

## **Some chemical applications (IR Spectroscopic Investigation and X-Ray Fluorescence scanning) for sediments and rock Samples collected from Al-Hamamah and Al- Haniyah areas at eastern side coast of (Libya)**

Hamad M. Adress Hasan<sup>1</sup>, Fatimah A. Abdulsayid<sup>2</sup>, Huda A. Egoil<sup>3</sup>

<sup>1,3</sup>Chemistry Department, Faculty of Science, Omar Al-Mukhtar University, Albaydha- Libya.

<sup>2</sup>Chemistry Department, Faculty of Science, Benghazi University, Alkufra-Libya.

---

### **ABSTRACT**

Different chemical analysis methods (XRF and IR,) were used in this study, for analysis some sediment and rock samples collected from some areas extended along eastern side of Libya including (Al-Hamamah and Al-Haniyah) locations. For both sediments and rock samples, the IR spectra display a significant peak that suggested that CaCO<sub>3</sub> is the main composition mixed with small amounts of CaO. In addition, the X-Ray analysis showed the presence of Al and Si metals in the majority of the samples. Introduction this is due to the presence of other ores such as feldspar or silica, but the presence of magnesium in the majority of cases is due to magnesium – calcite carbonate (Dolomite). This analysis generally concluded that the coast sediment and rocks consisted predominantly of calcite with minimal contents of other oxides.

**KEYWORDS:** Sediments and Rocks, XRF, IR, Al-Hamamah, Al- Haniyah, Libya.

---

Date of Submission: 12-05-2021

Date of acceptance: 25-05-2021

---

### **I. INTRODUCTION**

Weathering and erosion of rocks create sediments, which are brought to the shore by winds and rivers before being deposited on beaches by the action of waves and tides. Mineral assemblage composition is then connected to the source region's mineralogical composition, as well as a variety of other processes occurring during the sedimentation period, such as physical sorting, mechanical abrasion, and dissolution. It is possible to determine the provenance, distribution, and potential pollution hazards by analyzing sediments. Marine sediments provide details that can be used to recreate past oceanographic conditions and environmental changes<sup>[1][2][3][4][5]</sup>. Metal content and accumulation sediment have been described as a useful bioindicator for estimating the degree of pollution in marine ecosystems<sup>[6]</sup>. Sediments are also critical in the remobilization of contaminants in aquatic environments under favorable conditions, as well as in water-sediment interactions<sup>[7]</sup>. Many aquatic species reside in sediments, which often function as a big reservoir for many of the toxic chemical elements that can move back into the water<sup>[8][9]</sup>.<sup>[10]</sup>Using spectroscopic techniques to examine beach rock samples from Andaman Island, India, they concluded that the presence of mineral in beach rock samples can be identified using the FT-IR spectroscopic technique.

The XRD technique is used to validate the mineral constituents in the beach rocks. The non-destructive technique of energy dispersive X-ray fluorescence (EDXRF) spectrometry was used to investigate the element concentrations in beach rock samples. Al, Ca, K, Fe, Ti, Si, V, Co, Cu, Ba, Zn, Pb, Cd, and Mn concentrations are determined. There is a discussion of the geochemical activity of elements in the field. The cementing minerals and elemental compositions of beach rocks on Andaman Island, India, are exposed using spectroscopic techniques. The sample is typically ground to a fine powder for rocks, ores, sediments, and minerals. At this point, it may be analyzed directly in the case of trace element analyses.<sup>[11]</sup> In Cape Town Harbor, South Africa, I researched the geochemical assessment of sediment. Cu had a content of less than 1, indicating that its existence was mainly due to natural changes. The findings demonstrate how trace metals in runoff from domestic and urban drains, as well as inflow storm water, contribute to the overall amount of trace metals in the water. Ship repair activities proved to be a significant contributor to the increased metal pollution in dockyard areas.

This research was based on sediment and rock samples obtained from various locations along the Eastern coast of Libya for Al Gabal Al-Akhder (Libya). The key goals of this study can be summarized as follow: Firstly, using one of Nanotechnology techniques (X-Ray Fluorescence) to assess the types of chemical composition of the sediments and Rocks. Infrared spectra (IR) were used to identify the main functional group in

the considered rocks and sediments samples. Secondly, to consider the chemical compositions of the rocks and sediments of the area under examination and calculate the metal contents.

## **Experimental**

### **Sampling**

Four sediment and rock samples were obtained from two separate locations along the Eastern coast of the Al Gabal Al -Akhder locale (Libya). During the winter of 2015, sediment and rock samples were collected. At each segment Sediments and Rocks soil studies, samples were chosen from Al-Hamamah and Al- Haniyah. The samples were collected and placed in polyethylene bags before being moved to the central unit of chemical investigation, Faculty of Science, Omar El-Mukthar University.

