



Spectroscopy studies of archaeological pottery samples recently excavated From Pilaiyarpalaiyam site in Tamilnadu, India

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ABSTRACT

These studies focus on firing temperature and mineralogical analysis of the ancient pottery sample collected from the recently excavated site Pilaiyarpalaiyam in Tamilnadu, India. Clay was prepared which consists of quartz, kaolinite, illite, chlorite, feldspars and iron oxides. The samples were subjected analysis as in the received state. The characterization studies for the analysis of the composition of the pottery using FT-IR and XRD analysis reveals the skill and style of the artisan lived in the ancient civilization. The firing temperature and the firing conditions adopted at the time of manufacturing of the pottery also determined. The Pilaiyarpalaiyam samples might have been fired in the range of 800 °C.

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Introduction

Archaeologists have been, for many years, interested in the provenance of pottery fragments, since the pottery is the most abundant tracer in all archaeological excavation. The classification at any level of such manufactures has a key role in historical studies. The analysis of pottery can indeed supplement the information gathered from written documents to produce a better knowledge of trade routes linking populations of different areas, which is one of the essential in gradients for the comprehension of their history.

Analyses of archeological objects bring us much information on the development and propagation of the cultures and the technologies of the human event. Archaeometrical studies for ceramics focus on some topics such as (i) dating (when was the artifact produced?), (ii) provenance (where was the artifact produced?) and (iii) technology (how was the artifact produced?). The results of systematic researches in archaeometry may contribute to the archaeological documentation. This seems to be an important piece of information about the development of ceramics manufacturing throughout history. The use of trace element analysis to characterise geological samples is a regular practice within geological science and one which has also been effectively utilised in archaeological studies to match particular clay sources to archaeological ceramic building material such as pottery and tile (e.g. Mallory-Greenough et al., 1998; Meloni et al., 2000; Gomez et al., 2002; Montana et al., 2003) as well as pottery (e.g. Beier and Mommsen, 1994; Montana et al., 2003; Vince, 2004, 2007; Vince and Steane, 2004).

Provenance studies of these materials have been fundamental in reconstructing past resource procurement and utilization strategies (Bressy et al., 2008; Eerkens et al., 2007) and testing hypotheses regarding aspects of social organization such as trade

And mobility (Phillips and Speakman, 2009; Weisler, 1994; Weisler and Kirch, 1996; Weisler and Woodhead, 1995). Petrography, mineralogy, and geochemistry are useful tools in provenance and technology studies of ancient pottery, which are often debatable when based only on archaeological evidence. Although information on the spread of a given ceramic class

may be derived from regional correlation of potsherds from known stratigraphic contexts, the evidence of local production is generally rare and is connected with findings of pottery wastes in a kiln context. The identification of petrographic and geochemical reference groups, the analysis of lithologies and composition of inclusions, and the comparison with local clayey materials and rock types outcropping in the area surrounding the archaeological study site can all provide additional constraints to the provenance problem and to the identification of possible trades. When written documents are missing, pottery may actually represent the only available marker of provenance. In addition, analysis of mineral assemblages in the potsherds constrains identification of specific technological aspects, such as maximal temperature, redox conditions, and firing times (Bimson, 1969; Philpotts and Wilson, 1994). In the present work was focused on production technology of pottery bodies, raw materials used in manufacturing, firing temperature and firing environment.

Objectives

This study aims to determine the chemical and mineralogical characteristics of a collection of coarse wares from Pilaiyarpalaiyam in order to distinguish local products and imported ones. The identification of artefacts locally produced is the most important objective. The further identification of local products (the Pilaiyarpalaiyam and surroundings), this contexts may provide information about patterns of imports or exports over short, medium and long distances, firing temperature and firing atmosphere and also conformed skill of ancient artisans technological aspect there are used to making pottery.

Materials and methods

The Pottery samples were collected from archaeological site at Pillayarpalayam, Kanchipuram in Tamilnadu, India. The pottery samples of interest were collected at different depths and are named as PP1, PP2, PP3, PP4, PP5 and respectively PP6. The Fourier transform infrared spectra of the pottery samples were recorded in the mid frequency region 4000 - 400cm⁻¹ using Bruker FT-IR spectrophotometer by KBr pellet technique. The samples were palletized by mixing with the spectra grade KBr at

the ratio of 1:20 by weight. The KBr pellet of 13mm diameter was kept inside the sample holder and scanned at 2cm^{-1} resolution, which is commonly, used standard laboratory investigation as it covers almost all the Vibrational frequencies [1]. PP1-PP6 samples of the potsherd samples were used for the XRD analysis. The X-Ray Diffraction (XRD) was employed for the semi-quantitative mineral identification of the colored surfaces of the pottery slips. Samples were carefully placed horizontally on a special holder, so as to analyze the pigmented surfaces of the sherds non-destructively. The Powder X analytical software was used for the semi-quantitative determination of the mineral phases. The characterization studies for the analysis of the composition of the pottery using FT-IR and XRD analysis reveals the provenance, skill and style of the artisan lived in the ancient civilization. Table 1 shows Description of depth wise details of Pilaiyarpalaiyam Pottery sample.

