FT-IR SPECTROSCOPIC STUDIES ON COASTAL
SEDIMENT SAMPLES FROM NAGAPATTINUM
DISTRICT, TAMILNADU, INDIA.

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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, montmorlinite, calcite, aragonite and organic carbon. This result shows that FT-IR is a
promising technique for identifying and quantifying the mineral analysis.

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

1. INTRODUCTION

Sediments that 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, extent and also the possible hazards of contamination. Marine sediments preserve useful
information for reconstructing oceanographic conditions and environmental changes in the past [1-5].
Coastal sediments usually act as sinks of river borne metals released through weathering and human
activities in terrestrial environments [1-3].

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. FT-IR spectroscopy
applied to the mineral identification is studied by the many workers [1-7]. The mineralogical analysis of
coastal sediment with the application FT-IR spectroscopy is the main objective of the present work.

The heavy populated Nagapattinum district of Tamilnadu coast is chosen for the present work,
covering a distance of 120 Km in its fold (Fig-1). This coastal place is an important 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 make 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 10 kms. 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 which is near to sample site. The samples were placed in plastic pouches and transported to the laboratory. The location map is given in Fig-1.

![Sample collection location map](image)

**Fig-1. Samples collected Location Map of Nagapattinum District, Tamil nadu**

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:

The Perkin Elmer FT-IR spectrometer available in Department of Chemistry, Muthurangam Government Arts College, Vellore; Tamilnadu, India is used in the present work for recording the IR spectra of the samples at room temperature. The KBr pellet technique (1:20) was performed 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.

![Fig-2. A typical FT-IR spectrum of Coastal sediment samples of Nagapattinum district, Tamilnadu](image)

3.0. 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 detailed discussion about the different minerals is reported below.

3.1. Quartz
Quartz is a silicate mineral. It is an ubiquitous mineral and forms one of the most abundant constituent in all the samples of the Earth’s crust and it is also an important component of 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 IR absorption bands[1870-1875,1615-1620, 1080-1085, 795-800, 775-780, 695-700, 515-520 with 455-460 cm\(^{-1}\)] may suggest the presence of quartz in the samples, as can be seen in Table 1. The bending vibration at 700cm\(^{-1}\), symmetrical stretching vibration at 775cm\(^{-1}\) and symmetrical stretching vibration 800cm\(^{-1}\) are assigned. The pattern of absorption in quartz can be explained by ascribing the 455cm\(^{-1}\) region (Si-O asymmetrical bending vibrations), the bands 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).

There is maximum of three to five peaks that are observed in any 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 NAP and any of these peaks was noticed in 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\(^{-1}\). As 695 cm\(^{-1}\) peak is present in the spectra of all the samples, it can indicate that the quartz mineral in these samples is in crystalline form. Band assignments for different minerals of coastal sediment samples of Nagapattinum district are given in Table-2.

