

## Spectroscopic investigations of the selected pottery sample from Manappadu - Tamilnadu, South India

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### Abstract

This present work aims at investigating the presence of minerals, raw materials used and ceramic technologies adopted in making pottery during the ancient period belonging to one of the important archeological site Manappadu of Tamil Nadu, India. One pottery sample of the period 220BC is used for the present work. Fourier Transform Infra Red (FTIR) spectroscopy has been used for the studies. The presence of quartz, kaolinite, montmorillonite, haematite and magnetite in the selected pottery sample has been identified. The classification of the firing temperatures and firing features of pottery sample is also presented. The firing of pottery under reduced condition is judged from the magnetite and haematite contents establishing the ability of the ancient artisans of Tamilnadu to achieve controlled firing.

**Keywords:** FTIR, Kaolinite, Quartz, Haematite, Magnetite, Montmorillonite

### Introduction

The study of pottery through the ages is considered to be an essential requirement to identify, understand and characterize civilizations. The style of pottery, the clay minerals used, the firing temperature and firing techniques employed by ancient artisans, if known, can all be helpful in unraveling the cultural sequence of a particular archeological site, the trade and cultural links it had in the past, the technological advancement made and the historical periods involved. The characteristics of the ancient pottery sample obtained from excavations are mostly not known. So, investigations have to be made to assess the characteristics of ancient potteries so that the technological

knowledge, skills of the ancient artisans, the age of civilizations, cultural links, etc., can be understood. Extensive investigations have been made on the various aspects of ancient materials excavated from different sites in countries like Greece, Rome, Bulgaria, Egypt, Iraq and China<sup>1,2,3</sup>. But in India such studies are scanty and this is more so in South India. So in this work an attempt has been made to study the pottery sample obtained from Manappadu which is one of the important archeological site of Tamilnadu with a view to analyze the characteristics of the selected pottery sample which belongs to period of 220 BC.

A brief account of the available history of the selected site and their importance are given below.

## Manappadu

Manappadu is a coastal village in Thuthukudi District down south of Periapattinam of latitude 8°21'03"N and longitude 78°03'34"E in India. According to Archaeologists<sup>4</sup> this place might have been a connecting port in the east-west sea as there was a light house in the village. Fishing was the occupation in this sea coast village and a large quantity of salted fish were sent to the interior and even shipped to Sri Lanka and other countries. Apart from pottery shreds, a few stone pillars carrying some inscriptions stand as the only evidences of Manappadu's past. Potteries collected by Archaeological survey of India, Southern circle, Chennai indicate that Manappadu could have been once a flourishing port.

## Method

The selected Pottery sample has been analyzed by recording its vibrational spectra with the aid of FTIR spectroscopy using Perkin Elmer FTIR spectrophotometer model 1600 instrument in the range 4000-400  $\text{cm}^{-1}$  in the 16 scan mode as potassium bromide pellet.

## Results and discussions

The selected pottery sample has been studied in the "as received state"(ARS) and the FTIR spectrum obtained is shown in figure 1. Infrared frequencies in  $\text{cm}^{-1}$  of the pottery sample (as received condition) from Manappadu along with vibrational assignments are given in table1.

The spectrum shows that the sample has a broad band in the hydroxyl stretching vibrational region of 3700-3400  $\text{cm}^{-1}$  which is the characteristic clay mineral region. The existence of a wide band in the 3700-3400  $\text{cm}^{-1}$  region in the pottery sample may be taken to indicate the highly disordered nature of the clay minerals present in them<sup>5,6</sup>. Since the pottery is essentially a fired sample, it is but quite natural that the lay minerals are in a highly disordered state.

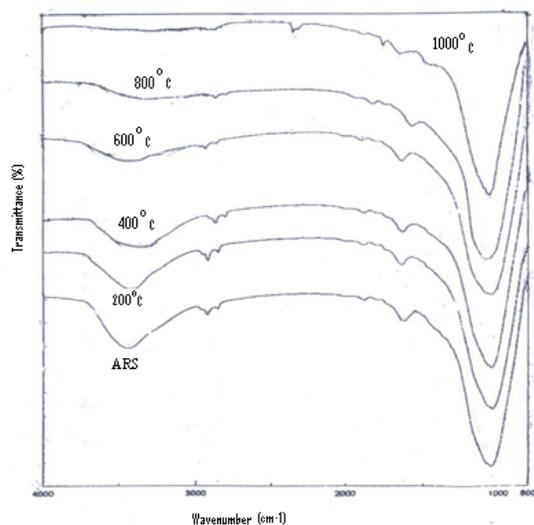
In the pottery sample a broad band appears around 3430  $\text{cm}^{-1}$ . This band taken together with the weak band around 1630  $\text{cm}^{-1}$  represent the O-H stretching and O-H bending due to adsorbed water. Miller<sup>5</sup> has shown that in the case of kaolinite, the 3718  $\text{cm}^{-1}$  peak is broadened and is shifted to around 3650  $\text{cm}^{-1}$  on heating the kaolinite to temperatures of the order of 820 °C and beyond when it is in the completely disordered form. The pure kaolinite has four bands in the O-H stretching region 3718  $\text{cm}^{-1}$ , 3686  $\text{cm}^{-1}$ , 3672  $\text{cm}^{-1}$ , and 3636  $\text{cm}^{-1}$ . Pure montmorillonite has bands in the O-H stretching region at 3650  $\text{cm}^{-1}$  and 3520  $\text{cm}^{-1}$ <sup>7,8</sup>.

