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Estimation of the firing temeparaure of arachaelocigical pottery excavated from Thiruverkadu, Tamilnadu, India by FT-IR spectroscopy

R.Ravisankar[1], S.Kiruba[2], A.Naseerutheen[3], A.Chandrasekaran[4], G.Raja Annamalai[5], M.Seran[6] and P.D.Balaji[6]

[1]Post Graduate and Research Department of Physics, Government Arts College, Thiruvanamalai, Tamilnadu, India
[2]Department of Physics, St.Joseph's College of Engineering, Chennai, Tamilnadu, India
[3]Department of Physics, C.Abdul Hakeem College, Melvisharam, Tamilnadu, India
[4]Department of Physics, Global Institute of Engineering &Technology, Vellore, Tamilnadu, India
[5]Department of Physics, Achariya College of Engineering technology, Villianur, Puducherry, India
[6]Department of Ancient History and Archeology, University of Madras, Chennai, Tamilnadu, India

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ABSTRACT

Archaeology is the study of past societies through the material remains left by those societies and the evidence of their environment. It studies a past material culture. The material analysis in the artifacts plays a dominate role in archeometry. In the present work FT-IR spectroscopy has been employed to identify the constituent of minerals in the pottery samples were recently excavated from the site Thiruverkadu of Chennai. The firing conditions (open/reduced atmosphere) and the iron mineral phase changes are studied from the FT-IR spectrum. From the analysis, it is found that the potteries were fired to a temperature greater than 800ºc in the oxidizing atmosphere.

Keywords: Ancient Pottery, FT-IR, Firing temperature Analysis.

INTRODUCTION

Archaeology is the study of past societies through the material remains left by those societies and the evidence of their environment. All remains and objects and any other traces of humankind from past times are considered elements of the archaeological heritage. The term archaeology is generally used for special part of historic sciences. Archaeology tries to reconstruct the culture and history of past societies, especially of those on which no or poor written sources exist and for information on everyday life is scare. Archaeology in its broad sense, studies a past material culture. Material analysis plays a dominate role in archeometry.

Ancient potteries are the most common artifacts found during excavation of archeological sites, so archaeologists are interested in the studies of pottery fragments. Most archaeologists have classified ancient artifacts (pottery) by their shapes and uses. The study performed on pottery

objects is relevant within several research fields and many questions have to be solved. The systematic and scientific study of the above artifacts reflects the technological development, civilization and trade links between different countries during the past .Various spectroscopic and magnetic studies are mostly widely used for the study of archeological artifacts like potteries, bricks and tiles.

Minerals of an archaeological artifacts were classified a the primary minerals- minerals that were present in the raw materials and have not undergo reactions in wide range of temperatures, and the firing minerals – that have been formed during the firing. The identification of firing minerals is an essential requirement for the elucidation of firing temperature of potteries. The absence of any firing minerals in the ceramic paste is a clear indication of a low temperature. The knowledge of firing temperature and condition of firing gives us better understanding of the civilization that created potteries and provides us the information for conservation and restoration techniques. A thermal transformation in constituent mineral of clay is considered irreversible. The change in the mineral composition will be observed only if the shred is fired above its original temperature applied by the potter. This is the key factor for the investigation of ancient potteries. By analyzing the mineral trapped in the sample one can elucidate its firing temperature.

Spectroscopic techniques are very useful tools to achieve a detailed knowledge of the art works. Using spectroscopic technique one can identify manufacturing techniques and functional relationships between specific resource manufacturing combinations. For bulk characterization of archeological shreds, Fourier Transform Infrared (FT-IR) spectroscopy is usually preferred to other analytical techniques such as X-ray diffraction (XRD) due to its non-invasiveness. Indeed, although a sampling object is needed (only~2 mg of material), FT-IR spectroscopy is common and well established tool for the ceramic body identification. The FT-IR approach with respect to the traditional one is tremendous in preparation (no acidic dissolution is necessary), experimental procedure, cleanliness and simplicity and analysis time. Many workers applied the FT-IR technique to study the ancient potteries [1-10]. The present work aimed to analysis the recently excavated archaeological pottery from Thiruverkadu, Tamilnadu by FT-IR technique and to estimate the firing temperature of the pottery.