### **Sample preparation:**

The samples were washed in distilled water, grounded in a mortar, and mixed together.

### **Samples analysis:**

XRF, IR, and a Flam photometer were used to analyze the samples.

### **X-Ray Fluorescence scanning (XRF):**

The samples were scanned using X-ray scanning at Alexandria University's Faculty of Science's central lab (X-Ray unit).

### **Infrared Red spectra (IR):**

The samples were analyzed using an infrared instrument IR instrument Type perklen at Faculty of Science, Omar El-Mukthar University.

### **Carbonate content:**

The carbonate content was calculated by titration with 0.1M HCl by Ph. Ph (indicator) method.

### **Major elements:**

0.5 gram of sample was prepared with 5 mL of concentrated HCl, filtered, and then transferred to a 100 mL measuring flask using distilled water (Sodium, Potassium, and Calcium) were measured by Flam phoetmetr, and magnesium was calculated by titration method with EDTA in the presence of EBT indicator.

## **II. RESULTS AND DISCUSSION**

### **Carbonate:**

In the marine world, the total carbonate content is definitely the most significant environmental factor and the equilibria system. In all animals, it plays an important role in building shells<sup>[12]</sup>. Photosynthesis controls the formation of  $\text{CaCO}_3$ <sup>[13]</sup>. While several calcite-rich sediments may have a primarily allergenic source of carbonate, many other sediments may have an allergenic source of carbonate. Many other carbonate sediments from the lacustrine region are truly androgenic. Their key constituents were precipitated from the water column directly.

In this study, the carbonate content in sediment and rock samples fluctuated in the following ranges of (54-59 %) and (44.1-53.12 %). Generally, the content of carbonate depends of the type of sediments. However, the sediments and rocks of investigated area are mainly calcite and magnesium calcite to explain the high carbonate content. The data suggested that these metals may be present in the forms of carbonate in the contaminated sediment.

### **Major cations:**

#### **Calcium:**

Calcium concentrations in sediment and rock samples from the study area (Tables 1, 2) and (Figure 1-4) were (39.9, 48.70 %) at Al-Hamamah and (42.5, 48.30 %) at Al-Haniyah, respectively. The higher values may be attributed to phytoplankton's ability to extract  $\text{CO}_2$  from water in order to boost the pH and precipitate  $\text{CaCO}_3$ , as well as the region's higher calcite material. The high values may be due to a biogenic origin, in which aquatic organisms readily absorb calcium to form their skeletal structure. As a result, when these species died, their skeletons began to decompose<sup>[14]</sup>. The biodetrital mixture of mollusks, coralline, algae, echinoids, formation studies, carbonate petetiods, and the deposition of  $\text{CaCO}_3$  from the water column are all potential causes of the change in calcium content.

#### **Magnesium:**

Magnesium is often released as soluble  $\text{MgCl}_2$  and  $\text{MgSO}_4$  during chemical weathering. It mostly sinks to the bottom of the sea and is partially precipitated as carbonate<sup>[15]</sup>. The concentrations of magnesium in sediment in the sample field. (Tables 1, 2 and Figures 1-4), were 1.50 mg/kg in Al-Hamamah and 2.70 mg/g in Al- Haniyah, and rock samples ranged from 1.90 mg/g in Al-Hamamah to 1.10 mg/g in Al- Haniyah, most likely due to  $\text{Mg}^{+2}$  precipitation as carbonate.

**Sodium:**

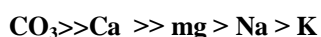
It is the sixth most abundant element in the lithosphere, and when leached from rocks, it is extremely reactive and soluble. Alkali metal content is comparable in deep-sea and near shore sediment, with the clay fraction responsible for the majority of these elements<sup>[16]</sup>.

The sodium concentrations in the sediment and rock of the study region (Tables 1, 2 and Figures 1-4) ranged from 0.37 to 0.60 mg/g at Al-Hamamah and from 0.19 to 0.10 mg/g at AL-Haniah. The small differences in sodium concentrations can be due to minor changes in sediment mineralogy or grain size. The ability of certain species to concentrate sodium may explain the high sodium content in marine sediment.

**Potassium:**

It is known as being involved in the aquatic world. The concentrations of K<sup>+</sup> in sediment and rock samples (Tables 1,2) were allocated to ranges of (1.50, 1.90 mg/g) at Al-Hamamah and (2.70, 1.10 mg/g) at Al-Haniyah, respectively. Changes in K<sup>+</sup> content at various sediment stations are largely dictated by the composition of the sediment.