**Table 1**

Wave number ( $\text{cm}^{-1}$ )	Assignments
3743.4	O-H Stretching of clay mineral
3431.9	O-H Stretching of adsorbed water
2360.3	Si-O of quartz
2137.3	Si-O of quartz
1017.0	Si-O of quartz of fine particle
728.8	Si-O of quartz
692.00	Si-O of $\text{SiO}_4$
641.69	Si-O bending mode in Si-O-Si
582.00	Fe-O of $\text{Fe}_3\text{O}_4$
534.90	Fe-O of $\text{Fe}_2\text{O}_3$
481.8	Si-O-Si bending of silicate

Similarly, the weak bands in the range of 3525-3570  $\text{cm}^{-1}$  obtained for the sample may be taken to indicate the possibility of the presence of some highly disordered montmorillonite or calcined montmorillonite in the sample. So a mixture of non-plastic kaolinite and more plastic montmorillonite appears to have been used as raw clay minerals in the manufacturing of pottery by the ancient artisans. According to Miller<sup>5</sup>, the bands at 1100  $\text{cm}^{-1}$  and 915  $\text{cm}^{-1}$  are due to the vibration of aluminum hydroxyl in the octahedral sheet structures. In highly disordered kaolinite the bands at 1100  $\text{cm}^{-1}$

and  $1035\text{ cm}^{-1}$  merge to give a broad absorption<sup>9</sup>. It is also found that there is progressive destruction of octahedral layer on account of heating accompanied by weakening of the  $915\text{ cm}^{-1}$  band.



**Figure 1**

The sample shows a doublet absorption bands around  $795\text{ cm}^{-1}$  and  $780\text{ cm}^{-1}$  and a peak around  $693\text{ cm}^{-1}$ . This doublet and the band at  $693\text{ cm}^{-1}$  are attributed to the Si-O modes of crystalline quartz. Farmer and Russell<sup>10,11</sup> have shown that the presence of a sharp band at  $694\text{ cm}^{-1}$  can be attributed thin particles/fine grains and in the case of thick particles/coarse grains this band would shift to  $689\text{ cm}^{-1}$ . The sample has hematite as indicated by the peak around  $535\text{ cm}^{-1}$  which is the characteristic peak of haematite. It has also a peak around  $571\text{ cm}^{-1}$  indicating the presence of magnetite<sup>12,13</sup>.

It has been found that the sample of Manappadu indicates the presence of strong well defined haematite and magnetite peaks. So it is likely that the sample would have been fired under reduced conditions.

Potteries are essentially fired clay materials. So an understanding of the thermal transformation occurring in clay materials when they are heated may help to infer the firing temperatures.

To get a clear idea about the firing temperature that could have been used in firing the selected pottery sample, a refiring study has been conducted. The refired pottery sample has been studied using the FTIR spectroscopic technique. It is an established fact that once a ceramic is fired at a certain temperature and altered, it “freezes” at this stage, which cannot be altered by subsequent refiring unless the original firing temperature is exceeded<sup>14,15</sup>. This property of the ceramic provides a method of assessing the firing temperature used in making a certain ceramic in antiquity. For estimating the firing FTIR spectroscopy through the refiring test, the sample has been refired in the laboratory in a furnace at the temperatures of  $200\text{ }^{\circ}\text{C}$ ,  $400\text{ }^{\circ}\text{C}$ ,  $600\text{ }^{\circ}\text{C}$ ,  $800\text{ }^{\circ}\text{C}$  and  $1000\text{ }^{\circ}\text{C}$ . The FTIR spectra obtained for the refired sample are shown in figure 1 along with the spectra for the ‘as received state’ sample<sup>16</sup>. Comparison of these spectra obtained at different firing temperatures for sample indicates that the peaks around  $3650\text{ cm}^{-1}$  and  $3550\text{ cm}^{-1}$  and the wide band in the hydroxyl region exist up to  $800\text{ }^{\circ}\text{C}$  and disappears at  $1000\text{ }^{\circ}\text{C}$ , the Si-O peak and wide band in the  $1100\text{--}900\text{ cm}^{-1}$  region remain more or less unaltered upto  $800\text{ }^{\circ}\text{C}$  and vanish at  $1000\text{ }^{\circ}\text{C}$ .

### Conclusion

The FTIR analysis shows that the pottery sample contains kaolinite, quartz, haematite and magnetite. The clayey matrix appears to be composed of highly disordered calcined montmorillonite.

The study has shown that the artisans used mixer of kaolinite and montmorillonite clays for making pottery and that in addition to the clay, quartz also formed raw materials. The study has also shown the technological capabilities of the artisans with respect to their ability to achieve the necessary firing temperature, their ability to adopt controlled firing and their understanding of the properties of clay and other materials they

used in making potteries. The study has brought to light the interesting fact that the ancient artisans of Manappadu region of Tamilnadu during the ancient period it self have adopted almost the same technologies which are being used in the modern 21<sup>st</sup> century for making potteries.

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