FT-IR Spectroscopic Studies on Coastal Sediment Samples from Nagapattinum District, Tamilnadu, India

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Authors’ contributions

This work was carried out in collaboration between all authors. Author RR designed the study, wrote the protocol, and wrote the first draft of the manuscript. Author SS managed the literature searches, analyses of the study performed the spectroscopy analysis and AC managed the technical process and JPPJ involved the geological guidance and aspects. All authors read and approved the final manuscript.

ABSTRACT

The mineralogical characterization was carried out to determine the major and minor constituents minerals present in the coastal sediment collected in and around Nagapattinum district Tamilnadu, India by FT-IR spectroscopy. The minerals were identified with the help of available literature from the IR absorption band or location of different peaks. The identified minerals are quartz, orthoclase, microcline, albite, kaolinite, montmorillonite, calcite, aragonite and organic carbon. This result shows that FT-IR is a promising technique for identifying and quantifying the mineral analysis.

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1. INTRODUCTION

Sediments are produced through weathering and erosion of rocks, are transported to the coast by winds and rivers, and finally deposited on beaches by the action of waves and currents. The composition of mineral assemblages is then related to the mineralogical composition of the source region, and also to several other processes during the sedimentation cycle, such as physical sorting, mechanical abrasion and dissolution. By analyzing sediments, it is possible to determine the provenance, distribution and also the possible hazards of contamination. Marine sediments preserve useful information for reconstructing oceanographic conditions and environmental changes in the past [1,2,3,4,5]. Coastal sediments usually act as sinks of river borne metals released through weathering and human activities in terrestrial environments [1,2,3].

The mineral analysis gives prompt area of research and gives an important tool in economic scale also. There are number methods are used to identify the minerals by the conventional techniques such thin section analysis, X-ray diffraction (XRD) and FT-IR spectroscopy. Among these techniques, FT-IR is screening tool for its accurate, inexpensive invariance, rapid, time consuming and sampling procedure is simple. It is also acts as finger print technique in mineral identification. Many workers applied the FT-IR spectroscopy for the mineral identification [1-7]. The present work deals the mineral analysis of the coastal sediment using IR spectroscopy.

The study area is chosen for the present work is Nagapattinum district (Fig. 1) which is covering a distance of 120 Kms from Kodiyampalayam to Kodiyakarai of Tamilnadu coast. This coastal place is catching center of fishery activities in Tamilnadu and also plays a major role in marine commodities. Numerous industries, chemical factories and aquaculture farms are also developing along this coast and it makes much attention for present and future research. In the present study, an attempt has been made to determine the constituent of minerals in the coastal sediments collected from Nagapattinum district of Tamilnadu using the potential tool of FT-IR spectroscopy.

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 Nagapattinum district. The samples collected from different sites under study were labeled as KDM, NPZ, NSI, NPB, TRGB, NGR, NAP, VLK, TPI, VKT, VED and KODI. The distance between each station falls around 10kms. At each sample site, covering a sampling area of $1m^2$, 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 which is close to sample site. The samples were placed in plastic pouches and transported to the laboratory. The location map is given in Fig. 1.
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 glass container which is free from the moisture 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

The Perkin Elmer FT-IR spectrometer available in Department of Chemistry, Muthurangam Government Arts College, Vellore; Tamilnadu, India for recording the IR 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 IR spectroscopy, the spectrum
should be recorded in the range of 4000–400 cm$^{-1}$. Such coverage range ensures that most of the useful vibrations active in the IR 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 FT-IR spectrum is shown in Fig. 2.

![FT-IR spectrum](image)

**Fig. 2. A representative FT-IR spectrum of coastal sediment samples from Nagapattinam district**

3. RESULTS AND DISCUSSION

The absorption frequencies of the peaks in the spectra of each site in wave number unit (cm$^{-1}$) are reported in Table 1. By comparing the observed frequencies with available literature [23-30], the minerals such as quartz, orthoclase, albite, Kaolinite and montmorlinite have been identified. The Mineral wise discussion is outlined is given below.

3.1 Quartz

Quartz is a silicate mineral. It forms most abundant mineral in the Earth’s crust. It is present in many sediments as well as sedimentary and igneous rocks. 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 often distorted and twins are common. It occurs in hydrothermal veins and pegmatite. The IR absorption peaks of quartz were reported by many workers [1-17]. 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 all samples and it is presented in Table 1. The bending vibration at 700cm$^{-1}$, symmetrical stretching vibration at 775cm$^{-1}$ and symmetrical stretching vibration 800cm$^{-1}$ are assigned. The band ascribing at 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 775 cm\(^{-1}\) (Si-O symmetrical stretching vibrations) and 795 cm\(^{-1}\) (Si-O symmetrical stretching vibrations).