Na<sup>+</sup> and K<sup>+</sup> are often found in clay in the geochemical cycle, but they can also be found in other mineral phases including alkali-feldspars. Since such minerals are almost entirely absent from the area's sediments, it's possible that Na<sup>+</sup> and K<sup>+</sup> occur as separate minerals in phases or are correlated with the main mineral components (carbonate minerals). In general, the following is the order of major cation concentrations in the sediments of the investigated area:

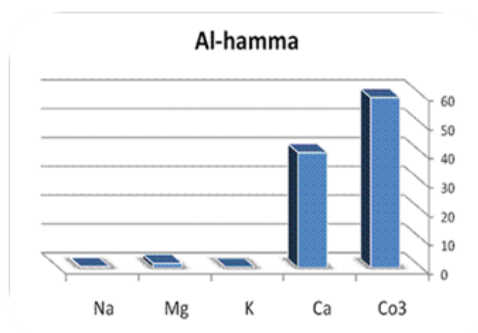


**Table (1):** Concentrations of major cations Ca% (Mg , Na and K) (mg/g) in sediment during winter (2015):

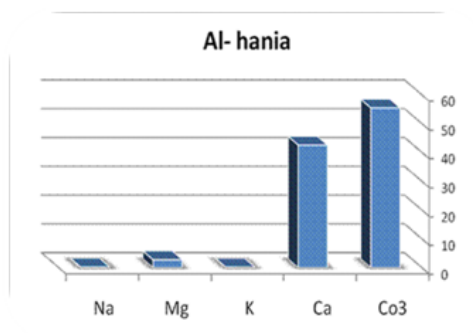
Location	Parameter				
	CO <sub>3</sub> %	Ca%	Mg (mg/g)	Na(mg/g)	K(mg/g)
Al-Hamamah	59	39.9	1.50	0.37	0.17
Al- Haniyah	55.4	42.5	2.70	0.19	0.13

**Table (2):** Concentrations of major cations Ca% (Mg, Na and K) (mg/g) in Rocks during winter(2015)

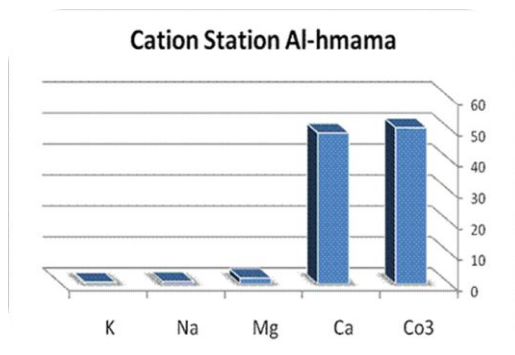
Location	Parameter				
	CO <sub>3</sub> %	Ca%	Mg (mg/g)	Na(mg/g)	K(mg/g)
Al-Hamamah	50.4	48.70	0.80	0.60	1.90
Al- Haniyah	50.90	48.30	0.19	0.10	1.10



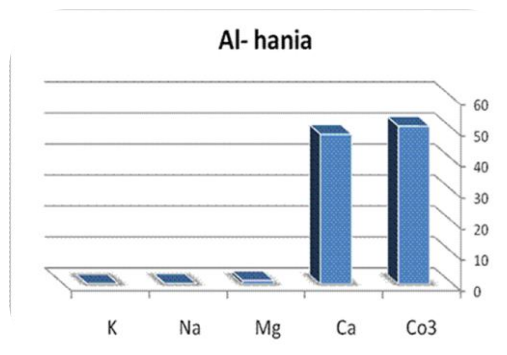
**Figure (1):** The carbonate and minerals concentrations in sediment at location Al-Hamamah.



**Figure (2):** The carbonate and minerals concentrations in sediment at location Al- Haniyah.



**Figure (3):** The carbonate and minerals concentrations in rock at location Al-Hamamah.

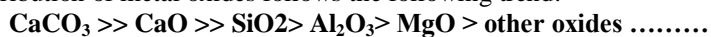


**Figure (4):** The carbonate and minerals concentrations in rock at location Al-Haniyah.

**X-ray Fluorescence (XRF).**

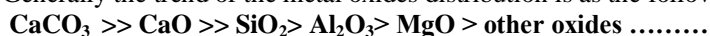
The contents of the elements oxides of the studied samples are shown in Figures (5 and 6) and curves (7-10) and represented in Table (3), the results of Al-Hamamah the data showed that the results at this location recorded oxide extant (K<sub>2</sub>O) in sediments sample, on the other the SiO<sub>2</sub> did not recorded in rocks sample at this station. Again, the extant carbonate very high of the other oxides remnant in this location.

In both Sediments and Rocks samples, the distribution of metal oxides follows the following trend:



At the location Al- Haniyah, the results at this location that recorded absence oxide (NaO) in Sediments sample and rocks sample. Also the levels of carbonate were very high compared with other of oxides in this location.

