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Mineral characterization of Coastal Sediments of East Coast of Tamilnadu, India using FT-IR Spectroscopy

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Abstract. The characterization of minerals in sediments collected from Pattipulam to Devanampattinam of East Coast of Tamilnadu, India was carried out using FT-IR spectroscopic technique. The minerals identification was done by using band position of IR absorption peaks from the available literatures. The minerals such as quartz, microcline, orthoclase, albite, kaolinite, montmorlinite, calcite, aragonite and organic carbon are identified. From the analysis. quartz was identified as major mineral and kaolinite, montmorlinite, calcite and aragonite accessory minerals from the presence of number of peaks. FT-IR spectroscopy was powerful tool for the mineral analysis of coastal sediments from the analysis.

Keywords: East Coast**,** Sediment, Minerals, FT-IR spectroscopy.

1.Introduction

Sediments are the principal carriers of the trace elements in the hydrosphere. Sediment particles are made up of derived from rock, soil, biological and anthropogenic inputs. The basic structural unit of inorganic sediment is silicate and aluminosilicate [1]. Sediment is an important reservoir of contamination and serves as the ultimate sink of elemental contaminants. Sediment quality is one of the factors that determine the environmental health of an aquatic system. The characteristic features of sediments depend on particle size distribution, porosity, organic matter percentage and sorption capacity of pollutants. The composition of sediments includes silicate minerals (quartz, and feldspar), iron oxide of hydroxides (gibbsite) and carbonate (calcite, aragonite, and dolomite) [2-4].

Minerals are crystalline elements or compounds that occur naturally in the earth. If a mineral contain sufficient quantity of metal which can be extracted profitably from it, it is known as ore minerals. Mineralogy is a fundamental part of a litho logical description but the analytical capabilities for accurate mineral analysis lag behind other parameters [5]. The mineral composition of lake, coastal and marine sediments is of broad interest because of its usefulness as an indicator of environmental change. The mineral analysis is the prominent area of research and It improves the economic growth of the country.

There are different methods for mineral analysis which include differential thermal analysis, X-ray powder - diffraction studies, ultraviolet-visible spectrometry, infrared spectrometry, etc. Fourier transform infrared (FT-IR) technique has the

greatest advantages over other techniques for its rapid, cheap and non destructive capabilities.

Fourier Transform Infrared Spectroscopy (FTIR) is a well established method for the characterization of mineralogical and geochemical properties of marine sediments. Fourier Transform Infrared Spectrophotometry (FTIR) spectra of minerals display characteristic features, usually absorption features, which can be related qualitatively to variations in the constituent minerals. Absorption features result from the detection of vibration modes, i.e. lattice vibrations and/or molecular group vibration modes. Qualitative mineral identification is possible because minerals have characteristic absorption bands in the midrange of the infrared, wave numbers 4000 to 400 cm^{-1}.

In the present study, a mineral analysis on coastal sediment samples collected from Pattipulam to Devanampattinam along the East Coast of Tamilnadu, India has been carried out using FT-IR technique. This coast is a densely populated area with variety of industrial activities and agriculture activities. So this research aims to investigate mineralogical composition of the coastal sediments using FT-IR spectroscopy.

2. Geomorphic and Environmental setting of the Study area

Sediment samples were collected along the Bay of Bengal coastline, from Pattipulam to Devanampattinam coast during pre-monsoon condition. The plain topography of the study area is predominant with thedeltaic and estuarine formation. The geomorphic future of sandy coastal area is characterized by several strand lines, lagoons, mangrove swamps, salt marshes, estuaries, creeks, barrier, dunes, spits and beach terraces. The beach sand comprises brown and reddish grey, silty clay and fine sands as inter distributary flood basins occupy it. The coastal environment is vital for nation's economy by the resources, productive habitats and rich biodiversity. Pitchavaram has well-developed mangrove ecosystem. Sand dunes, spits were also located in the study area. Coastal developments like urban agglomerations, industrialization (Cuddalore), Tourism (Mahabalipuram), Energy production unit (Madras power station at kalpakkam) were serving to the nation located in the study area. The coastal water gets polluted by many domestic and industrial discharges of assorted nature.