For any samples, minimum three to maximum five peaks are observed. 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 NAP and any of these peaks was noticed in the remaining samples. 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\(^{-1}\). The peaks at 695 cm\(^{-1}\) indicate crystalline form of quartz in the samples. Band assignments for different minerals of coastal sediment samples of Nagapattinam District are given in Table 2.

3.2 Feldspar

Feldspar is an abundant of rock minerals, which constitute 60% of the earth’s crust. 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. Feldspar is found in association with all rock types including granite, gneiss, basalt and other crystalline rocks and constituents of the most igneous rocks. It crystallize from magma in both intrusive and extrusive rocks; they occur as compact minerals, as veins, and are also present in many types of metamorphic rock. They are also found in many types of sedimentary rocks. Feldspar weather to yield a large part of clay found in soils.

From the Table 1 the IR absorption peaks appearing at 1050-1055, 1040-1045, 990-995, 785-790, 765-770, 740-745, 720-725, 645-650, 640-645, 585-590, 580-585, 535-540, 465-470, 460-465, 430-435, 425-430, 420-425, 405-410 cm\(^{-1}\) were assigned to feldspar mineral. The peak appearing around 535 cm\(^{-1}\) is due to Si-O asymmetrical bending vibrations and the other peak around at 642 cm\(^{-1}\) is due to Al-O-coordination vibrations. The feldspar group of minerals was analyzed by FT-IR technique and reported by many workers [1,2,3,6,14-23]. The different types of feldspar minerals are given below.

(a) Microcline

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

(b) Orthoclase

The peaks at 1040-1045, 765-770, 645-650, 580-585, 535-540, 465-470 & 430-435 cm\(^{-1}\) are observed for Orthoclase in the Samples.

(c) Albite

The observed peaks of Albite are 990-995, 785-790, 720-725, 420-425, 405-410 cm\(^{-1}\).
<table>
<thead>
<tr>
<th></th>
<th>Location</th>
<th>Sample ID</th>
<th>Silicate Minerals</th>
<th>Feldspar</th>
<th>Clay Mineral</th>
<th>Organic carbon</th>
<th>Carbonate Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Kodiyam pallayam</td>
<td>KDM</td>
<td>455,700,780,1875</td>
<td>426, 1060, 1011</td>
<td>77, 787, 993</td>
<td>3425</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>Pazhayar</td>
<td>PZR</td>
<td>695,775, 1095,1875</td>
<td>644, 434, 740</td>
<td>525</td>
<td>935,3425</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>Sirkazhi</td>
<td>NSI</td>
<td>695,780, 1125,1875</td>
<td>428, 469, 534</td>
<td>790,995</td>
<td>939</td>
<td>3443</td>
</tr>
<tr>
<td>4.</td>
<td>Poombukar</td>
<td>NPB</td>
<td>696,780, 1092,1160, 1875</td>
<td>532</td>
<td>990</td>
<td>1030</td>
<td>3441</td>
</tr>
<tr>
<td>5.</td>
<td>Tharan gambadi Nagore</td>
<td>TRGB</td>
<td>455,780, 1875</td>
<td>530, 648</td>
<td>787,993</td>
<td>920,3425</td>
<td>-</td>
</tr>
<tr>
<td>6.</td>
<td>Vettai Karan Thoppu</td>
<td>VED</td>
<td>457,698, 1095,1160, 1875</td>
<td>426, 532, 640, 1051</td>
<td>525,785,990</td>
<td>939</td>
<td>3440</td>
</tr>
<tr>
<td>7.</td>
<td>Akkarai pettai</td>
<td>NAP</td>
<td>455,695,780, 795,1875,</td>
<td>586, 642, 1126</td>
<td>467, 922</td>
<td>1645, 3445</td>
<td>-</td>
</tr>
<tr>
<td>8.</td>
<td>Velan kanni</td>
<td>VLK</td>
<td>517,695,780, 1615,1875</td>
<td>530, 640, 1144</td>
<td>-</td>
<td>422,577</td>
<td>920,3422</td>
</tr>
<tr>
<td>9.</td>
<td>Thiru poondi</td>
<td>TPI</td>
<td>515,695,775, 1616,1875</td>
<td>534, 640, 1055</td>
<td>-</td>
<td>790,995,1095</td>
<td>940</td>
</tr>
<tr>
<td>10.</td>
<td>Vettai Karan Thoppu</td>
<td>VKT</td>
<td>695,780, 1165,1620, 1875</td>
<td>532, 640, 1055</td>
<td>990</td>
<td>940,3425</td>
<td>478</td>
</tr>
<tr>
<td>11.</td>
<td>Vedaraniurr</td>
<td>VED</td>
<td>457,698, 1095,1160, 1875</td>
<td>426, 532, 640, 1051</td>
<td>525,785,990</td>
<td>939</td>
<td>3440</td>
</tr>
</tbody>
</table>