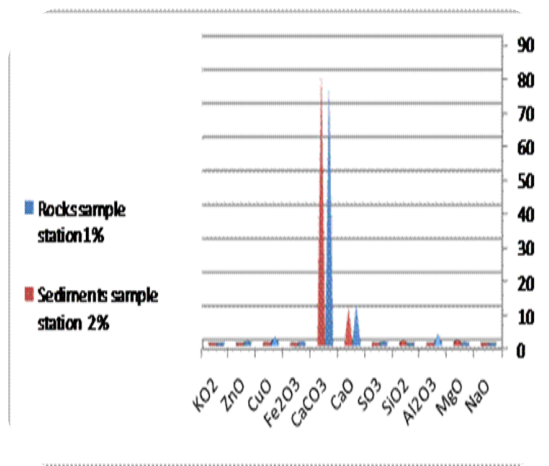
Generally the trend of the metal oxides distribution is as the following order :



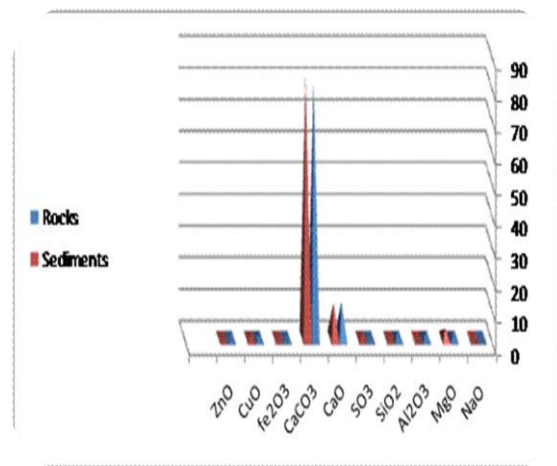
in both Sediments and Rocks samples.

**Table (3):**The values of the metal oxides % in Sediments and Rocks samples of locations (AL-Hamamah and Al-Haniyah).

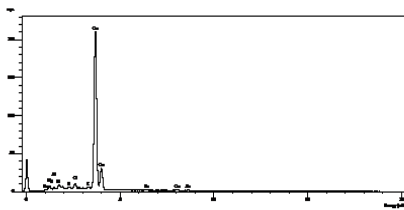
Metal	Samples			
	Al-Hamamah		Al- Haniyah	
	Sediments	Rocks	Sediments	Rocks
NaO	0.2	0.2	-	-
MgO	1.6	0.7	2.9	1.5
Al <sub>2</sub> O <sub>3</sub>	0.6	3.1	0.0	1.5
SiO <sub>2</sub>	1.3	-	0.3	1.4
SO <sub>3</sub>	0.6	0.9	0.7	0.4
CaO	10.8	11.8	11.1	11.4
CaCO <sub>3</sub>	80.7	77.3	82.5	80.8
Fe <sub>2</sub> O <sub>3</sub>	0.2	0.8	0.2	0.2
CuO	0.7	2.2	0.7	0.9
ZnO	0.5	1.1	0.2	0.5
K <sub>2</sub> O	0.5	-	-	-



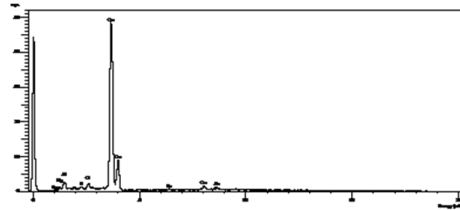
**Figure (5):** The oxides contents at location Al-Hamamah.



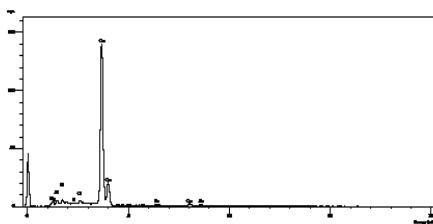
**Figure (6):** The oxides contents at location Al- Haniyah.



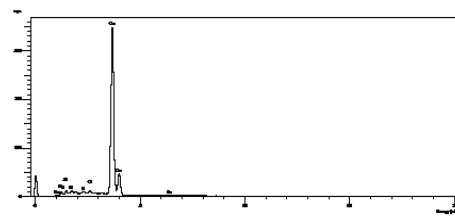
**Figure (7):** XRF curve of Sediments sample Al-Hamamah.