3. Materials and Methods

3.1. Samples Collection

Sediment samples were collected along the Bay of Bengal coastline, from Pattipulam to Devanampattinam coast during the pre-monsoon season. These samples were collected, when sediment texture and ecological conditions can be clearly observed, when erosional activities are predominant and sediments were not transported from the river and estuary towards the beach and marine. In order to ensure minimum disturbance of the upper layer, samples were collected by a Peterson grab sampler from 10 m water depth parallel to the shoreline. The grab sampler collects 10 cm thick bottom sediment layer from the seabed along all the 22 stations (Fig. 1). Sampling locations were selected to collect representative samples from the study area.

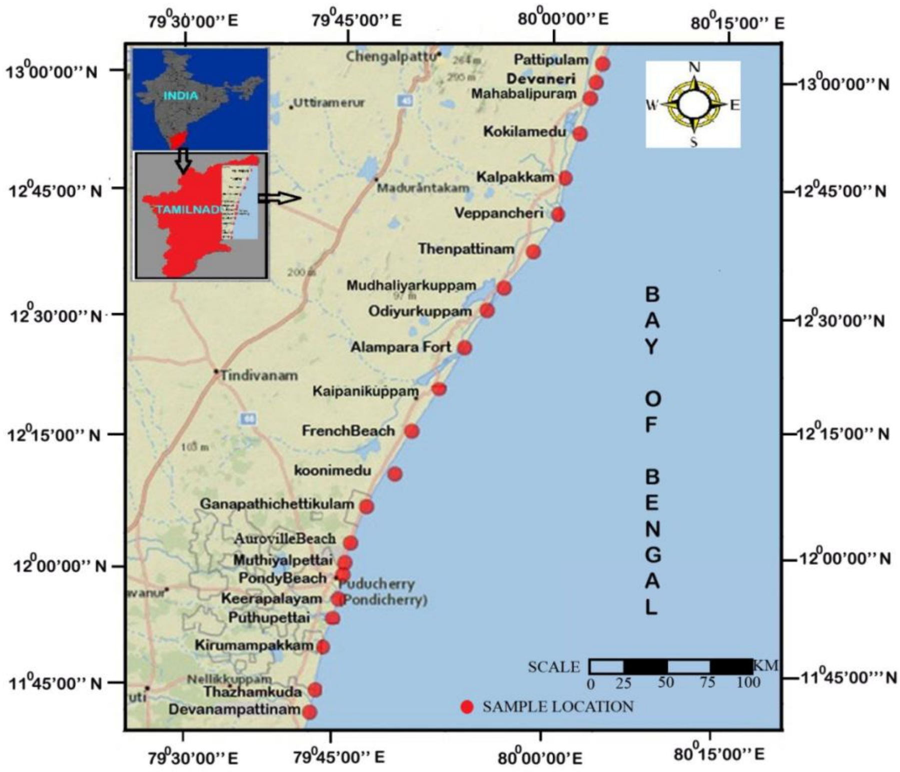

Figure (1) Location Map of the Study area

Table 1 represents the latitude and longitude for all the sampling locations in the study area. The sampling locations were selected based on the prevailing stress and included areas near the urban and domestic effluent discharge points. Uniform quantity (about 2 kg) of sediment samples were collected from all the sampling stations .Care was taken to ensure that the collected sediments were not in contact with the metallic dredge of the sampler, and the top sediment layer was scooped with an acid washed plastic spatula. Sediment samples were stored in refrigerated at -4ºC until analysis. Then pebbles, leaves and other foreign particles were removed. The samples were dried at 105°C for 2 hrs to obtain constant dry weight.

Table -1 Latitude and longitude of sampling Locations

Locations	Sample ID	Latitude (N)	Longitude (E)
Pattipulam	PPM	12°40'51.27"	80°15'19.35"
Devaneri	DVN	12°39'19.32"	80°14'49.68"
Mahabalipuram	MAM	12°37'55.53"	80°14'13.14"
Kokilamedu	KKM	12°34'56.33"	80°13'22.37"
Kalpakkam	KPM	12°30'57.52"	80°11'50.57"
Veppancheri	VPC	12°27'58.97"	80°11'16.29"
Thenpattinam	TPM	12°24'42.28"	80° 9'48.29"
Mudaliyarkuppam	MKM	12°21'26.51"	80° 6'52.67"
Odiyurkuppam	OKM	12°19'35.89"	80° 5'44.70"
Alampara fort	APT	12°16'19.80"	80° 3'16.00"
Kaipanikuppam	KPK	12°12'42.65"	80° 1'32.40"
French beach	FBH	12° 9'2.75"	79°59'11.44"
Koonimedu	KMU	12° 4'59.37"	79°55'53.55"
Ganapathichettikulam	GCM	12° 2'45.84"	79°56'46.86"
Auroville beach	ABH	11°59'51.98"	79°55'31.39"
Muthiyalpet	MPT	11°57'43.22"	79°52'42.65"
Pondy beach	PBH	11°56'38.16"	79°52'17.45"
Keerapalayam	KEP	11°54'23.61"	79°51'49.37"
Puthupettai	PPT	11°52'45.44"	79°51'19.75"
Kirumampakkam	KIP	11°50'23.50"	79°51'54.44"
Thazhankuda	TKA	11°46'28.21"	79°49'31.03"
Devanampattinam	DPM	11°44'41.37"	79°49'23.01"

