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Determination of firing temperature of some ancient potteries of Tamil Nadu, India by FT-IR Spectroscopic technique

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Abstract
Archaeological artifacts such as potteries, bricks and tiles are the source of information about the ancient civilization, their technological skills and cultural trade etc. Pottery is one of the oldest human technology and art-form that remains as a major industry even today. The potteries are made of clay minerals and kaolinte is the common mineral in pottery making. The firing temperature of ancient potteries is based primarily on changes of physical characteristics occurring when clay minerals are heated. The study of thermal transformations of the clay minerals can thus help in determining the firing temperatures of the potteries. In the present work, the estimation of firing temperature of the recently collected potteries from Melchittamur of Tamil Nadu is determined by FT-IR spectroscopic technique. The mineral composition and firing condition are inferred from the FT-IR spectrum. To estimate the upper limit of firing temperature of pottery fragments, the specimens were refried at different temperatures and the FT-IR spectrum was recorded from the samples. The interpretation of results is made from the IR characteristics absorption bands. Results are discussed and the conclusion is drawn.

Keywords: Ancient pottery, clay, FT-IR, firing temperature.

Introduction

One of the most important areas of archeology is the identification of the source and the origin of ancient artifacts. Archeological artifacts like potteries, bricks and tiles are of the earliest and most significant innovation of mankind. The systematic scientific study of the above artifacts reflects the technological development, their civilization and trade links between different countries during the past. Archaeometry includes studies about dating, authentication, conservation and restoring, as well as provenance and the achievement of technological information about handmade article manufactures. Various spectroscopic and magnetic studies are mostly widely used for the study of archeological artifacts like potteries, bricks and tiles.

Most archaeologists have classified ancient artifacts (pottery) by their shapes and uses. The main ingredients of pottery are clays to which tempering materials are some time added during manufacture. The clay, shell, sand etc from which pottery were fashioned can have a chemical composition which is unique and thus reveals the local source from which they were taken. The potteries are made of clay minerals and the common major clay mineral used in making potteries is kaolinte. Firing clays, which contain 40-80% of silica, makes pottery. Thermal transformations in clay materials during firing provide a means to estimate the firing temperature of the artifacts. Several methods of thermal analysis are used in the laboratory to determine, the firing temperature of ancient potteries which are based primarily on changes of physical characteristics occurring when clay minerals are heated. The firing temperature of the ancient pottery provides basics for understanding many aspects of ancient technology such as manufacturing techniques and functional relationships between specific resource manufacturing combinations.

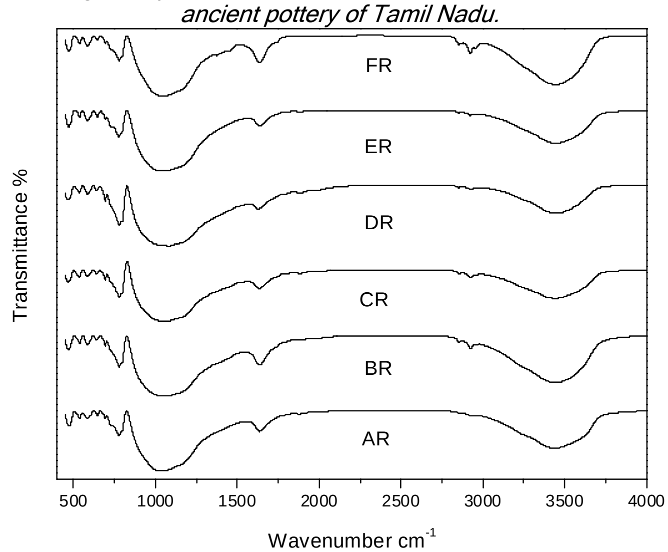
To study the materials used for firing, the technology of firing (either controller firing or open firing) and art of controlling the firing spectroscopic techniques are widely used. The transformation of iron bearing minerals during the firing of ancient wares by Tominaga *et al.* (1978), Kostikas *et al*. (1976), Makundi *et al.* (1979), Eissa *et al*. (1979), Longworth and Tite (1977) using Mossbauer spectroscopy. Infrared spectroscopic studies on archaeological materials were carried out by Eissa *et al.* (1979) and Maniatisa *et al.* (1972). In the present study infrared spectroscopy is used to study the firing temperatures achieved by the ancient people and the firing techniques employed by them. The dehydroxylation of kaolinte minerals was first studied by Ross and Kerr (1981). According to their Differential thermal analysis (DTA) results, dehydroxylation takes place at temperatures between 400°C and 525°C. A small amount of water can persist up to 750°C or 800°C at which dehydroxylation is complete. Dehydroxylation of kaolinte was studied by Prost *et al*. (1989) also using infrared spectroscopy. They observed that among the hydroxyl bands in 3700-3800 cm^{-1} region the bands at 3675, 3650 and 3630 cm^{-1} persist after firing to temperature of 327°C. According to Elass and Oilver (1978) on heating, kaolinte the intensity of bands of 3700-3800 cm^{-1} region decreases and at 500°C only a weak broad band remains in the 3600 cm^{-1} region. The thermal behavior of the bands due to hydroxyl groups in clay artifacts were studied by Maniatis *et al.* (1972) also. They observed that the clay minerals begin to lose their crystalline hydroxyl groups and start disorganizing at temperatures in the range 400-600°C and for some minerals it can continue up to 800°C. According to them the persistence of a weak band around 3600 cm^{-1} indicates the presence of iron hydroxyl still in the clay body and points to incomplete dehydroxylation.