**Figure (8):** XRF curve of Rocks sample Al-Hamamah.



**Figure (9) :** XRF curve of Sediments sample Al- Haniyah.

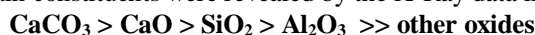


**Figure (10) :** XRF curve of Rocks sample Al- Haniyah.

**Discussion of XRF results:**

The concentration levels of the metal oxides that determined by XRF in Table (3) showed relatively lowest concentration  $\text{SiO}_2$  was observed at location Al- Haniyah in sediments with values of 0.3 %, and not extant observed at location Al-Hamamah in sample rocks. The high levels were recorded at location Al-Hamamah for  $\text{Al}_2\text{O}_3$  in rocks 3.1 %. On the other side, the lowest concentration for  $\text{Al}_2\text{O}_3$  was observed at location Al-Hamamah in sediments with 0.6 %. The relatively high levels that recorded at location Al-Hamamah for MgO in marine sediments 1.6 %. and relatively lowest concentration for MgO observed at location Al-Hamamah in rocks 0.7 %. The high levels that recorded of (0.9 and 0.7%) for  $\text{SO}_3$  was observed at location Al-Hamamah in rocks, and location Al- Haniyah in sediments, respectively. While lowest concentration for  $\text{SO}_3$  observed at location Al- Haniyah in rocks 0.4%. The high levels 11.8 % for CaO observed at location AL-Hamamah in rocks. Calcite is a calcium carbonate mineral with a cumulative concentration of  $\text{CaCO}_3$  in all samples at all sites. At all sites, ZnO concentrations were typically lower than CuO concentrations.

The presence of Al and Si in the samples is due predominantly to SiO<sub>2</sub> (Quartz), and the presence of Al in all X-ray spectra is most likely due to clay minerals such as potash feldspar ( KAlSiO<sub>8</sub>) and/or Kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>). It's likely that the low Mg content is due to the presence of small quantities of dolomite. The slight differences in metal content from one place to the next are largely due to the presence of the above ores in various concentrations. The main constituents were revealed by the X-Ray data in the following order:



**Infrared analysis( IR):**

Figures (11-14) display infrared spectra, and Table (4) lists the fundamental bands. In mineralogy, infrared spectra are widely used for quantitative analysis and identification of various minerals, including complex mixtures. It is based on the absorption bands' positions and shapes<sup>[16]</sup>. All of the samples under examination have nearly identical spectra, suggesting that the constituents are nearly identical. The hydrogen bonding of the structural OH- groups is one of the most prominent characteristics of the soil absorption spectra. M-O vibrations in the tetrahedral, octahedral sub-layers, and other associated oxide mineral sublayers<sup>[17]</sup>.

The samples from the investigation area Table (4) and Figure (11-14) revealed a wide band at (3616 - 3696 cm<sup>-1</sup>) attributed to the O-H stretching vibration of H<sub>2</sub>O, which was quickly lost when heated. These areas are often made up of calcareous soils of amorphous silica. Carbonate mineral absorption is characterized by weak bands at 2529 cm<sup>-1</sup> (calcite and magnesium calcite). Furthermore, all samples' spectra had a clear broad feature at (2500 cm<sup>-1</sup>), which is typical of the carbonate radical. The band characteristic of pure calcite has been reported to appear at 1400 cm<sup>-1</sup>. In the sediment samples, the in plane bending vibration band at 1080 cm<sup>-1</sup> for O-H occurs in all areas. The bands at 863 cm<sup>-1</sup>, on the other hand, reflect the bending in plane vibration band of O-H groups in MgAlOH. The wave number of the M-CO<sub>3</sub> stretching band at 715 cm<sup>-1</sup> is used to classify carbonate minerals in all sediments. At 450 cm<sup>-1</sup>, the symmetric Si O-Si stretching appeared as weak bands. Metal oxides are allocated to the bands between (500 – 650 cm<sup>-1</sup> ). In the presence of silicon and calcite or calcium oxide, the IR spectra are usually in accordance with the XRF study, with the exception of the presence of different peaks that may be connected to metal oxides<sup>[18]</sup>.

**Table (4):** Fundamental infrared bands (cm<sup>-1</sup>) of soils samples.

Infrared bands (cm <sup>-1</sup> )	Assignment
3619 - 3696	v OH
3424 - 3442	v SiO <sub>4</sub>
2500	CO <sub>3</sub> Minerals
1797 - 1798	δ H <sub>2</sub> O water deformation
1629 – 1938.2	v CO <sub>3</sub> coordinated
1030 - 1033.6	O-H in plan vibration
873.1 – 876.7	δ Al OH or Mg Al OH in plane vibration
694.53 – 796.11	v M-CO <sub>3</sub>
470.87 - 535	M – O