3.2. Sample Preparation

The dried samples were subjected to grain size separation by dry sieving though ASTM mesh sieve. The samples were sieved into 200µm for homogenization of the samples. Separated grains were ground well by dry grinding with agate mortar and then dried in a hot air oven at 110°C to remove moisture content. A pellet of 1mm in thickness and 13 mm in diameter is prepared. 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 [6].

3.3. Fourier-transformed infrared spectroscopy

The KBr pellet technique was followed by mineral analysis. A sample of 2 mg is mixed with 40 mg of spectroscopic KBr in the ratio 1:20 using a mortar and pestle. Before mixing, the necessary amount of KBr powder is dried at 120°C for 6 hours in an oven. Otherwise the broad spectral peak due to free OH will seriously affect the interpretation of the bound hydroxyls associated, with any of the minerals. The major and minor minerals are qualitatively determined by FT-IR technique. For each sample five to six pellet specimens are prepared and the spectra were taken in the mid region of 4000-400cm^{-1}. The instrument scans the spectra 16 times in 1 min and the resolution is ±5cm^{-1}. A typical FT-IR spectrum is shown in Fig-2.

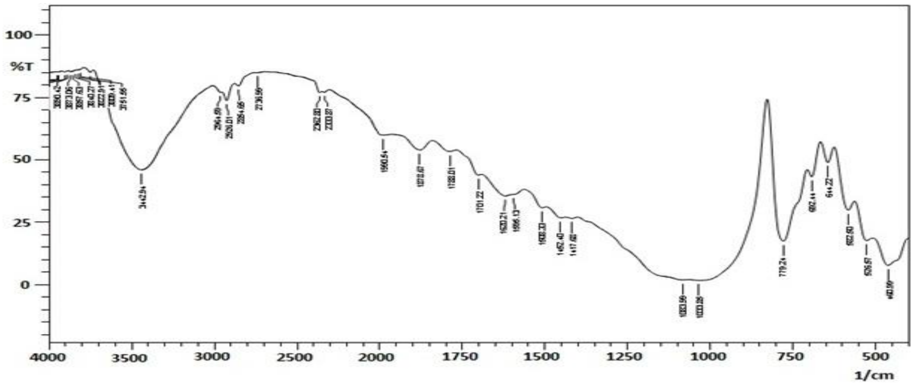

Figure (2) A typical FT-IR spectrum of coastal Sediment sample

4. Results and Discussions

The observed wave number unit (cm^{-1}) from all spectra is given in table-2 along with their corresponding minerals. By comparing the observed frequencies with the available literature, the minerals identified are quartz, microcline, orthoclase, albite, Kaolinite, montmorlinite, calcite and aragonite [1-4,6-12].The mineral wise discussion is as follows.

4.1. Quartz

Quartz is a silicate mineral and its chemical formula is SiO_2. Quartz forms the major constituent of metamorphic, sedimentary, granite, limestone, etc. In the present study, it is confirmed that the most dominant of all the minerals present is quartz from the appearance of IR absorption bands in Table 2. Many workers reported the IR absorption peaks of quartz using FT-IR study [1,3-4,6,13-16].The presence of IR absorption bands at 1870-1875, 1615-1620, 1080-1085, 795-800,775-780,695-700, 515-520 & 455-460 cm^{-1}indicate quartz in the samples and it is reported in Table 2.The band assignments of different minerals in coastal sediment samples are given in Table 3.

