Karsh regions, where the dissolution and reprecipitation of carbonates lead to the formation of caves, stalactites and stalagmites. The carbonate class also includes the nitrate and borate minerals.

Many workers have suggested that i.r absorption band appearing at 2982, 2519, 1433, 875 & 715 cm^{-1} is assigned to calcite [1,5,7-8,10-11,14-17,22,25,28,33-35].

From table 2.1, the i.r absorption bands at 875-880, 1420-1425 & 1795-1800 cm^{-1} are found to be calcite. Aragonite is identified in the samples by the FTIR. Absorption peaks at 855-860, 1785-1790 cm^{-1} [1,3,6,16-17,23,33,36-39].

(v) Organic Carbon:

From the spectra of all the samples in Table 2.1 a very weak absorption band present at 2850-2855 and 2925-2930 cm^{-1} may suggest the presence of organic carbon [17]. These bands are due to C-H absorption contaminants present in the samples.

3. CONCLUSION

FTIR spectroscopy seems to be a useful method for the mineral analysis of coastal sediments quartz, microcline, orthoclase, albite, kaolinite, montmorillonite, calcite, aragonite and organic carbon. Among these minerals quartz is considered as major mineral for its FTIR absorption peaks whereas feldspar is minor mineral. The accessory minerals are identified as kaolinite, montmorillonite, calcite and aragonite from the IR study. The performed analyses provided useful information about the mineralogical composition of the sediments. This is a fundamental step in gaining knowledge about the constituent of minerals. The FTIR approach with respect to the traditional one is tremendous due to preparation (no acidic dissolution is necessary), experimental procedure, cleanliness and simplicity and analysis time.

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*Biographical Sketch



*Dr. R. Ravisankar, did his B.Sc (Physics) in C. Abdul Hakeem College, Melvisharam, Vellore Dist, Tamilnadu, India and completed his M.Sc in Physics from Voorhees College, Vellore, Tamilnadu, India. He obtained his M.Phil and Ph.D degree from Annamalai University, Chidambaram, Tamilnadu, India. He has completed B.Ed and M.Ed degree from Madras and Annamalai University, respectively. He did his research work in Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam for his Ph.D programme. During his Ph.D programme, he was awarded the **Best paper Award** in Nuclear and Radio analytical Symposium (NUCAR) organized by Department of Atomic Energy for his research work in Instrumental Neutron Activation Analysis in the year 2003. He got the **Best Teacher Award** from Aruni Engineering College, Tiruvannamali, Tamilnadu during his teaching work in the institution. He got the **Best Researcher Award** from SSN College of Engineering, Chennai, Tamilnadu during his inspiring teaching with research in this institution. He is having teaching experience of more than nine years in college levels. His research area of interest is Radiation Physics, Environmental Physics, Spectroscopy and Material Science. Dr. Ravisankar is conducting research in the field of Radiation physics in collaboration with Indira Gandhi Centre for Atomic Research (IGCAR), kalpakkam, Tamilnadu since the year 2000. His research area of interest is Spectroscopy, Environmental Physics and Material Science. He has published more than 70 papers in National and International conferences. He has published more than 40 papers in peer reviewed journals for his credit in research career. He has guided more than ten students in obtaining M.Phil degree and currently guiding eight Ph.d scholars from various universities of Tamilnadu, India. At present he is working as Assistant Professor of Physics, Government Arts College, Tiruvannamali, Tamilnadu, India.*