MATERIALS AND METHODS

2.1. Sample Collection:

The pottery samples were recently excavated from the site Thiruverkadu (lat.13º 48'N; long 80º 10"E) of Chennai, Tamilnadu, India by the Department of Ancient History and Archeology, University of Madras, Chennai. Tamilnadu, India. The pottery shreds of Thiruverkadu belonging to the first century AD to 200 AD. Red slipped ware and Red ware were collected in the site. The typical collection of pottery samples is shown in Fig-1. The samples are labeled as TVD RS 1, 2, 3, 4 & 5 (Red slipped ware) and TVD R1 & TVDR2 (Red ware). After removal of surface layers, the pottery shreds were grounded into fine powder using agate mortar. They were sieved using a 90µm mesh. The major and minor minerals were qualitatively determined by FT-IR technique.

2.2. Sample Analysis:

The KBr pellet technique was followed for the mineral analysis. Sample of 2 mg is mixed with 40 mg of spectroscopic KBr in the ratio 1:20 using a mortar and pestle. Before mixing, necessary amount of KBr powder is dried at 120°C for six hours in an oven. Otherwise the broad spectral peak due to free OH will seriously affect the interpretation on the bound hydroxyls associated,

with any of the minerals. The major and minor minerals are qualitatively determined by FT-IR technique. The Bruker Alpha FT-IR spectrometer is available in Department of Chemistry, Government Arts College, Tiruvanamalai, Tamilnadu, India is made use of in the present work for recording the i.r. spectra of the samples at room temperature. For each samples five to six pellet specimens are prepared and the spectra were taken in the mid region of 4000-400cm^{-1}. The instrument scans the spectra 16 times in 1 minute and the resolution is 5cm^{-1}. This instrument is calibrated for its accuracy with the spectrum of a standard polystyrene film. Every time, before the spectrum of sample is obtained; the spectrum of the polystyrene film is taken and checked for the accuracy and transmittance. The best spectrum for each site was considered as a representative spectrum of the site. The typical spectrum is given in Fig-2.

RESULTS AND DISCUSSION

3.1. Mineral Analysis by FT-IR study

By comparing the observed frequencies with the available literature, the different types of inclusions were identified in the potsherds such as quartz, orthoclase, albite, kaolinite, montmorlinte and hematite. The assignments have been made on the basis of characteristics IR absorption bands of the minerals [5-9]. The observed IR absorption frequency in the region of 400-4000 cm^{-1}of the ancient potteries of Thiruverkadu together with minerals identification is given in Table-1. The main constituents of mineral in potsherds were quartz with the bands detected at 795, 775 & 695cm^{-1}.The clay minerals such as kaolinte and montomorilinte were identified by the presence of the peak at 1035, 1635 & 3440cm^{-1} respectively. The presence of orthoclase (640 & 545cm^{-1}) and albite (435 & 405cm^{-1}) indicates feldspar group of minerals in the samples. The iron oxide mineral hematite (475 & 540cm^{-1}) is inferred from the i.r. absorption bands. Our results are good in agreement with the reported value of the mineral composition of pottery by De Benedetto et al [10]. Table 2 list the infrared absorption frequencies and Probable assignment of ancient potteries of Thiruverkadu, Tamilnadu

The FT-IR spectra of the received state shows no characteristics absorption band for the inner hydroxyl water at 3700 and 3630cm^{-1} indicating that these samples would have been fired to a temperature of 800ºc . The bands appeared at 3440cm^{-1} along with 1635cm^{-1} attributed to adsorbed water molecules during long burial or during records the spectra [11].