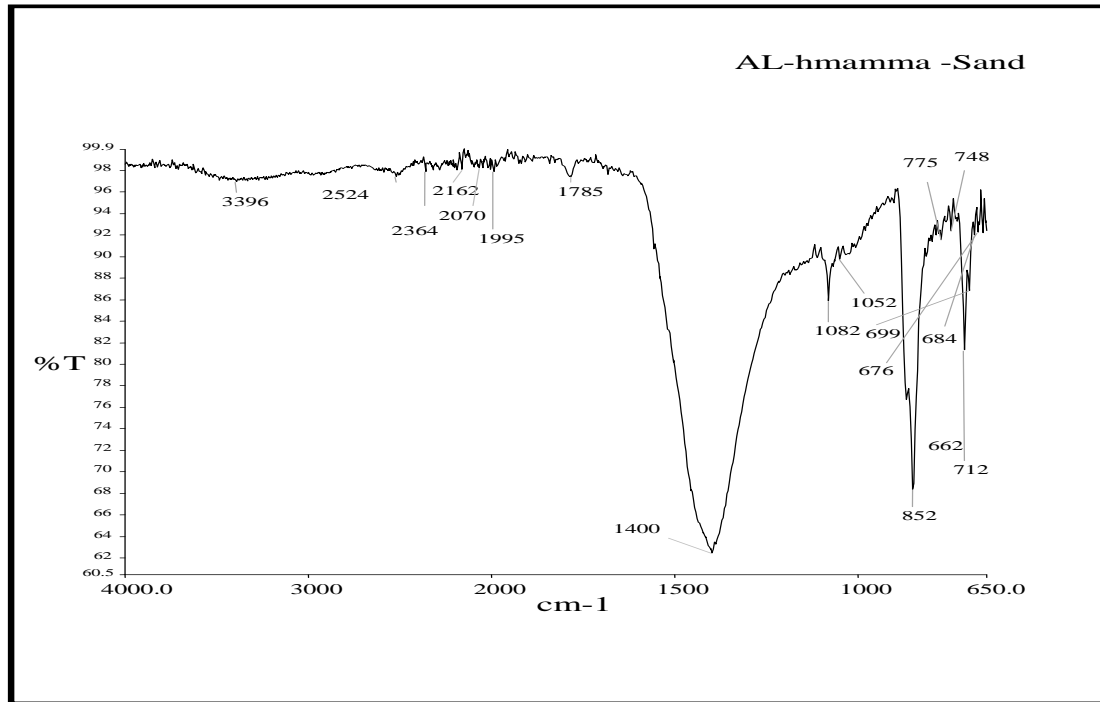


Figure (11): IR analysis for sample Al-Hamamah Sediments.

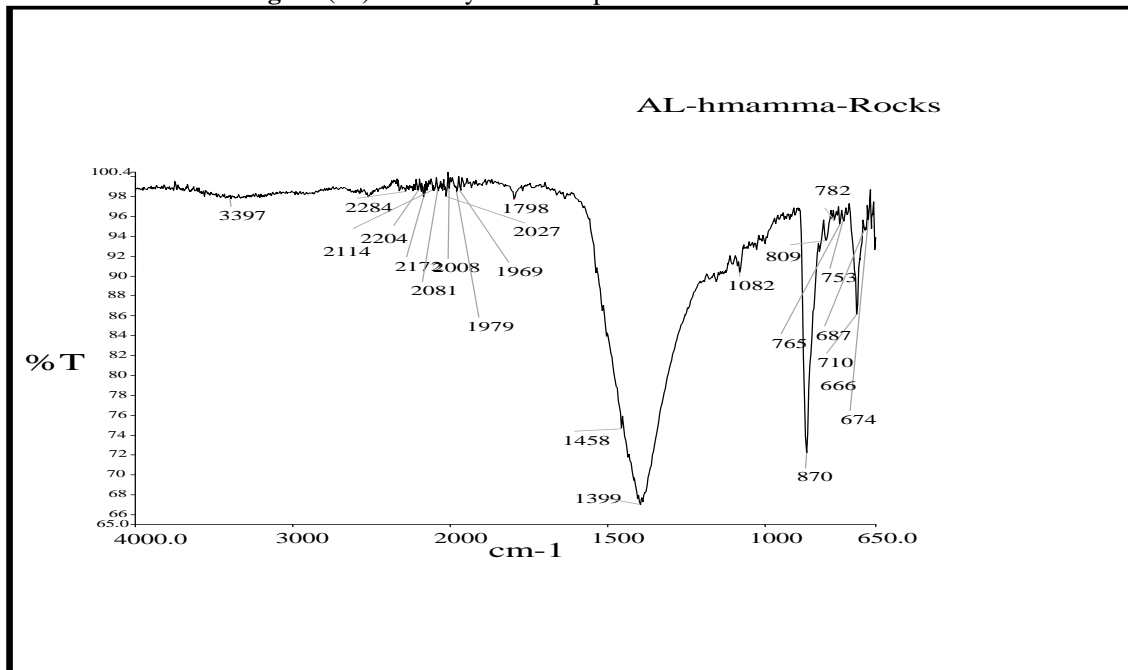


Figure (12): IR analysis for sample Al-Hamamah Rocks.

