



PHYSICS

## SPECTROSCOPIC STUDIES OF SOME FIRED CLAY ARTIFACTS RECENTLY EXCAVATED AT TITTAGUDI IN TAMILNADU

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### Abstract

This paper presents the preliminary results of an investigation on pottery shreds using Fourier Transform Infrared (FT-IR) spectroscopy. The analysis has lead to initial characterization of the pottery shreds collected from the archaeological site Tittagudi in Caddalore district.

**Keywords:** Pottery shreds, FT-IR spectroscopy, Clay minerals

### Introduction

Archaeology is the study of ancient human society, by reconstructing environmental settings and cultural systems, typically from their physical remains (masonry, pottery, coins, engravings, etc). More knowledge about the great civilization is brought out with archaeological excavations. In recent times, science and technology have been applied to the world of cultural heritage, conservation and preservation<sup>1</sup>.

Various techniques are in use for the identification and characterization of different clay minerals. Vibrational spectroscopy represents a powerful method to study and characterize art objects. Among the several techniques recently improved, Fourier Transform Infrared Spectroscopy (FT-IR) is efficacious tool which is able to yield quantitative information to identify the clay minerals in the studied samples<sup>2</sup>. In the present work, FT-IR spectroscopy has been employed extensively to characterize and define the mineralogy of the clay samples collected from the archaeological site Tittagudi in Caddalore district in Tamilnadu which is one of the most important archaeological places. This site was excavated by the Department of Epigraphy and Archaeology, Tamil University, Thanjavur<sup>3</sup>.

### Materials and Methods

The pottery samples of interest were collected at different depths and are named as TTK1, TTK2, TTK3, TTK4 and TTK5 serially and Fourier transform infrared spectra of the pottery samples were recorded in the mid region 4000-450cm<sup>-1</sup> using Avatar 360 FT-IR spectrophotometer with 1cm<sup>-1</sup> resolution in its 100 scan mode using KBr pellet technique. Each sample is mixed with Spectra grade KBr in powder form and finely ground using agate mortar at the ratio 1:20 by weight. The sample of 4mg mixed with 80mg of spectra

grade KBr. The pellets of 13mm diameter were prepared at a pressure of 8 atmosphere<sup>4</sup>.

### Results and Discussion

Potteries are made up of clay materials, which include primary, secondary, accessory minerals and amorphous materials. Clay minerals are made up of chains of SiO<sub>4</sub> tetrahedral and AlO<sub>6</sub> octahedral, which are the basic structural units of silicates<sup>5</sup>. Silicon is tetrahedrally surrounded by oxygen atoms and the hydroxyl groups to form a hexagonal network which is repeated infinitely. The tetrahedral are arranged so that all their apexes (O or OH) point in the same direction and their bases are in the same plane.

On the other hand the oxygen and hydroxyls on the free apexes are coordinated to Al ions forming octahedral sheets. Accessory minerals generally are the various iron oxides and oxyhydroxides. These are often found dispersed as finely divided particles or as surface coatings. Minute quantities of these minerals, can influence the morphological and mineralogical properties of the clay minerals<sup>2</sup>.

The infrared spectra recorded for five samples collected from Tittagudi site are presented in the Fig 1. The absorption observed in the spectra with their relative intensities and the tentative assignments are given in the Table 1.

In the present study, the sample TTK2 shows a very weak band at 3624cm<sup>-1</sup> which may be assigned to O-H stretching due to crystalline hydroxyl group<sup>6</sup>. According to Russell<sup>7</sup> very strong to medium absorption band in the region 3427-3441cm<sup>-1</sup> and strong to weak bands in the region 1629-1639cm<sup>-1</sup> in all the Tittagudi samples are due to adsorbed water<sup>7</sup>. As stated by Maritan and Columbini<sup>8,9</sup> Very weak bands around 2920cm<sup>-1</sup> and 2852cm<sup>-1</sup> in the samples TTK1-TTK5 may be observed as C-H stretching band

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probably induced by residuals of organic matter (Wood, Flour etc) adsorbed by the material.