The presence of organic matter was identified in the samples by the presence of the peaks at 2855 & 2925cm^{-1}. This indicates that the amount of organic contribution is higher in red part. As stated by Maritan and Columbini [12-13] weak bands around 2925cm^{-1} and 2855cm^{-1} in all the samples may be observed as C-H stretching probably induced by residuals of organic matter (Wood, Flour etc) adsorbed by the material. The amount of organic contribution is higher in red part in comparison with the black decoration part. The bands observed at 2925cm^{-1} and 2855cm^{-1}(γCH) in all the samples indicates the presence of organic contribution and hence the samples in our study is red part may contain higher amount of organic contribution.

A strong band at 1100-1000cm^{-1} region centered at 1035cm^{-1} indicates the presence of silicates (Si-O) in clay materials. This strong band around 1035cm^{-1} has been assigned to Si-O stretching of Silicate band. This band indicates that the clay is in disordered condition, possibly due to the iron substitution which leads to red clay [14]. Quartz is the most common abundant mineral in the constituent of clay mineral. The presence of the i.r. absorption band at 775cm^{-1} is quartz and it is assigned the Si-O quartz band [11]. Quartz and feldspar are often present in clays or added as temper.

The well resolved peak at 475cm^{-1} in the spectra of the received state in the samples reveal the presence of iron oxide (hematite) which also confirms the firing temperature as above 600ºc.This peak indicate the presence of hematite. The potteries collected from the Thiruverkadu were Red slipped/Red ware in colour and shows that the presence of hematite and hence fired in the oxidizing atmosphere at the time of the manufacture [15]. The presence of band at 540cm^{-1} attributed to Si-O-Al bending vibration is due to the presence of residual Al in octahedral sheet. This band is attributed to hematite and being an indicative of iron oxides formed during firing processes, due to the replacement of aluminum by irons around 600ºc [16-17].

It is obvious from the analysis that the pottery samples collected at Thiruverkadu is made of secondary mineral quartz and various accessory minerals albite, orthoclase, kaolinte & montmorlinite, iron oxide mineral such as hematite. By analyzing the mineral trapped in the sample one can elucidate its firing temperature. The detailed discussion about the estimation of firing temperature of the pottery is discussed below based on the IR absorption band in the received state of the ancient pottery.

3.2. Firing temperature Analysis using FT-IR study

Potteries are made up of clay minerals which are found in sheet structure. When the pottery is fired, the sheet structure gets collapsed depending on the level of temperature of firing and firing conditions, which can be monitored by using FT-IR study.

The band at 3700cm^{-1} is due to symmetric stretching vibrations of the hydroxyl groups. On firing the clay, the onset of dehydroxylation of octahedral layer of clay minerals is clearly reflected by a marked alternation and disappearance of the above bands in between 400-600ºc. When clay is fired between 300ºc and 500ºc dehydroxylation of octahedral layers of most clay minerals takes place [18] and at 600ºc, silicate structure collapses and a broad symmetry band is observed at 1030cm^{-1} for red clay and 1080cm^{-1} for white clay [14]. According to Mendelovici et al [19] the absorption band around 3630cm^{-1} is due to crystalline hydroxyl groups which persist only up to 800ºc.

The FT-IR spectra of the received state samples taken for the present study do not show any absorption band at 3630cm^{-1} indicating that these samples would have been fired to a temperature of 800°c or above. The presence of band around 1035cm^{-1} in the received state indicates that the samples have been fired above 600 ºc and made up of disordered clay. The above results can also be confirmed with the bands at 915 and 875cm^{-1}. The band at 915cm^{-1} is due to Al (OH) vibrations in the octahedral sheet structure which begins to disappear with increasing temperature, and at 500°c the bands disappear completely [20-21]. None of the samples taken for the present study showed the band at 915cm^{-1}. This implies that all the samples were fired above 500°c. According to Yariv and Mendelovici [22], a shoulder band at 875cm^{-1} indicates dehydroxylation of kaolinte minerals which are completed at 800°c and the octahedral sheet structure in the clay minerals disappeared. None of the samples showed the presence of the peak at 875cm^{-1} indicating that the samples were fired above 800 ºc.