3.2 Feldspar

Feldspar an abundant group of rock minerals, which constitute 60% of the earth’s crust. The general formula for feldspar can be written as \(WZ_4O_8\) in which W may be a Na, K, Ca, and /or Al, the Si:Al ratio ranging from 1:1 to 3:1. Chemically the feldspar is silicates of aluminium 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 an essential constituents of the most igneous rocks. Feldspar 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 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, 990-995,1040-1045,1050-1055cm\(^{-1}\) were assigned to feldspar mineral. The peak pertaining to the region around 535cm\(^{-1}\) is due to Si-O asymmetrical bending vibrations and the one around 642cm\(^{-1}\) is due to Al-O-coordination vibrations. The feldspar group of minerals was analyzed by IR technique and reported by many workers [1- 3, 6, 14 - 23]. The different types of feldspar minerals are given below.
<table>
<thead>
<tr>
<th>S. No.</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></td>
<td></td>
<td></td>
<td>Quartz</td>
<td>Microcline</td>
<td>Orthoclase</td>
<td>Albite</td>
<td>Kaolinite</td>
</tr>
<tr>
<td>1.</td>
<td>Kodiya pallayam</td>
<td>KDM 455,700,780,1875</td>
<td>426,106</td>
<td>536,101</td>
<td>577,787</td>
<td>3425</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>Pazhaiyar</td>
<td>PZR 695,775,1095,1875</td>
<td>644,740</td>
<td>434,538</td>
<td>525</td>
<td>935,3425</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>Sirkazhi</td>
<td>NSI 695,780,1125,1875</td>
<td>428,534</td>
<td>469,538</td>
<td>790,995</td>
<td>939</td>
<td>3443</td>
</tr>
<tr>
<td>4.</td>
<td>Poombukar</td>
<td>NPB 696,780,1092,1160,1875</td>
<td>532</td>
<td>-</td>
<td>990</td>
<td>1030</td>
<td>3441</td>
</tr>
<tr>
<td>5.</td>
<td>Tharan gambadi</td>
<td>TRGB 455,780,1875</td>
<td>530,105</td>
<td>648</td>
<td>787,993</td>
<td>920,3425</td>
<td>-</td>
</tr>
<tr>
<td>6.</td>
<td>Nagore</td>
<td>NGR 795,1615,1875</td>
<td>428,534,742</td>
<td>469</td>
<td>579,787</td>
<td>940,1115,3425</td>
<td>-</td>
</tr>
<tr>
<td>7.</td>
<td>Akkarai pettai</td>
<td>NAP 455,695,780,795,1875</td>
<td>586,642,112</td>
<td>467</td>
<td>422</td>
<td>-</td>
<td>1645,3445</td>
</tr>
<tr>
<td>8.</td>
<td>Velankanvi</td>
<td>VLK 517,695,780,1615,1875</td>
<td>530,640,114</td>
<td>422,577</td>
<td>920,3422</td>
<td>480</td>
<td>2926</td>
</tr>
<tr>
<td>9.</td>
<td>Thiruppondi</td>
<td>TPI 515,695,775,1616,1875</td>
<td>534,640,105</td>
<td>534,640,105</td>
<td>790,995</td>
<td>940</td>
<td>3443</td>
</tr>
<tr>
<td>10.</td>
<td>Vettai Karan Thoppu</td>
<td>VKT 695,780,1165,1620,1875</td>
<td>532,640</td>
<td>438,584</td>
<td>990</td>
<td>940,3425</td>
<td>478</td>
</tr>
<tr>
<td>11.</td>
<td>Veda ranium</td>
<td>VED 457,698,1095,1160,1620,1875</td>
<td>426,532,640,105</td>
<td>525,785,990</td>
<td>939</td>
<td>3440</td>
<td>2855,292,5</td>
</tr>
<tr>
<td>12.</td>
<td>Kodiya karai</td>
<td>KODI 520,695,779,1875</td>
<td>463,640</td>
<td>434,582</td>
<td>528</td>
<td>472,1020,1115</td>
<td>3441</td>
</tr>
</tbody>
</table>
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></td>
</tr>
<tr>
<td></td>
<td>645</td>
<td>Al-O- Co-ordination vibrations</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>1040</td>
<td>Si-O asymmetrical stretching vibration</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>1120</td>
<td>Si-O asymmetrical stretching vibration</td>
<td>[18]</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>Fe3+ (Al-OH)</td>
<td>[16]</td>
</tr>
</tbody>
</table>

(a) Microcline

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

(b) Orthoclase

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

(c) Albite

The observed peaks of Albite are 405-410, 420-425, 720-725, 785-790, & 990-995 cm\(^{-1}\).

3.3 Clay minerals

The presence of kaolinite, illite and montmorillonite indicate clay minerals in samples. Kaolinite is a mineral with this chemical composition Al\(_2\)Si\(_2\)O\(_5\)(OH)\(_4\). It is layered silicate mineral, with one tetrahedral sheet linked through oxygen molecules to one octahedral sheet of alumina octahedral. Kaolinite a clay mineral crystallizing in the monoclinic system and forming the chief constituent of china clay and Kaolin. It is soft, 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 peaks appearing at 470-475,915-920,935-940,1015-1020,1030-1035,1115-1120\& 3420-3425cm\(^{-1}\) in the samples indicate kaolinite. Absorbance at 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 -17, 19, 22,24-30].

Montmorilinite is a very soft phyllosilicate mineral that typically forms in microscopic crystals, forming clay. Chemically it is hydrated sodium calcium aluminium magnesium silicate hydroxide (Na, Ca)x(Al, Mg)y(Si\(_{4}\)O\(_{10}\))(OH)\(_{2}\).nH\(_{2}\)O. Montmorilinite, 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 IR absorption bands at 875-880, 1640-1645 and 3440-3445cm\(^{-1}\) show the presence of montmorilinite in the samples [1,3,14,16,17,20,25,31,32]. The band typically centered at 3400cm\(^{-1}\) is due to O-H stretching of water molecule present in the interlayer region of montmorilinite.

### 3.4 Carbonate Minerals

The carbonates consist of those minerals containing the anion (CO\(_{3}\))\(^{2-}\) and include calcite and aragonite (born calcium carbonate), dolomite (magnesium/calcium carbonate) and siderite (iron carbonate).

Carbonates are also found in evaporates settings and also in karst 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 & 715cm\(^{-1}\) is assigned to calcite [1,4 - 8,10,14,16,17,22,25,28,33-35].

From table - 1, the IR absorption bands at 875-880, 1420-1425\& 1795-1800cm\(^{-1}\)are found to be calcite. Aragonite is identified in the samples by the i.r. absorption peaks at 855-860,1785-1790 cm\(^{-1}\) [1,3,15-17,23,33,36-39].

### 3.5. 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 of contaminants present in the samples.

### 3.6. 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. Hence the 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.

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