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FT-IR Spectroscopic Investigations of some Archaeological Pottery Excavated from Thamaraiikulam, Dindigul Dist, Tamil Nadu, India.

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The FT-IR spectroscopic analysis was performed to characterize pottery corresponding to the Iron Age grave period from Thamaraiikulam village, Dindigul District, Tamil Nadu, India. The main goal was to point out the potentiality of the Fourier Transform Infrared spectroscopic (FT-IR) technique as a non-invasive analytical tool in archaeometry. The elemental compositions and its various mineralogical phases and firing temperature of red, red and black and black polished pottery samples were measured. The raw material, the firing temperature and firing conditions were identified by presence of mineralogical composition in the samples by FT-IR study. The results of FT-IR study revealed that archeological pottery was fired to a temperature greater than 750 °C.

Keyword: Ancient Pottery, FT-IR Mineral Analysis, FT-IR Firing Temperature

1. Introduction

Ceramics have a long history and are found in almost all societies. They are not perishable, and are often found in large quantities in archaeological excavations. For these reasons, ceramics play a central role in archaeological theories and methods. Infrared Spectroscopy (IR) analysis has been used to study material composition, especially in the case of archaeological materials. In particular, in the case of arts and archaeology, this technique is the most suitable non-destructive method to determine the elemental profile of artefacts, paintings and manuscripts. For archaeological purposes, major elements and traces contents are good enough to characterize the pottery material and to determine the clay and its sources. From this knowledge, information about trade routes and relationships between cultures, and social changes in ancient societies can be established^[1]. Many analytical techniques, based on different theories and giving complementary information, are usually employed in the study of archaeological objects. In particular, spectroscopic techniques are very useful analytical

tools to characterize a detailed knowledge of artworks^[2-6]. Among the different available analytical techniques the ones being capable to perform mineralogical determinations are advantageous. FT-IR analysis is perhaps the technique that has been more extensively applied to the analysis of archaeological materials. In the present work the elements present in some pottery fragments of Thamaraiikulam and firing temperature of pottery have been analysed by FT-IR spectroscopy.

2. Material and Methods

2.1 Sample Collection

Thamaraiikulam (Long: 10°25'25"N; Lat: 77°28'40"E) is one of the Village in Palani Taluk in Dindigul District in Tamil Nadu State. Thamaraiikulam is 51.3 km far from its District Main City Dindigul. It is 416 km far from its State Main City Chennai. Nearest Towns are Thoppampatti (14.2km), Kodaikanal (24.5km), Oddanchatram (25.7k.m.), Vathalakundu (41.2km). The pottery samples were recently excavated from the site Thamaraiikulam is a small village in Palani Taluk,

Dindigul District, Tamil Nadu state, India, by the Department of History, School of Social Sciences & International Studies, Pondicherry University, Puducherry, India. The pottery shreds of Thamaraiikulam belonging to 5th century BC. Black and Red ware, Red ware and Black polished ware were collected in the site. The samples are labeled as TK 1, 2, 3 & 4.

2.2 FT-IR Analytical Technique

FT-IR spectra on the pottery samples were recorded on a Bruker Alpha FT-IR spectrometer available in

department of chemistry, Government Arts College, Tiruvannamalai, Tamil Nadu, India, using KBr pellets technique in the wave number range from 4000 cm^{-1} to 400 cm^{-1} . The KBr pressed pellet technique was used by mixing the powdered samples with KBr in weight proportion of 1:20. The spectra were recorded in the mid region of 4000-400 cm^{-1} in the 'as received state' as well as refired state. The precision of the instrument is $\pm 5\text{cm}^{-1}$. Fig-1 shows the representative FT-IR spectrums of as received and refired potsherds of Thamaraiikulam.

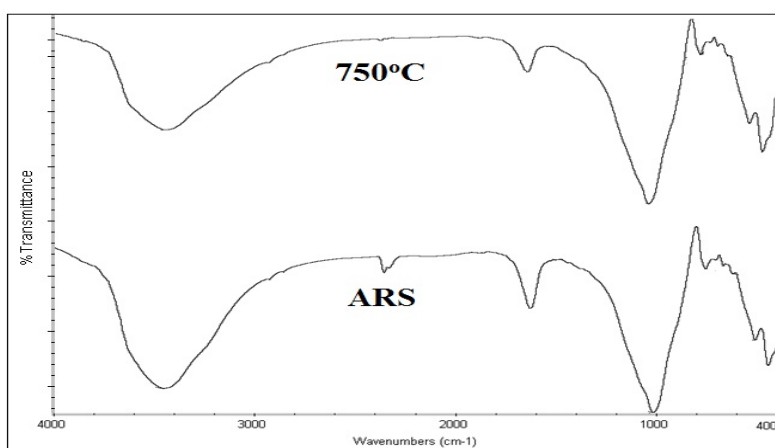


Fig 1: Representative FT-IR spectrums of as received and refired potsherds of Thamaraiikulam.