The well resolved and distinct peak at 540cm^{-1} with weak intensity attributed the presence of hematite and reveals the presence of iron oxide which also confirms the firing temperature as above 600ºc. The presence of hematite indicating that these samples were fired in the open air or perfectly oxidizing atmosphere at the time of the manufacture [23]. At the same time, air has been allowed at a higher temperature during cooling which enabled the oxidization of iron components formed during reduced atmosphere, the reason or the red color of the pottery. Further the red colouration is due to hematite.

The colour of the pottery is due to the content of iron oxides which acts as the coloring agent. Yariv and Mendelovici[22], Mirti et al [24-25] and Piero Mirti and Patrizia Davit [26] observed that colour of the potteries is due to hematite which is red brown solid and decides the atmospheric conditions (oxidizing/reducing) where the artifacts were fired. The potteries collected from the Thiruverkadu were Red slipped/Red ware in colour and shows that the presence of hematite and hence fired in the oxidizing atmosphere. The presence of hematite in the in the studied samples of the mineral analysis supports the above statement. Table-3 lists the estimation of firing temperature of ancient pottery shreds excavated at Thiruverkadu.

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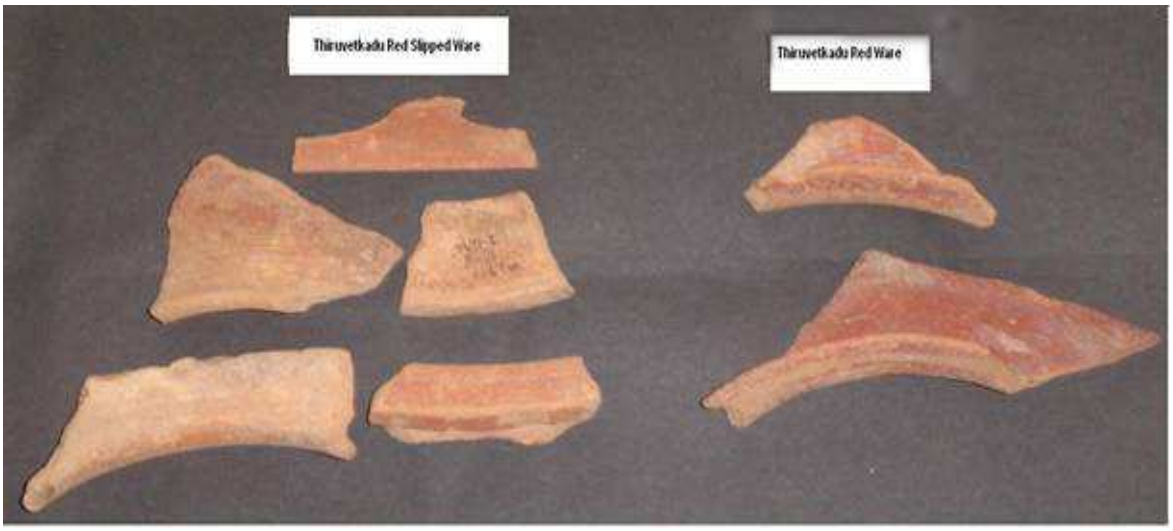

Fig-1. Typical Collection of Potsherds of Thiruverkadu of Tamilnadu

Table-1 Observed Absorption Frequency in the region of 400 – 4000 $cm^{-1}$of the ancient potteries of Thiruverkadu together with minerals identification

Sample No	Silicate Mineral	Feldspar Mineral		Clay Minerals		Iron Oxide Mineral
	Quartz	Orthoclase	Albite	Kaolinite	Montomorilinte	Hematite
TVDRS1	775 795	545 640	405 435	1035	1635 3440	475
TVDRS2	775	545	435	1035	1635 3440	475
TVDRS3	775 795	545 640	405 435	1035	1635 3440	475
TVDRS4	775	545	435	1035	1635 3440	475
TVDRS5	775 795	545 640	435 405	1035	1635 3440	475
TVDR1	695 775	545 640	435 405	1035	1635 3440	475 540
TVDR2	695 775	545 640	435 405	1035	1635 3430	475 540