Quartz is identified with reference to Si–O bonds and this Si–O bond is stronger in silicate minerals. The Si–O bond in the region 900–1100 cm^{-1} is due to stretching mode and in the range 400–800 cm^{-1} is due to bending mode is widely used for quartz identifications. The pattern of absorption band inquartz can be explained by ascribing the 455cm^{-1}region(Si-O asymmetrical bending vibrations), the band in the region 695cm^{-1}(Si-O symmetrical bending vibrations),the bands in the region 775cm^{-1}(Si-O symmetrical stretching vibrations) and 795cm^{-1}(Si-O symmetrical stretching vibrations).

Minimum three to six peaks of quartz are observed in all samples. The characteristic feature of quartz is doublet appearing at or around 800 cm^{-1}and 780cm^{-1}. Such a clear observation of doublet was noticed in the samples (PPM,MAM, KPM, VPC, MKM, OKM, KMU, ABH, PBH, KIP, &DPM) and any of these peaks was noticedin remaining samples(DVN, KKM, TPM, APT, KPK, FBH, GCM, MPT, KEP, PPT& TKA). Any slight shift in the peak may be due to impurities, crystal defects or isomorphous substitutions [17]. The absence of peak at 780cm^{-1} in samples may be very weak. The peak appearing at 695 cm^{-1} is most useful to determine in crystalline form. The crystallinity of quartz may give a clear indication on the crystalline forms of other minerals. The 695 cm^{-1} is present in most of the samples indicate that quartz mineral are well in crystalline form [1].

4.2. Feldspar

Feldspar is the name given to a group of minerals distinguished by the presence of alumina and silica (SiO_2) in their chemistry. This group includes aluminum silicates of soda, potassium, or lime. It is the single most abundant mineral group on Earth. They account for an estimated 60% of exposed rocks, as well as soils, clays, and other unconsolidated sediments, and are principal components in rock classification schemes. The minerals included in this group are the orthoclase, microcline and plagioclase feldspars. The general formula for feldspar can be given as WZ_4O_8 in which W may be a Na, K, Ca, and/or Al. Chemically the feldspar is silicates of aluminum containing sodium, potassium, iron, calcium or barium or combinations of these elements. The feldspar group of minerals was analyzed by FT-IR technique and reported by many workers [14-16, 18-22]. From the Table 2, the i.r. absorption peaks appearing at 405-410, 420-425, 425-430, 430-435, 460-465, 465-470, 535-540, 575-580, 580-585, 585-590, 640-645, 645-650, 720-725, 740-745, 765-770, 785-790, 990-995, 1010-1015, 1040-1045 & 1050-1055cm^{-1} was assigned to feldspar mineral. The peaks appearing at 465-470cm^{-1}, 535-540cm^{-1}& 640-645 belong to Si-O-Si bending, Si-O asymmetrical bending vibration and Al-O coordination vibration respectively.

4.2.1. Microcline

The presence of microcline is identified by the peaks at 425-430, 460-465, 535-540, 585-590, 645-650, 740-745 and 1050-1055 cm^{-1}. The spectra of microclines present a band at about 536-538 cm-1 which is attributed to the coupling between the O-Si-O bending vibration and the K-O stretching vibration and it is shifted to lower wave numbers than the bands in orthoclase and sanidine attributed to the same vibrations [23-24]. An inverse behavior presents the band that is appeared at about 646-648 cm-1 in the spectra of microclines. This band is attributed to the OSi(Al)-O bending vibrations and is shifted to higher wavenumbers than the bands attributed to the same vibrations in the spectra of orthoclases and sanidines [23-24]

4.2.2. Orthoclase

The peaks at 430-435, 465-470, 540-545, 580-585, 640-645,765-770, 1010-1015 and 1040-1045cm^{-1}areobserved for Orthoclase in all the samples. The peak appearing at 540-545 is attributed to coupling between the O-Si-O bending vibration and the K-O stretching vibration (Iiishi et al., 1971; Matteson and Herron, 1993). The presence of the band at640-645 attributed to the O-Si(Al)-O bending vibrations (23-24).

4.2.3. Albite

The observed peaks of albite are 405-410, 420-425, 575-580, 720-725, 785-790 and 990-995cm^{-1}.

