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Multi - Analytical Approach of Archaeological Pottery Excavated from Thoppur, Thiruvannamalai Dist, Tamilnadu, India.

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Abstract : A three pieces of pottery samples Red slipped ware and Red ware excavated from the site Thoppur, Thiruvannamalai District of Tamilnadu, India. In order to characterize and classify these earth ware samples, mineralogical and elemental concentrations were studied with FTIR, XRD and SEM-EDS analysis. Fourier Transform Infrared spectrometry method can be used for the study of characteristic reactions, associated with the course of firing and also used to distinguish between different types of clay minerals and derive information concerning their composition. XRD analysis gives the confirmation about the findings of FT-IR results. From the above analyses, firing temperature and firing conditions of archaeological pottery were determined. The microstructure and elemental composition of the pottery sample evaluated from their microphotograph by Scanning Electron Microscope along with energy dispersive spectrometer (SEM-EDS).

Keywords : Ancient Pottery, FT-IR, Firing Temperature, XRD, SEM-EDS.

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1. Introduction

The cultural heritage research field experienced great development during last decades. Many papers about multidisciplinary studies on artistic objects were published so underlying the importance of the co-operation between humanistic and scientific efforts. Infrared (IR) Spectroscopy has been for decades a frequently used method to investigate the structure, bonding and chemical properties of clay [1]. Clay minerals are hydrated aluminum silicates with very strong fine particle size, usually <2µm. They have layered structure formed by tetrahedral sheets linked to an octahedral sheet through sharing of apical oxygen. Kaolinite and Montmorillonite are the most widely used clay mixture in the manufacturing of pottery. In the unfired matrix, it is possible to find, as major components, clay minerals mixed with quartz, feldspar and firing produces differences in the products as a result of the initial composition and of the different operative conditions. The best known clay minerals of the layer type are the smectite group. Smectites are widely used in various branches of industry. For instance, hematite is produced during pottery firing only if the process is carried out in oxidizing conditions [2].

Among various instrumental techniques, X-ray analytical methods, including X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), Thermo gravimetric analysis (TGA) and Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM-EDX), may successfully address the above issues [3-4]. Since the introduction of Fourier Transform instrumentation the application of the IR spectroscopy greatly increased in many spheres of clay research. The improved performance of the FTIR spectrometers made it possible to design sample-handling accessories that were impractical (or) difficult to implement on older instruments [5].

XRD is a technique that allows identifying the crystalline substances present in the studied sample, through an investigation of the properties marking the different mineral kinds. The method of analysis used by X-ray spectroscopy, such as X-ray diffraction is used to estimate the mineralogical composition. XRD is therefore a destructive technique [6]. The SEM with EDS analysis is non-destructive and capable of offering precise chemical compositional information towards the characterization of archaeological pottery artefacts; it is also an excellent tool and it has been found useful in many applications to characterize the archaeological potteries [7].

In the present paper, we report and discuss the experimental results obtained through FTIR transmittance measurements performed on a set of three shreds found during archaeological excavation in Thoppur, Tiruvannamalai Dist, Tamilnadu, India. For a detailed characterization of the shreds, X-ray diffraction measurements, using CuKα radiation as a source, have been performed and their analysis is in progress to obtain a complete description of the findings. The identification of FTIR joined with XRD analysis is further confirmed by SEM-EDS patterns.

2. Materials and Methods

2.1. Sample Collection

The pottery samples were recently excavated from the site Thoppur (12°29′N; 78°77′E) of Chengam Taluk in Tiruvannamalai Dist, Tamilnadu, India, by the Department of History, Pondicherry University, Puducherry, India. The pottery shreds of Thoppur belonging to 5th century BC. Red ware and Red slipped ware were collected in the site. The samples are labeled as TPP1, TPP2 &TPP 3. The typical collection of pottery samples are shown in Figure - 1.