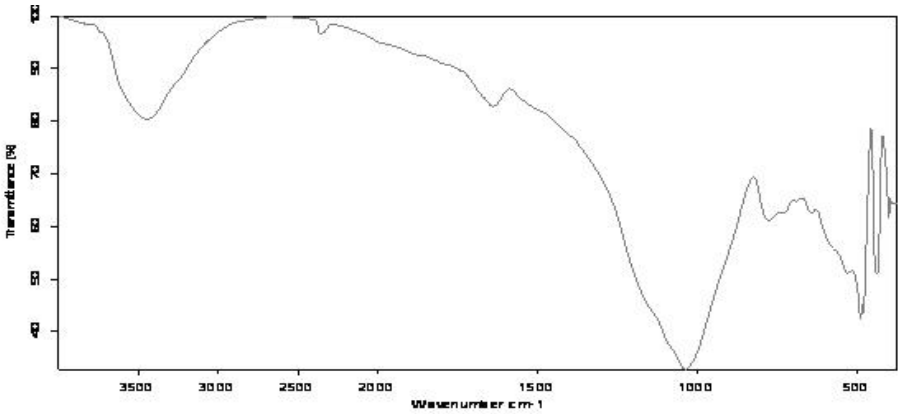

Fig-2. A typical FT-IR spectrum of Ancient pottery o f Thiruverkadu

Table.-2 Infrared absorption frequencies and Probable assignment of ancient potteries of Thiruverkadu, Tamilnadu

Frequency (cm^{-1})	Mineral Name	Tentative Assignment	Reference
3440	Montmorillonite	O-H- Stretching of absorbed water molecule	Ravisankar et al (2010) {8]
1035	Kaolinte	Si-O-Stretching of clay mineral	Ravisankar et al (2010) {8]
775	Quartz	Si-O symmetrical stretching vibration	Ravisankar et al (2010) {8]
545	Orthoclase	Fe-O of Fe3O4	, Ravisankar et al (2010) {8]
475	Hematite	-	Ravisankar et al (2010) {8]-
455	Quartz	Si-O asymmetrical bending vibration	Ravisankar et al (2010) {8]-
435	Albite	Si-O of mixed vibration	Ravisankar et al (2010) {8]-
405	Albite	-	--

Table 3 Estimation of firing temperature of Pottery Shreds excavated at Thiruverkadu

Sample ID	Colour	Type of the clay	Atmosphere Prevailed	Octahedral sheet structure	Estimation of firing temperature
TVD RS1	Red Slipped Ware	Red clay	Oxidizing	Completed	>800ºc
TVD RS2	Red Slipped Ware	Red clay	Oxidizing	Completed	>800ºc
TVD RS3	Red Slipped Ware	Red clay	Oxidizing	Completed	>800ºc
TVD RS4	Red Slipped Ware	Red clay	Oxidizing	Completed	>800ºc
TVD RS5	Red Slipped Ware	Red clay	Oxidizing	Completed	>800ºc
TVD R1	Red Ware	Red clay	Oxidizing	Completed	>800ºc
TVD R2	Red Ware	Red clay	Oxidizing	Completed	>800ºc

CONCLUSION

The mineral characterization studies on recently excavated ancient potteries of Thiruverkadu. Tamilnadu was carried out by FT-IR technique. The performed analysis revealed the presence of minerals in potteries. Quartz, orthoclase, albite, hematite and kaolinte were detected in the samples. The potteries collected from the Thiruverkadu were Red ware in colour and shows that the presence of hematite and hence fired in the oxidizing atmosphere. From the above analysis, one can say that the artisans have fired the samples greater than 800°c under open atmosphere which is also reflected from the red color of the sample. Red clay was used for making of the pottery samples.

Application of FT-IR spectroscopic for the study of the archeological pottery shows great potential for understanding technological conditions implemented for the production of pottery and was found to give useful information about the mineral composition of the pottery. The future work plans to determine the firing temperature studies and dating of the potteries using different techniques.

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