4.3. Clay Minerals

Kaolinite is a mineral with a chemical composition $Al_2Si_2O_5$. It is layered silicate mineral, with one tetrahedral sheet linked through oxygen molecules to one octahedral sheet of alumina octahedral. Kaolinite mineral is crystallizing in the monoclinic system and forming the chief constituent of china clay and Kaolin. It is softly, earthy, usually white mineral, produced by weathering of feldspars.

The IR absorption peaks of kaolinite are reported by many workers[25-29].The observed peaks at 470-475, 935-940, 1030-1035, 1115-1120 and 3420-3425 cm^{-1} are attributed to kaolinite. The broad absorption band observed at 1030 cm^{-1} belongs to Si–O stretching of kaolinite (clay mineral) [18-19].

Montmorillonite is a very soft phyllosilicate mineral. Chemically it hydrated sodium calcium aluminium magnesium silicate hydroxide $(Na.Ca)x\ (AlMg)_2\ (Si_4O_{10})\ (OH)_2.nH_2O$.The observed i.r absorption bands at 475-480, 825-830,1640-1645 and 3440-3445 cm^{-1} in the spectrum of the samples suggested the presence of montmorilinite in the samples [1,6,18-19,25-29].The band typically centered at 3400cm^{-1} is due to O-H stretching of water molecule present in the interlayer region of montmorillonite. The strong peak observed at 1635 cm^{-1} in the samples suggests the possibility of water of hydration in the adsorbent.

4.4. Carbonate Minerals

Carbonates are commonly deposited in marine settings. This class also includes the nitrate and borate minerals. Many workers have reported that i.r absorption band appearing at 2982, 2519, 1795, 1410, 1433, 875 and 715cm^{-1} is assigned to calcite [1,3,7,9,12,14-16,18-19]. The calcite shows the i.r. absorption bands appearing at 2515-2520, 1790-1795, 1415-1420, 875-880-cm^{-1}& 710-715cm^{-1} in the samples. From Table 2, the IR absorption bands at 855-860, 1455-1460, 1475-1480 and 1785-1790cm^{-1} are found to be aragonite [1,4,6-7,11-12,18-19].

4.5. Organic Carbon

The absorption bands present at 2925-2930 and 2850-2855 cm^{-1} suggest the presence of organic carbon in the samples [15-16, 21]. These bands are due to C-H absorption of contaminants present in the samples and this band belongs to carbon and oxygen double bonded linkage (C=O).

Table (3).Band assignments for different minerals

Minerals	**Frequency (cm^{-1})**	**Tentative assignments**	**References**
Quartz	459	Si - O asymmetrical bending vibration	[1,6,13,16,20]
	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	[3,18-20]
	642	Al - O - Co-ordination vibration	
Kaolinte	1030	Si-O Stretching	[25-27]
	935	O-H deformation	
Montmorlinite	3440	O-H Stretching of absorbed water molecule	[6,14,20]
Calcite	875	Fe^{3+} (Al-OH)	[14-16]

Table (2).FT-IR observed absorption bands (cm^{-1}) of sediment samples of East Coast of Tamilnadu

Locations	Sample ID	Silicate Mineral	Feldspar Minerals			Clay Minerals		Organic arbon	Carbonate Minerals	
		Quartz	Microcline	Orthoclase	Albite	Kaolinte	Montmorlinite		Calcite	Aragonite
Pattipulam	PPM	459, 695, 778, 795, 1616, 1875	425, 460, 535, 740	432, 765	405, 725, 990	471, 935, 1030, 3420	480, 1640	2854, 2926	715, 1414, 1795	855, 1475
Devaneri	DVN	455, 695, 780 1875	427, 585, 645	765, 1010	787, 990	471, 1030, 3425	1640, 3440	2850, 2930	715, 1420	1460, 1790
Mahabalipuram	MAM	455, 695, 775,798, 1616, 1875	464, 535, 645, 740	469	405, 425,720	1030, 3425,	480,1640, 3440	2851, 2925	715, 878, 2515	856, 1788
Kokilamedu	KKM	457, 695, 775, 1082, 1875	428, 464, 535, 742	434, 1040	425, 579, 787, 995	939, 1030, 3425	480, 3440	2854, 2929	875, 1795	1476, 1790
Kalpakkam	KPM	458, 697, 779,795, 1873	428, 535, 640, 745	430, 1010	405, 575,725	475, 1030, 3420	1643, 3445	2851, 2925	1412, 1795	1785
Veppancheri	VPC	455, 775, 795, 1080, 1875	463, 587, 1051	465	425, 578, 990	475, 935	1645, 3440	2857	715, 1416	855
Thenpattinam	TPM	458, 695, 776, 1616, 1873	462	435, 467, 581	405, 725, 993	920, 1035, 3425	480, 826	2855, 2930	715, 875, 2515	1460,1789