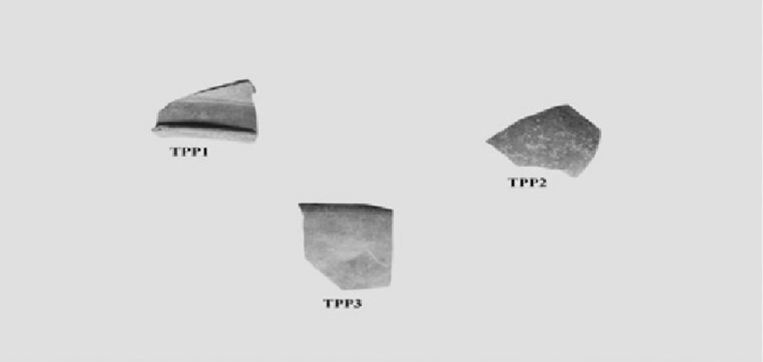

Figure 1 - Visual characteristics of ancient pottery samples from Thoppur

2.2. Analytical Techniques

The infrared spectra were recorded in the mid IR region 400-4000 cm^{1}using Bruker Alpha FT-IR spectrometer available in Department of Chemistry, Government Arts College, Tiruvannamalai, Tamilnadu, India was made use of in the present work for recording the IR spectra of the samples at room temperature. The KBr pellet technique was used to record the spectrum. The crushed samples were grounded before making the KBr pellet. The samples were mixed with KBr in the proportion of 1:20.For each of the samples five to six pellet specimens were prepared and the spectra were taken. The instrument scans the spectra 16 times in 1 minute and the resolution is $\pm 5 cm^{-1}$.

Samples for X-ray powder diffraction (XRD) studies were packed in shallow cavities in glass slides to minimize preferred orientation. The X-ray patterns of powdered pottery and refired samples were recorded at room temperature by using X-ray diffractometer (D500, Siemens) having a curved graphite crystal diffracted monochromator, with a source of CuKα radiation and NaI(Tl) scintillation detector. Diffraction patterns were obtained by continuous scanning from 10 to 70°. Qualitative mineralogy of the studied samples is determined with the standard interpretation procedures of XRD.

The microphotographs of the samples were recorded using SEM Quanta FEI, Netherland. The maximum magnification possible in the equipment is 3,00,000 times with the resolution of 3nm. The elemental analysis was done using the Oxford INCA Energy Dispersive Spectrometer (EDS). The fresh fracture surface of the potteries in the received state (ARS) that were coated with a thin layer of gold was examined using SEM, typically setting at a magnification of X2000 for all the samples of the study.

3. Results and Discussion

3.1. FT-IR Analysis

Table-1
Mineralogical composition of the 'as received state' samples of Thoppur by FT-IR study

ID	Silicate Mineral	Feldspar Mineral			Clay Minerals		Iron Oxide Mineral		OC	Cal
	Q	Mi	Or	Al	Kao	Mon	He	Ma		
TPP1	460,777	-	471	640, 723	1038	1636	539	580	2926, 2854	715
TPP2	779,460	467	-	638, 723	1039	1636	539	586	2920	-
TPP3	778, 459	591	645	635, 723	1040	1636	541	-	2920	715

NOTE: Q = Quartz, Mi = Microcline, Or = Orthoclase, Al = Albite, Kao = Kaolinite, Mon = Montmorillonite, He = Hematite, Ma = Magnetite, OC = Organic Carbon and Cal = Calcite.

The representative FT-IR spectrum of infrared spectra of three samples is shown in Figure 2. The FTIR analysis was used to analyze the archaeological potteries TPP1, TPP2 (Red slipped ware) and TPP3 (Black and Red ware).