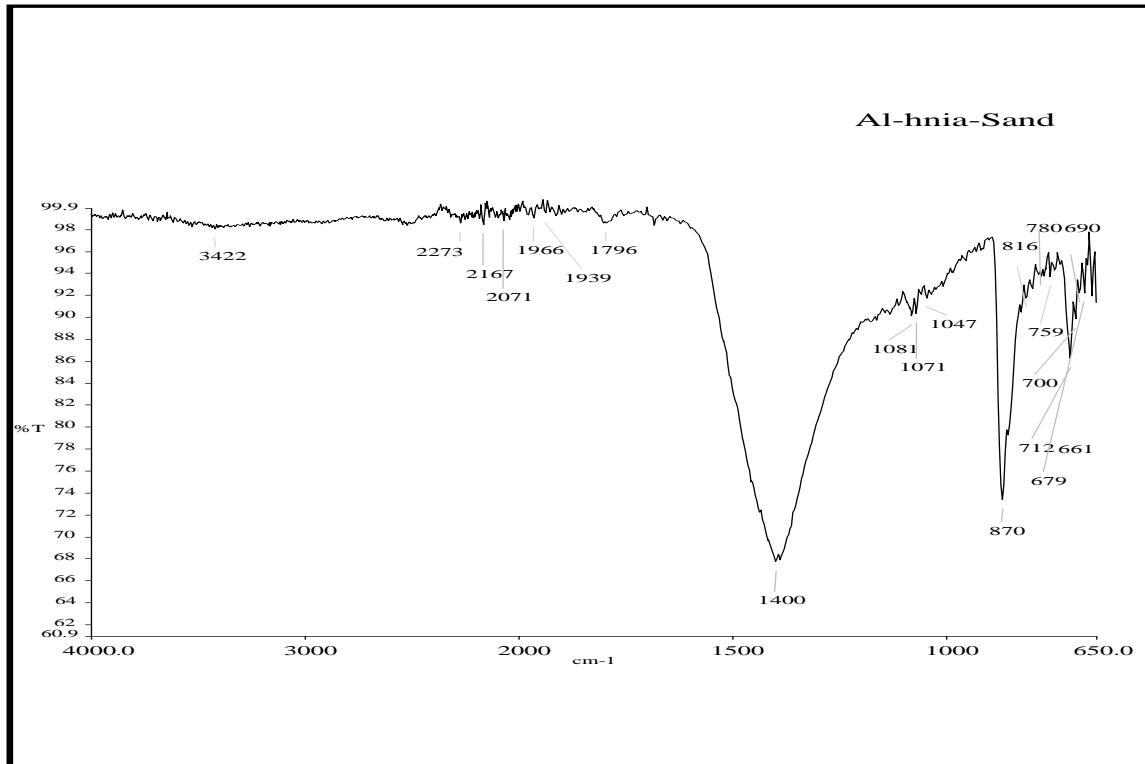


Figure (13): IR analysis for sample Al- Haniyah Sediments.