Locations	Sample ID	Silicate Mineral	Feldspar Minerals			Clay Minerals		Organic arbon	Carbonate Minerals	
		Quartz	Microcline	Orthoclase	Albite	Kaolinte	Montmorlinite		Calcite	Aragonite
Mudaliyarkuppam	MKM	515, 695, 775, 795	428, 590, 743	765	575, 785, 1095	475, 1030, 3425	478, 1640	2852, 2925	715, 1417, 1798	855, 1785
Odiyurkuppam	OKM	457, 780, 796, 1085	426, 745	1040	405, 420, 990	475, 935, 3425	1640, 3440	2929	875, 1418	1480, 1790
AlamparaFort	APT	455, 698, 1620, 1875	535,1615	469, 765	405,578, 995	427, 1030, 3425	476, 1643, 3445	2855, 2926	715, 1795	855, 1785
Kaipanikuppam	KPK	455, 695, 775, 1080, 1875	463, 587,	434, 466, 582	405, 420, 575	935, 1120, 3425	480, 825	2854, 2926	715, 1420, 2515	855, 1460, 1790
French beach	FBH	456, 780, 1080, 1615, 1875,	425, 586	536, 765	408,422,787, 990	472, 1035 3420	825,1640, 3440	2855, 2926	715, 1415, 1795	855
Koonimedu	KMU	458,780, 795 1160,1875	426,535,740	-	420.575,1090	473, 1030	480, 825, 3440	2855	715,1795	-
Ganapathichettikulam	GCM	458,515,695, 775	465,586, 1055	435,470	422,785	471, 1120, 3425	1640, 3440	2855	875, 1795, 2515	1480. 1789
Auroville beach	ABH	455, 775, 798, 1615, 1875	430, 535, 740	435, 645	405, 579, 725,	475, 938, 1033, 3420	480, 826, 1640, 3440	2855, 2926	715, 1412, 1795,	1476

Locations	Sample ID	Silicate Mineral	Feldspar Minerals			Clay Minerals		Organic arbon	Carbonate Minerals	
		Quartz	Microcline	Orthoclase	Albite	Kaolinte	Montmorlinite		Calcite	Aragonite
Muthiyalpet	MPT	515, 780, 1615, 1875	465, 740	1010	425, 788, 995	935, 1030, 3425	480, 825	2926	715,1420	855, 1475
Pondy beach	PBH	455, 695, 780, 795, 1616, 1875	430, 535	465, 536, 1011	405, 423, 575	475, 935, 1120	480, 1640	2855, 2926	715, 2515	855
Keerapalayam	KEP	455, 776, 1615	462, 535, 745	434,765	425, 585, 990	915, 1033, 3420	1640, 3433	2855	-	-
Puthupettai	PPT	455, 515, 697, 1870	535, 586	465, 540	405, 722, 993	471, 1030, 3425	825, 1640	2855, 2926	715, 875, 1795	855, 2515
Kirumampakkam	KIP	455, 775, 795, 1615	428,465	540, 1040	425, 579, 785	935, 1035, 3425	480, 825	2855	717, 878	855, 1790
Thazhankuda	TKA	455, 695, 797, 1090, 1875	427,461, 585	432, 645	405, 425, 990	475, 935, 1115,3420	475, 826,1640	2855, 2926	715, 1420, 1795	1475, 1790
Devanampattinam	DPM	459,520,695,778,795, 1616	425, 461, 740	435,470, 650	405, 583. 720, 990	471, 935, 1030, 3425	480,825, 1640, 3440	2855, 2926	715, 1420	855

5. Conclusion

FT-IR spectroscopic technique was used to identify the constituent of minerals present in coastal sediments. FTIR study revealed the presence of quartz, microcline feldspar, orthoclase feldspar, kaolinite, montmorillonite, calcite, aragonite and organic carbon in sediments. Among the studied minerals, quartz, feldspar and kaolinite are major and calcite and aragonite is trace on the basis of their presence and intensities of corresponding peaks in the samples. The performed analyses provided useful information about the mineralogical composition of the sediments.

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