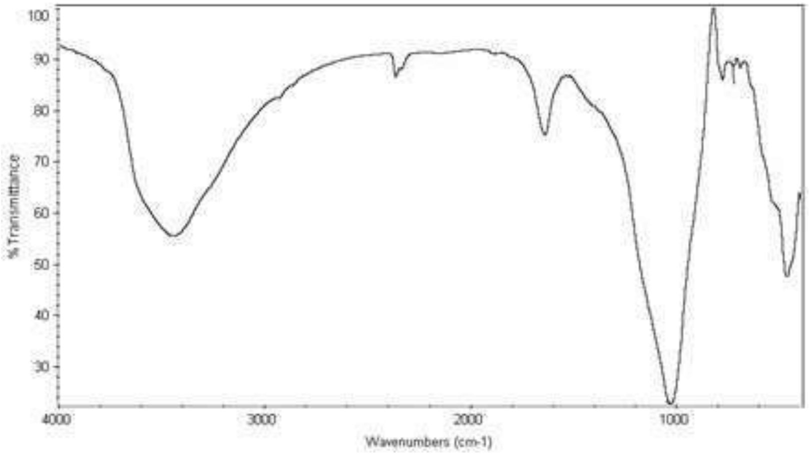

Figure 2 A typical FT-IR spectrum of Thoppur potsherd of TPP1

The FTIR spectra recorded for the samples in as received state. First of all, the typical peaks of quartz were detected in all the investigated samples. The presence of bands at 795 and 775 cm^{-1} along with 695 cm^{-1} in the sample is quartz [8]. The main SiO2stretching peak at 1080 cm-1and the distinctive doublet at 777 and 798 cm^{-1}. Furthermore in the low-frequency (below500 cm^{-1}) it was possible to detect the other typical peak associated to quartz (460 cm^{-1}). Quartz is major mineral in all the pottery samples. Calcite in trace was revealed in the samples TPP1 and TPP3 by the presence of the typical band centered at 715 cm^{-1}. Besides the above mentioned minerals, it was possible identify the presence of feldspar (Table-1). The revealed feldspar showed peaks centered at 467, 475, 595, 635, 645 and 725 cm^{-1}. Regarding the microcline we revealed the contributions at 467 and 595 cm^{-1} could be associated to orthoclase (471 and 645 cm^{-1}) and albite (635 and 725). The feldspar group minerals are minor. The weak band 640 cm^{-1} is attributed to Al-O coordination vibration. The Si-O-Al bending vibration observed at 530 cm^{-1} is the most sensitive band to the presence of residual Al in octahedral sheet [9]. During firing, no perceptible changes are observed in this region up to 450°C; above this temperature as iron replaces aluminium, the intensity of the band at 530 cm-1decreases with the appearance of the band at 540 cm^{-1} along with the weak shoulder peak at 580 cm^{-1} attributed to iron oxides. At 800°C, the increase intensity of the band at 580 cm^{-1} indicates that it is due to oxidation and crystallization of hematite [10]. These two peaks were observed in the samples due to presence of iron oxides [hematite and magnetite] as minor minerals.

The presence of weak broad band around 3440 cm^{-1} and less intensive absorption at 1636 cm^{-1} in all representative potsherds can be attributed to the adsorbed water and OH vibrations [11]. Two weak peaks observed at 2852 and 2926 cm^{-1} are due to C-H stretching mode and reveal the presence of some organic contribution. Thus, in the present study, a very weak band in the region 2927 and 2853 cm^{-1} are observed in all the samples can be assigned to C-H stretching of organic matter. The two peaks that can be observed at 2853 and 2927 cm^{-1} are due to some organic contribution, probably present in the mixture used for the preparation of the pigments [12]. In all the samples, the absence of bands at 3700 and 3620 cm^{-1} indicates that they have been fired above 450°C. The band at 915 cm^{-1} is due to Al(OH) vibrations in the octahedral sheet structure which begins to disappear with increasing temperature and at 500°C the band disappears completely [13]. None of the samples taken for the present study showed the sharp shoulder band at 915cm^{-1}. This implies that all the samples were fired to the temperature above 500°C. The broad symmetry band centered at 1035 cm^{-1} in all the samples, indicates that the samples were made of red clay and subjected to a firing temperature of above 600°C during manufacturing [3]. The peaks are observed at 540 and 580 cm^{-1} due to iron oxides, the samples might have been fired under oxidizing atmospheric condition with firing temperature of above 800°C. According to Yariv and Mendelovici; (1979), a shoulder band at 875 cm^{-1} indicates dehydroxylation of kaolinite minerals which are completed at 800°C and octahedral sheet structure of clay mineral disappeared [14]. This again confirms that all the samples from Thoppur were fired to the temperature above 800°C. Hematite is one of the most colouring materials in potteries. The presence of hematite gives reddish colour to the pottery. The red color of the pottery also reflects the oxidizing atmosphere followed by during manufacturing [4].