Result and Discussion

FT-IR Spectral analysis

FT-IR spectroscopy has been a frequently used method for to investigate the structure, bonding, Mineral composition and chemical properties of clay minerals [2]. To get the final products of the pottery are heated to higher temperatures and as a result thermal changes are taking place mainly on structure and bonding of the clay minerals, which can be studied using FT-IR spectroscopy [3]. The FT-IR spectra of the samples recorded in the range of 4000 to 400cm^{-1} collected from Pilaiyarpalaiyam for present study.

The recorded FT-IR spectra of the samples PP1, PP2, PP3, PP4, PP5 and PP6 respectively are shown in Fig. 2. The tentative Vibrational assignments of IR peaks as received state of the samples are given in Table 2. From FT-IR spectra of the pottery samples of firing temperature estimated. According to Ross et.al (1931), The FT-IR absorption band around 3630cm^{-1} is due to hydroxyl groups which persist up to 800°C . Pilaiyarpalaiyam pottery samples did not show on absorption band at 3630cm^{-1} this result indicating that they would have been fired to temperature 800°C . The above result can also confirmed by the bands present at 915cm^{-1} and 875cm^{-1} . The band at 915cm^{-1} Al (OH) vibrations in the octahedral sheet which begin to disappear with increasing temperature. At 500°C band is completely absent [4].

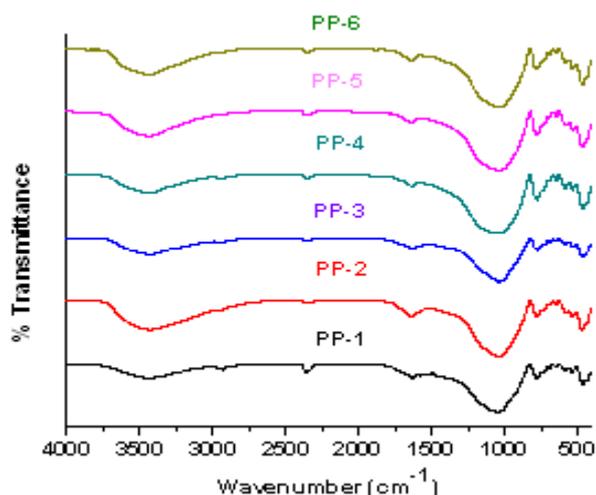


Fig. 2. FT-IR spectra of PP1-PP6

None of the samples of the present study showed the band at 915cm^{-1} implying that all samples were fired above 500°C . The samples PP1-PP6 have Si-O stretching clay minerals, which

indicated due to the absorption bands at around 1040 and 1042cm^{-1} [5,6]. The FTIR spectra were recorded at room temperature. As shown in Fig. 2, the Si-O stretching band shifts towards higher frequencies and broadens with increasing temperature 1042cm^{-1} at 800°C . This evolution of the FTIR spectra with temperature, as well as the changes in the position and width of the Si-O stretching band and its splitting pattern are in very good agreement with the existing literature (Shoval, 1994). To be precise two different absorptions of wave number around 1040cm^{-1} caused by silicate band indicate that the firing temperature ranges achieved would be 800°C [7]. According to Velraj et al, it is reported that the absorption band around 535cm^{-1} is due to hematite present in the shred [8]. Therefore the band observed at 535cm^{-1} in the present samples PP-1, PP-4, PP-5, and PP-6 shows presence of hematite and this band does not appear in PP-2 and PP-2 indicates the absence of hematite in the sample.

The IR spectra of the all the samples shows a medium band around 466cm^{-1} which indicates the presence of microcline (Kieffer S W, 1979 and Ciancio 1994). The broad band absorption bands at 580°C and 540°C have been indicated that the magnetite and hematite (Barillaro et.al) reducing and oxidation atmosphere condition adopted in firing pottery samples. The amount of magnetite and hematite indicate that skill of ancient people using firing condition of the clay samples fired.

XRD spectral analysis

The XRD patterns taken on the specimens of ancient pottery excavated from Pilaiyarpalaiyam are presented in Fig.3. The patterns thus obtained are compared with standard dataset of the Joint Committee for Powder Diffraction Standards (JCPDS), for the identification of crystalline mineral phases and the results are depicted in Table 2. Quartz, Feldspar is present in all the PP1-PP6 samples. The XRD analysis for identifying the composition of minerals and firing temperature. From the observed diffraction peaks it is identified that the samples having minerals such as Feldspar (4.202A°), Kaolinite (3.755A°), Gluconite (3.691A°), Quartz (3.316A°), Plagioclase (3.202A°), Sepiolite (3.153A°), Dickite (2.907A°), Orthopyroxene (2.473A°), Illite (2.291A°), and Silicon oxide (1.973A°).