3. Results and Discussions

3.1 Ftir Mineral Analysis

The FTIR spectroscopy is a physical method applied to study the mineralogy and mineralogical change of clay materials due to firing. Minerals obtained from recorded FT-IR spectra of four pottery samples of Thamaraiikulam are tabulated in table-1. The absorption peaks of quartz were detected in all the samples RTK1- RTK4. The presence of quartz can be explained by Si-O symmetrical stretching vibrations at around 780 cm^{-1} in all the received state samples while symmetrical bending vibrations arise around 692 cm^{-1} due to low level of Al for Si substitution in the sample RTK1. The presence of the sharp band at 692 cm^{-1} indicates that thin particles and in the case of thick particles, this band has shifted to 685 cm^{-1} [7]. Since the sample RTK1 shows that this band at 692

cm^{-1} it is clear that this clay contains quartz of thin particle size and the sample RTK2 shows the band at 685 cm^{-1} it is clear that this clay contains quartz of thick particle size. Russell reported that the presence of bands around at 1870, 775, 695 along with 460 cm^{-1} indicate that the pottery fragments due to quartz [8].

From Table-1, the broad absorption band at 3440 cm^{-1} along with the weak band around at 1640 cm^{-1} in all the samples due to absorbed water [9]. The inter layer hydrogen bonding in clay is assigned by a characteristic band at 3625 cm^{-1} . Most of the bands such as 3625, 3670, 3625

and 1035 show the presence of kaolinite. Kaolinite is the major constituent of clays which gives sharp bands in the region 3700-3600 cm^{-1} .

Table 1: Mineralogical composition of the ‘as received state’ samples of Thamaraiikulam by FT-IR study

ID	Silicate Mineral	Feldspar Minerals			Clay Minerals		Iron Oxide Minerals		Calcite	Organic Carbon
	Q	Mic	O	Al	K	Mon	H	Mag		
RTK1	+++	+	-	-	+	++	+	-	-	++
RTK2	+++	+	+	-	+	++	+	-	Tr	++
RTK3	+++	++	+	-	++	++	+	+	Tr	++
RTK4	+++	++	-	-	++	++	+	-	-	++

Q = Quartz, Mic = Microcline, O = Orthoclase, Al = Albite, K = Kaolinite, Mon = Montmorillonite, H = Hematite and M = Magnetite.

Abundant = +++, Present = ++, Little present = + and trace = tr.

A strong band at 3695 cm^{-1} is related to in phase symmetric stretching vibration. Inner hydroxyl groups, lying between the tetrahedral and octahedral sheets gives the absorption near 3625 cm^{-1} . The band at 1040 cm^{-1} is due to asymmetric stretching vibrations of silicate tetrahedron^[8]. The presence of montmorillonite is shown by the characteristic peaks centered at 3440 and 1640 cm^{-1} . These two peaks are observed in all the samples. Hence, we conclude that both montmorillonite and kaolinite are present in all the samples represented by all the samples RTK1-RTK4^[6].

The red color of the potteries is due to presence of high amount of hematite, black and grey colors are due to magnetite^[10]. From this, the relative amount of hematite and magnetite is responsible for the color of the potteries. The variations in the amount of these oxides give important information regarding the nature of the environment in which the potteries were made. The amount of magnetite and hematite decides atmosphere whether reducing or oxidizing for firing the artifacts. In the present study the atmospheric condition of the sample fired at the time of manufacture is identified by the ratio of iron oxides (magnetite and hematite) present in the sample. If the amount of magnetite present in the sample is large then it may be fired at reducing atmosphere. If the amount of hematite is high it may be fired at oxidizing atmosphere^[11]. To determine the concentrations of the magnetite and hematite present in the sample I/I₀ method was used. For this method the absorption bands at 540 and 580 cm^{-1} were used. These two bands have been attributed to magnetite and hematite respectively^[12]. In this I/I₀ method ‘I’ represents the value of intensity of magnetite and I₀ represents value of intensity of hematite of IR bands. If I/I₀ value is more than 1 the samples contain more amount of magnetite and visually black in color, which indicates that the reducing atmosphere was

prevailed by the artisans at the time of manufacturing. The sample RTK3 contains the ratio ‘I/I₀’ more than ‘1’ visually black in color. If I/I₀ value is less than 1 the samples contain more amount of hematite and visually red in color, which indicates that the oxidizing atmosphere was prevailed by the artisans at the time of manufacturing. The sample RTK1, RTK2 and RTK4 contain the ratio ‘I/I₀’ less than ‘1’ visually red in color.