3.2. XRD Analysis

Semi - qualitative results of mineralogical analysis of the pottery samples are obtained from XRD spectrum. The representative XRD spectrum of three samples is shown in Figure 3. The presence of minerals is identified by comparing 2θ values with JCPDS file [15]. The diffractometric analysis pointed out a very rich presence of quartz in each of the three samples.

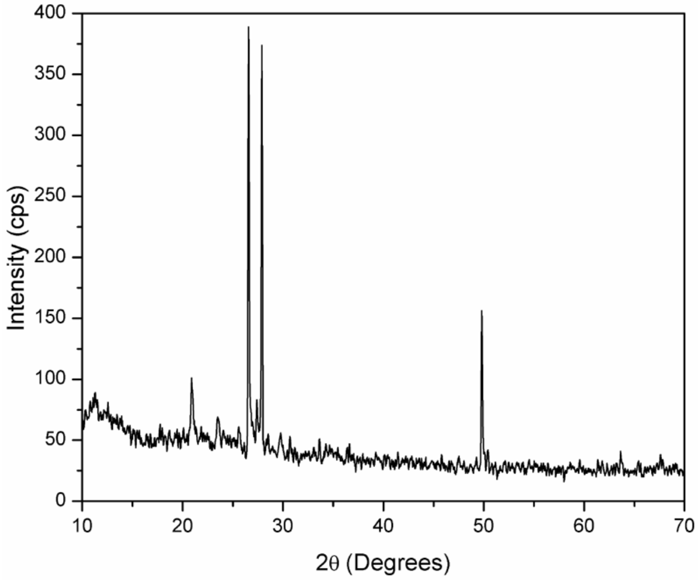

Figure 3 A typical XRD spectrum of Thoppur potsherds of TPP2

From the analysis, quartz is found as major mineral in all the samples. The quantities of feldspar are abundant. The diffractograms also show a small quantity of iron oxide mineral, which is little present in the samples TPP1 and TPP2. Calcite is present in traces in the sample TPP3. The peaks of quartz are high and narrow (especially d = 3.34, 4.25 and 1.82 A°), showed a good crystal state and these peaks are characteristics of α-quartz. But feldspar had wide peaks (especially d = 3.19 and 3.31 A°), showed a worse crystal structure. Since small quantity of calcite, we consider a firing temperature is greater than 800°C [16]. The presence of Fe (III)-containing hematite in most samples suggests that the artefacts were fired at a temperature greater than 800°C and manufactured by firing in an oxidizing kiln atmosphere. The results of XRD analysis of pottery fragments were also evidenced by FTIR.

3.3. SEM-EDS Analysis

The microstructure of the potsherd TPP3 is shown in Figure 4. According to SEM measurement, the size of the particle is situated of the between 10 to 20 μm. The careful examinations of microphotograph of TPP3 reveal that the particles were heterogeneously shaped with lot of incisions.

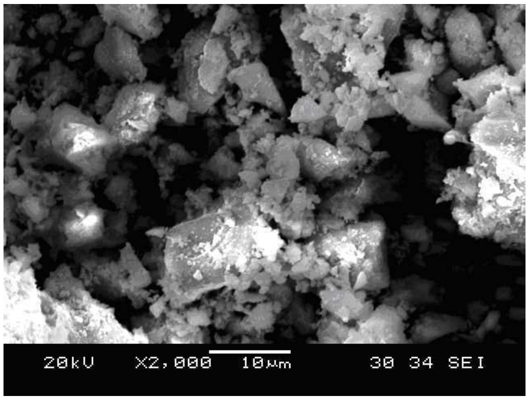

Figure 4 A typical SEM microstructure of Thoppur potsherds of TPP3

If the potsherd less than 6% of Ca, the clay used for the make is of non-calcareous in nature [17]. The clay was in continuous vitrification stage of non - calcareous type and fired in the oxidizing atmosphere in the range of 850-900°C. The SEM results of the sample TPP3 consist with the FTIR and XRD results obtained on the same sample.