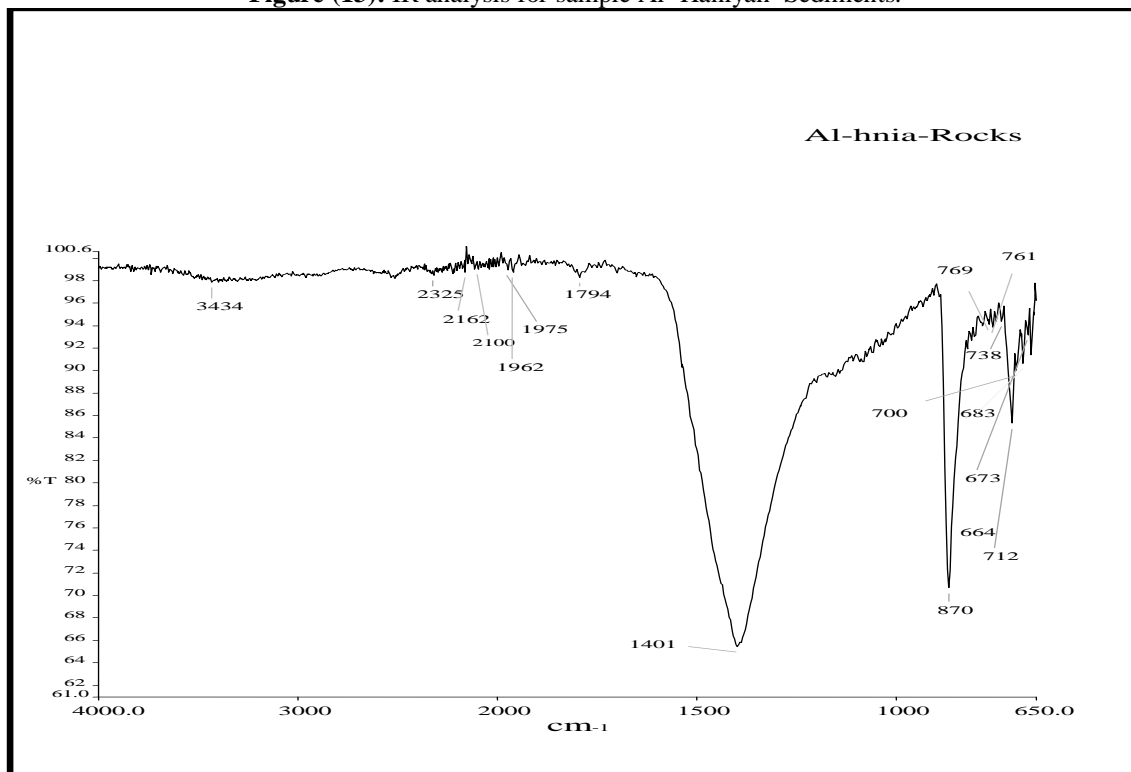


Figure (14): IR analysis for sample Al- Haniyah Rocks.



## REFERENCES

- [1]. Ravisankar R. (2009) Application of Spectroscopic techniques for the identification of minerals from beach rocks of Tamilnadu. *EARFAM*. 19:272.
- [2]. Farmer VC. (1974) *The IR Spectra of Minerals*. Mineralogical Society. London. 1974:182.
- [3]. ClarenceKarr. Jr, (1974). *Infrared and Raman Spectroscopy of Lunar and Terrestrial Minerals*. Academic Press: Newyork..
- [4]. Pichard C, Frohlich F. (1986) Quantitative IR analysis of sediments, Example of Quartz and Calcite determination. *Revue de l'InstitutFrancais du Petrol*;41:6.
- [5]. Herbert TD, Brian A, Tom, Burnett C. (1992) ;Precise major component determinations in deep sea sediments using Fourier Transform infrared Spectroscopy. *Geochimica Cosmo chimica Acta*. 56:1759.
- [6]. Alahverdi, M. and Savabieasfahani, M. (2012). Metal Pollution in Seaweed and Related Sediment of the Persian Gulf, Iran. *Bull. Environ. Contam. Toxicol.*, 88, 939–945.
- [7]. Ghrefat, H. A., Abu-Rukah, Y. and Rosen, M. A. (2011). Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Kafra Dam, Jordan. *Environ. Monit. Assess.*, 178, 95–109.
- [8]. Feng, H., Han, X. F., Zhang, W. G. and Yu, L. Z. (2004). Apreliminary study of heavy metal contamination in Yangtze River intertidal zone due to urbanization. *Mar. Pollut. Bull.*, 49, 910 – 915.
- [9]. Adekola, F. A. and Eletta, O. A. A. (2007). A study of heavy metal pollution of Asa River, Ilorin, Nigeria; trace metal monitoring and geochemistry. *Environ. Monit. Assess.*, 125, 157–163.
- [10]. Chandrasekaran A a, A. Rajalakshmi a , R. Ravisankar b, S. Kalarasai (2015), Analysis of beach rock samples of Andaman Island, India by spectroscopic techniques.
- [11]. Okoro, Olalekan S. Fatoki1, Folahan A. Adekola2 , Bhekumusa J. Ximba1 and Reinette G. Snyman (2014) Assessment of Metal Contamination in Surface Sediments of Jiaozhou Bay, Qingdao, China. *Clean*, 35 (1), 62–70.
- [12]. Serruya, C.(1970). Problems of sedimentation in lake of Geneva. *Vert. Int.Limnol*.
- [13]. Lermman, A.(1978).Lakes, chemistry .Geology,Physics,Spiger voltage ,New York ,356 pp.
- [14]. Honisch ,B, A. Ridgwell, D.N. Schmidt, E. Thomas, and S.J. Gibbs (2012)The Geological record of ocean acidification, *Science* 335 ,1058.
- [15]. Foran E, S. Weiner, M. Fine, (2013). Biogenic Fish-gut calcium carbonate is a stable amorphous phase in the Gilt-head seabream, *Sparus aurata*, *Scientific Reports* 3 1700.
- [16]. Vagenas. N. V, A. Gatsouli, C. G. Kontoyannis, Quantitative analysis of synthetic calcicum carbonate polymorphs using FTIR spectroscopy, *Talanta* 59 (2003) 831–836.
- [17]. Chandrasekaran A a, A. Rajalakshmi a, R. Ravisankar b, S. Kalarasai (2015), Analysis of beach rock samples of Andaman Island, India by spectroscopic techniques.
- [18]. Sivakumar R., Ravisankar R., A. Chandrasekaran3 and J. Prince Prakash Jebakumar (2013), FT-IR Spectroscopic Studies on Coastal Sediment Samples from Nagapattinum District, Tamilnadu, India.