Going on with the discussion of the present FTIR transmittance data, on the basis of the obtained results, as far as feldspars are concerned, the FTIR analysis showed that the presence of microcline and orthoclase. These two minerals have a similar spectrum but some differences in the frequencies of their characteristic peaks. In particular, orthoclase prevails in the case of RTK2 and RTK3, as it is proved by the detection of the main contributions centered at 650 and 1045 cm^{-1} , instead microcline is mainly present in all the samples with the characteristic peaks centered at 640 and 730 cm^{-1} . finally both of the minerals are identified in the samples RTK2 and RTK3 (see Table-1).

From spectra of all the samples Table-1, a weak absorption bands centered at 2925 and 2920 cm^{-1} suggest the presence of organic carbon^[3]. These bands are due to C-H stretching vibrations of some organic carbons. Carboxyl groups were the most important functional groups in natural organic matter. The organic substances have the high specific surface and good molding capacity, improving the plasticity of the clays.

The presence of IR absorption peaks centered at 1415 cm^{-1} in the sample RTK2 and 2515 cm^{-1} in the sample RTK3 are identified by calcite^[13]. The presence of calcite (CaCO₃) in the finds may occur, essentially for two reasons; a low process firing temperature (or) post burial deposition process. Calcite exists up to $800\text{ }^{\circ}\text{C}$, when the CaO

formation is promoted, followed by the followed by the formation of the high temperature crystalline phase made of Ca-silicates or Ca-Al-silicates such as gehlenite, diopside and anorthite. The calcite is present in calcareous clays only. Clearly, in non-calcareous clays, calcite is not expected.

3.2. Firing Temperature of Refired Sample

The FTIR spectra of the refired archaeological samples were recorded with corresponding minerals are tabulated in Table-2.

Table 2: Mineralogical composition of the refired state samples of Thamaraiikulam by FT-IR study.

ID	Silicate Mineral	Feldspar Mineral			Clay Minerals		Iron Oxide Minerals		Calcite	Organic Carbon
	Q	Mic	O	Al	K	Mon	H	Mag		
FTK1	460,524, 775	734	648	-	1029	3435	-	-	-	2856, 2924
FTK2	460,695, 779	644,730	-	-	1035,3690	3440	-	578	2513	2856, 2924
FTK3	460,775, 1872	644,732	1041	-	-	3437	534	580	2511	2856, 2924
FTK4	460,695,779, 1874	644,730	1045	-	-	3442,1635	-	-	-	2856, 2924

Q = Quartz, Mic = Microcline, O = Orthoclase, Al = Albite, K = Kaolinite, Mon = Montmorillonite, H = Hematite and M = Magnetite.

For the purpose, the samples were fired in the laboratory to temperature 750 °C for 2 hours using muffle furnace. The spectra are then recorded with these refired samples. The spectra of refired samples compared with that of the 'as received state samples'. The absence of inner hydroxyl bands at 3700 cm⁻¹ and the band at 915 cm⁻¹ indicate that all the samples were fired above 500 °C. At 500 °C the band is absent due to the complete destruction of clay mineral present in the pottery samples^[7]. The presence of weak broad band at 3440 cm⁻¹ coupled with 1640 cm⁻¹ in all the received state sample and in refired sample FTK4 indicate that the presence of absorbed water molecules which are due to long burial. Abroad symmetry band centered at 1035 cm⁻¹ observed in the received state samples RTK1, RTK3 and RTK4 as well as refired samples FTK1 and FTK2 indicates that the samples were made of red clay and subjected to a firing temperature of above 650 °C during manufacturing^[14]. Further increase of temperature causes increase in the intensity of hematite. The FTIR spectra remained relatively unchanged up to 700 °C. Firing at 700 °C results in the appearance of iron components either poorly crystalized or substituted hematite^[15]. In all the 'as received state' samples and refired samples the absorption band around at 540 cm⁻¹ attributed to iron oxide component hematite and in the as received state sample RTK3 and in the refired samples FTK2 and FTK3 the band centered at 580 cm⁻¹ indicates the iron oxide component magnetite.

In the refired samples, the presence of bands at 540 and 580 cm⁻¹ at 750 °C indicate the completion of reoxidation of iron compounds. In all the refired samples, sharp bands observed at 540 cm⁻¹ exist up to 750 °C indicates that complete oxidation of iron compounds which reveals the oxidizing atmospheric condition with firing temperature of above 750 °C during manufacturing. From the above discussion, by comparing absorption bands of both the as received state samples and refired samples around at 540 and 580 cm⁻¹ which indicate presence of iron oxide (hematite and magnetite), the samples might have been fired around at 750 °C in oxidizing atmosphere.

4. Conclusion

A set of four pottery fragments, coming from archaeological excavation in Thamaraiikulam, was investigated by FT-IR transmittance measurements. The study showed that the FT-IR technique permits a rapid sequential determination of mineralogical compositions such as quartz, feldspar, clay minerals, iron oxides and organic carbon present in the archaeological materials. As far as the production technology is concerned, the firing temperature was supposed to be greater than 750 °C. The whole set of samples shows a general similarity in the mineralogical composition.

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