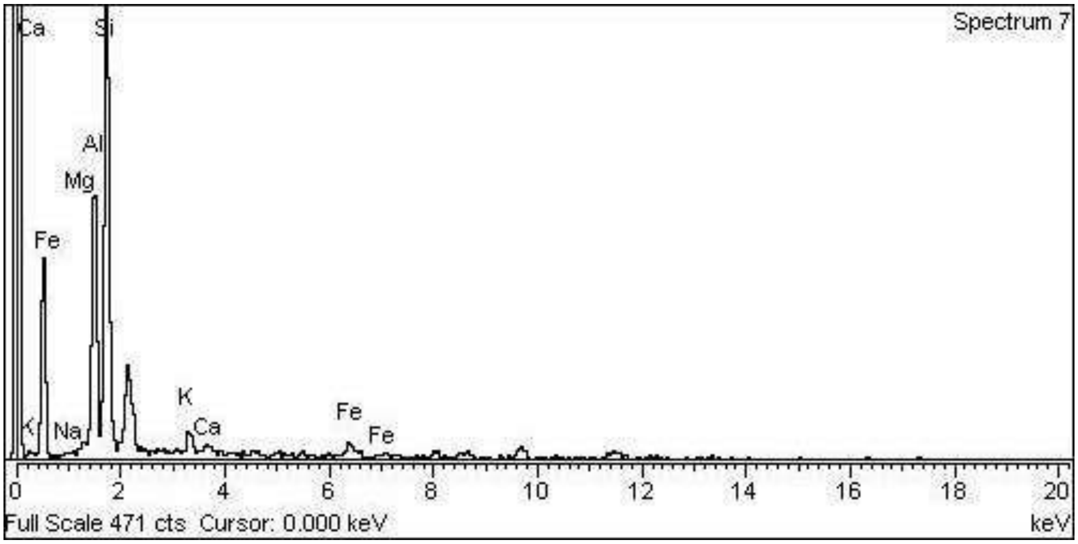

Figure 5 A typical EDS spectrum of Thoppur potsherds of TPP3

As shown in Figure 5, Energy Dispersive Spectrum of the sample TPP3 which is collected from the energy characteristic X-ray that is emitted when electrons strike a solid specimen enabled to identify the main elements that were present in the pottery samples. For quantitative analysis of mineral composition of the sample was determined by EDS analysis. Drawbacks of this technique are that small fragments must be removed from the objects and that minor elements below 1 wt% cannot be detected. The EDS measurement demonstrated that the sample consists mainly SiO_2, Al_2O_3 and Fe_2O_3 (iron oxide). Oxides such as Na_2O_3 and MgO comprised a total amount of smaller than 6wt%. Although the sample contain a small amount of Na_2O_3, MgO, K_2O and CaO (<10wt%), the amount of alkali oxides was systematically higher than that of the earth alkali oxides. This indicates that the alkalis were not only introduced as impurities from the siliceous ingredient, but that an additional alkali source has been used as well, probably potassium or sodium rich plant ashes [18]. From the study of the color and firing temperature of the pottery shreds excavated at the site, it is clear that oxidizing atmospheric conditions were used for firing in reduced kiln atmosphere by the ancient artisans. So the people lived at the time of manufacture of the potteries in the respective areas of the excavations aware of the technology of perfection to achieve good quality of their product. They might have used clay containing hematite rich composition to produce red color potteries [19]. The presence of red color on the pottery samples studied may be attributed the process of firing at reduced atmosphere.

4. Conclusion

Archaeological pottery samples excavated from Thoppur, Thiruvannamalai District in Tamilnadu were characterized by FTIR, XRD and SEM-EDS techniques. The mineralogical composition, the firing methods and firing conditions are inferred from characteristic peaks of the FT-IR spectrum. The XRD analysis of pottery fragments were also evidenced by FTIR. Further Scanning Electron Microscopic technique (SEM) was carried out to study the internal morphology and firing temperature of the pottery fired at the time of manufacturing. In addition to EDS analysis, which inspects identification of main constituent elements in the potsherds. The results obtained from the above techniques showed good agreement with one another. Spectroscopic results indicated that the potteries were fired to a temperature above 800ºC.

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