Table 1. FT-IR observed frequencies (cm\(^{-1}\)) of coastal sediment samples of Nagapattinum district with mineral identifications
Table 2. Band assignments of minerals

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Frequency</th>
<th>Tentative Assignments</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>455</td>
<td>Si-O asymmetrical bending vibration</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>515</td>
<td>Si-O asymmetrical bending vibration</td>
<td></td>
</tr>
<tr>
<td></td>
<td>695</td>
<td>Si-O symmetrical bending vibration</td>
<td></td>
</tr>
<tr>
<td></td>
<td>775</td>
<td>Si-O symmetrical stretching vibration</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>795</td>
<td>Si-O symmetrical stretching vibration</td>
<td></td>
</tr>
<tr>
<td>Feldspar</td>
<td>420</td>
<td>Si-O bending vibrations</td>
<td>[1],[2]</td>
</tr>
<tr>
<td></td>
<td>430</td>
<td>Si-O bending vibrations</td>
<td>[1],[2]</td>
</tr>
<tr>
<td></td>
<td>535</td>
<td>Si-O asymmetrical bending vibration</td>
<td>[11],[19]</td>
</tr>
<tr>
<td></td>
<td>585</td>
<td>O-Si(Al)-O bending vibrations</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>645</td>
<td>Al-O- Co-ordination vibrations</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1040</td>
<td>Si-O asymmetrical stretching vibration</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1120</td>
<td>Si-O asymmetrical stretching vibration</td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>935</td>
<td>O-H deformation</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>1020</td>
<td>Si-O symmetrical stretching vibration</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>1030</td>
<td>Si-O stretching</td>
<td>[7]</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>3440</td>
<td>O-H stretching of absorbed water molecule</td>
<td>[15],[16]</td>
</tr>
<tr>
<td>Calcite</td>
<td>875</td>
<td>Fe$^{3+}$ (Al-OH)</td>
<td>[16]</td>
</tr>
</tbody>
</table>
3.3 Clay Minerals

The presence of kaolinite, illite and montmorillonite indicate clay minerals in samples. Kaolinite is a mineral with a chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. It is layered silicate mineral, with one tetrahedral sheet linked through oxygen molecules to one octahedral sheet of alumina octahedral. 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. 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.

The IR absorption bands appearing at 3420-3425, 1115-1120, 1030-1035, 1015-1020, 935-940, 915-920 & 470-475 cm$^{-1}$ in the samples indicate kaolinite. Absorbance in 1030 cm$^{-1}$ is attributed to Si-O stretching of clay minerals. The IR absorption peaks of kaolinite are reported by many workers [1,3,6,12-30].

Montmorillonite is a very soft phyllosilicate mineral that typically forms in microscopic crystals, forming clay. Chemically it hydrated sodium calcium aluminium magnesium silicate hydroxide ($\text{Na, Ca}_x(\text{Al, Mg})_2\text{Si}_4\text{O}_{10}\text{(OH)}_2$) $n\text{H}_2\text{O}$. 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 bands appearing at 875-880, 1640-1645 and 3440-3445 cm$^{-1}$ show the presence of montmorillonite in the samples [1,3,14-32]. The band typically centered at 3400 cm$^{-1}$ is due to O-H stretching of water molecule present in the interlayer region of montmorillonite.

3.4 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 also found in evaporatic settings and also in karst regions, where the dissolution and reprecipitation of carbonates lead to the formation of caves, stalactites and stalagmites. This class also includes the nitrate and borate minerals.

Many workers have suggested that IR absorption band appearing at 2982, 2519, 1433, 875 & 715 cm$^{-1}$ is assigned to calcite [1,4,5,6,7,8,10,14-35].

From Table 1, the IR absorption bands at 875-880, 1420-1425 & 1795-1800 cm$^{-1}$ are found to be calcite. Aragonite is identified in the samples by the IR absorption peaks at 1785-1790, 855-860 cm$^{-1}$ [1,3,15-17,23,33-39].

3.5 Organic Carbon

From the spectra of all the samples in Table 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 of contaminants present in the samples.
4. CONCLUSION

FT-IR spectroscopic analysis performed on the coastal sediment samples taken from the different locations of Nagapattinum district Tamilnadu, India allowed to identify the constituents of minerals. The results revealed quartz and feldspars as the major components while the content of clay minerals was rather low. This FT-IR technique was highly useful in identifying different minerals in sediment. The FT-IR 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. The future work plans to confirm the minerals by X-ray diffraction.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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