Fig.1. FT-IR Spectrum of Tittagudi Samples

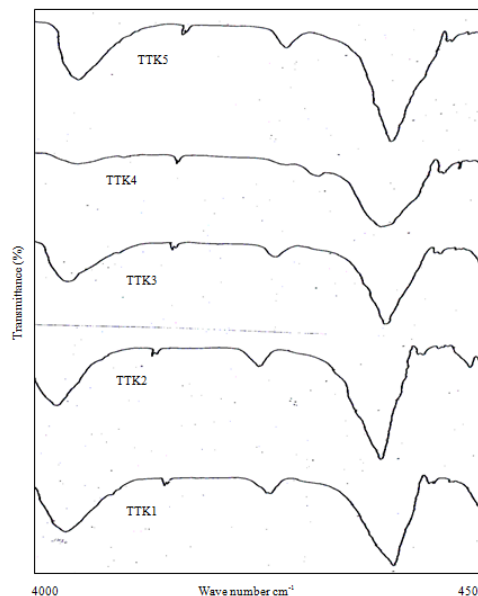


Table1. Tentative vibrational assignment

TTK1	TTK2	TTK3	TTK4	TTK5	Tentative vibrational assignment
	3624 VW				O-H str. Crystalline hydroxyl
3438 VS	3441 M	3430 VS	3427 VS	3437 S	O-H Str.adsorbed water
2923 VW	2923 VW	2918 VW	2918 VW	2923 VW	C-H Stretching
2847 VW	2858 VW	2847 VW	2847. VW	2852 VW	C-H Stretching
1634 S	1629 W	1638 M	1639 M	1637 M	O-H adsorbed water
	1429 VS				Calcite
	1040 VS			1039 VS	Si-O Str.clay minerals
		1031 VS	1034 VS		Albite
	876 S				Calcite
776 VS	779 S	776 S		778 S	Si-O Quartz
	716 VW		733 VW		Muscovite
			694 VW	694 VW	Calcite
	640 VW				Si-O Quartz
585 VS	585 VS				MnO
					Magnetite-FeO- Fe <sub>3</sub> O <sub>4</sub>
	542 M		541 M		Hematite-FeO- Fe <sub>2</sub> O <sub>3</sub>
		525 VS			Hematite-FeO- Fe <sub>2</sub> O <sub>3</sub>
476 VS	464 S	467 VS	466 S	465 VS	Hematite-FeO- Fe <sub>2</sub> O <sub>3</sub>

VS-Very Strong; S-Strong; M-Medium; W-Weak; VW-Very Weak

Quartz is a common constituent of most clay minerals. The absorption band centered around 777cm<sup>-1</sup> in the samples belonging to Tittagudi site except in TTK4 and very weak band around 694cm<sup>-1</sup> in TTK4 and TTK5 are due to Quartz<sup>10</sup>.

The substitution of Fe, Mg or other metals in the octahedral lattice alters the structure of clay minerals.

Calcite occurs as an impurity in clays. With reference to Benedetto<sup>11</sup>, a very strong band at 1429cm<sup>-1</sup> corresponding to TTK2 and a strong and very weak band at 876cm<sup>-1</sup> and 716cm<sup>-1</sup> in TTK2 are due to the presence of Calcite<sup>11</sup>. A strong band at 1100-1000cm<sup>-1</sup> region centered at 1040cm<sup>-1</sup> indicates the presence of silicates (Si-O) in clay materials. A very strong band

around  $1040\text{cm}^{-1}$  in Tittagudi samples TTK2 and TTK5 have been assigned to Si-O stretching of Silicate band<sup>12</sup>. Albite and Microcline are both known as alkali feldspar, Na and K end member compositions, respectively, and have similar occurrence in rocks, such as granite, rhyolite, etc<sup>13</sup>. The strong bands at about  $1032\text{cm}^{-1}$  and  $990\text{cm}^{-1}$  have been assigned to the accessory mineral Albite<sup>11</sup>. The presence of accessory mineral Albite<sup>11</sup> is found from the observation of band around  $1032\text{cm}^{-1}$  in TTK3 and TTK4. A very weak band at  $733\text{cm}^{-1}$  in TTK4 may be assigned to Muscovite<sup>11</sup>. A small shoulder of the band at  $640\text{cm}^{-1}$  in TTK2 may be assigned to Manganese Oxide<sup>13</sup>.

The region  $400\text{--}700\text{cm}^{-1}$  is characteristic of Fe-O group. The iron oxides i.e. Magnetite<sup>7</sup> is identified by the bands around  $580\text{cm}^{-1}$  and Hematite<sup>7,14</sup> which are present in the samples are identified by the bands around at  $540\text{cm}^{-1}$  and  $460\text{cm}^{-1}$ . These iron oxides are of low abundance in clay minerals and sometimes it may be difficult to identify in the infrared spectra due to the overlap of absorption bands of silicates. The very strong band at  $585\text{cm}^{-1}$  in the samples TTK1 and TTK2 indicates the presence of Magnetite<sup>7</sup>.

A very strong band at  $525\text{cm}^{-1}$  in TTK3 has been assigned to Hematite<sup>14</sup>. The medium absorption bands around  $540\text{cm}^{-1}$  in TTK2 and TTK4 reveal the presence of Hematite<sup>14</sup>. The strong and very strong band in the region  $464\text{--}476\text{cm}^{-1}$  in all the samples is also due to Hematite<sup>14</sup>.

It is obvious from the above analysis that the pottery samples collected from Tittagudi site is made of secondary mineral Quartz and various accessory minerals Calcite, Albite, Muscovite, Manganese oxide and iron minerals such as Magnetite and Hematite. These minerals have greater influence on clay structure. Our results show the usefulness of Infrared spectroscopy in the chemical analysis of pottery samples. The results are most informative when backed up by other techniques such as XRD, SEM and EDX

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