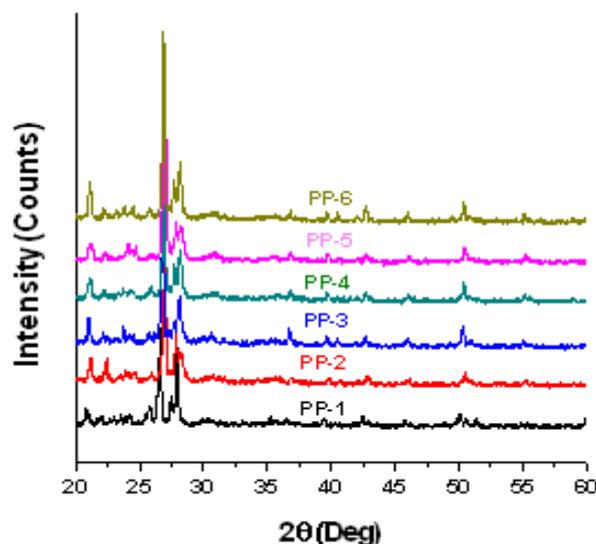


Fig. 3. XRD Pattern of PP1-PP6 Pottery sample

Calcite decomposition into CaO and CO_2 begins around 650°C and it is completed upto 900°C .

Table 1. Description of pottery samples excavated in Pillayarpalayam

Sample code	Depth (m)	Physical characteristics
PP1	1.20	Red ware, Both the surfaces are polished, thickness 5 mm.
PP2	1.33	Red ware, Both the surfaces are polished, thickness 4 mm.
PP3	1.50	Red ware, Both the surfaces are polished, thickness 5 mm.
PP4	1.65	Red and Black ware, Both the surfaces are unpolished, thickness 6 mm.
PP5	2.07	Black ware, Both the surfaces are unpolished, thickness 5 mm.
PP6	3.50	Red and Black ware, Both the surfaces are unpolished, thickness 7 mm.

Table 2. Infrared absorption frequencies (cm⁻¹) of Pillayarpalayam Pottery samples with tentative Vibrational assignments

PP 1	PP 2	PP 3	PP 4	PP 5	PP 6	Tentative Vibrational Assignments
Frequency (cm ⁻¹) & Relative intensity						
3444 S	3423 S	3424 S	3442 S	3443 S	3442 S	H-O-H bending of water.
1628 M	1632 M	-	1630 M	1636 M	1639 M	H-O-H bending of water.
1042 S	1039 S	1035 S	1042 S	1041 S	1039 S	C-O stretching vibrations
776 S	776 S	777 S	777 S	777 M	776 S	Si-O quartz
-	-	-	646 W	646 W	646 W	Si-O-Si bending. Gehlenite
582 S	-	-	583 M	-	-	Fe-O of Magnetite
535 S	-	-	537 M	532 M	533 S	Fe-O of Hematite
464 S	463 S	463 S	463 S	464 S	465 VS	Si-O microcline

V.S – Very Strong; S – Strong; M – Medium; W – Weak; V.W – Very Weak;

Trindade et al. concluded that the decarbonation of calcite may extend to 1100 °C for calcite rich systems [9]. On the other hand, secondary calcite may occur in ceramics as a result of post-burial deposition processes due to recarbonation of lime [10]. Dolomite decomposes in two stages beginning at around 650 °C. After the decomposition of dolomite into calcite and magnetite, decarbonation of dolomite is completed up to 750–800 °C [11–13].

When both calcite and Fe are present during firing, it is also established that the new formation minerals gehlenite (Ca₂Al(AlSi)O₇), wollastonite (CaSiO₃), and diopside (CaMgSi₂O₆) can incorporate. Powder XRD pattern have good evidence with supported in FT-IR studies in this result indicate the firing temperature below 800 °C all samples [14]. Since the presence of Feldspar, Quartz and Dickite in all the samples, these might have been fired at below 900 °C. Besides the mineral kaolinite presents in the samples PP2-PP6 informed that these might have been fired below 800 °C because Kaolinite starts to decompose at 800 °C [15–16]. These results are good correlation with FTIR results.

Conclusion

The hematite present in the samples confirms the oxidation atmosphere presences by the artisans and the magnetite present in the samples confirm the reducing atmosphere adopted by the artisans during the time of manufacturing the pottery. The firing temperature achieved by the artisans at this site around 800 °C and also they were well aware of firing the pottery both oxidizing atmosphere and reducing atmosphere (close kiln).

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