The transformation of the clay minerals during heating is reflected in the 1100-1000 cm^{-1} region also. As the temperature is increased there is gradual destruction of the layer structures of the mineral. The bands at 1100cm^{-1} and 915 cm^{-1} due to Al(OH) vibration (Prost *et al.,* 1989) in the octahedral sheet structure begin to disappear with increasing temperature and at 500°C the band at 915cm^{-1} disappears completely (Miller, 1961; Elass & Oilver, 1978). This dehydroxylation is followed by crystal frame work collapse and tetrahedral sheet disorder can be seen from the broadening of the Si-O stretching band in this 1100-1000 cm^{-1} region. The weak shoulder band observed at 875 cm^{-1} in the spectra of iron rich clay minerals have been attributed to Fe(AlOH) group present in the clay mineral (Mendeluvici *et al.,* 1979). The presence of this group indicates the persistence of the octahedral sheet structures in the clay mineral, indicating incomplete dehydroxylation and thus firing temperatures below 800°C as at 800°C the dehydroxylation of kaolinte mineral are completed (Maniatisa *et al.,* 1972; Ross & Kerr, 1981). However, this band is observed only in iron rich clay minerals (Mendeluvici *et al.,* 1979). Based on the above discussion, it is obvious that IR study of potteries one can characterize the structural composition of clay minerals, mineral constituents, determine the firing temperature of the specimens and trace the origin of the specimens from the nature of the clay minerals used. All these information provides a clue to the trade and cultural links of the artisans. So the present work aims to identify the constituent of mineral present in the ancient potteries and also to estimate the firing temperatures using FT-IR technique.

Material and methods

The samples were collected from the recent excavation site Melchittamur of Tamil Nadu, India at different depths and the site named as AR, BR, CR, DR, ER, FR, GR, HR, IR, JR, KR, LR and MR for identification. The samples were taken at depth of 0.14m, 0.20m, 0.21m, 0.22m, 0.24m, 0.25m, 0.29m, 0.31m, 0.37m, 0.45m, 0.70m, 0.71m and 1.08m from soil surface. After removal of surface layers, the potsherds were grounded into fine powder using agate mortar. They were sieved using a 90 µm mesh to obtain uniform particle size for different analysis. The major and minor minerals are qualitatively determined by FT-IR technique. The Perkins Elmer-1600 series available in sophisticated analytical instrument facility in Indian Institute of Technology, Chennai, Tamil Nadu, India is made use for recording i.r. spectra of the samples at room temperature in the received state. The KBr pellet technique (1:20) pellets were followed for the mineral analysis. For each samples five to six pellet specimens are prepared and the spectra were taken in the mid region of 4000-400 cm^{-1}. The refired samples are also recorded by the same technique and the representative of spectrum is shown in Fig.1.

Fig. 1. A typical FT-IR spectrum of refired samples of ancient pottery of Tamil Nadu.



Results and discussion

Mineral analysis

By comparing the observed frequencies with the available literature, the different types of inclusions were identified in the potsherds such as quartz, orthoclase, albite, hematite, magnetite, kaolinite, calcite, gypsum, montmorillonite and illite. Table 1 lists the infrared absorption frequencies and probable assignment of potsherds of Tamil Nadu. The main constituents of minerals in potsherds were quartz with the bands detected at 795,775, 695 and 455cm^{-1}. The presence of orthoclase (635 & 545cm^{-1}), albite (435 & 405cm^{-1}) indicates feldspar group of minerals in the samples. Hematite (535 & 475cm^{-1}), magnetite (585cm^{-1}), kaolinite (3630, 3445, 1635, 1035 & 935cm^{-1}) and calcite (875 & 715cm^{-1}) were inferred from the IR absorption bands. The assignments have been made on the basis of characteristics IR absorption bands of the minerals (Farmer, 1974; Karr, 1974; Ghosh, 1978; Lyon,1967; Russell, 1987; Tuddenham, 1960; White, 1971; Xu *et al.,* 2001; Ravisankar, 2009; Ravisankar *et al.,* 2010). Our results are good in agreement with the reported value of the mineral composition of pottery by De Benedetto *et al.* (2002).

Firing temperature analysis

The firing temperature study of potteries is reported by many workers (Palanivel & Velraj, 2003; Tite, 1969; Velraj *et al.,* 2009; Velraj *et al.,* 2009). From the spectrum of the received samples from Melchittamur shows the absorption of kaolinte band around at 3630 cm^{-1} and 3445

Table 1. Infrared absorption frequencies & probable assignment of potteries of TN.

Frequency (cm^{-1})	Mineral name	Tentative assignment
3630	Kaolinte	O-H- Stretching of inner hydroxyl
3445	Montmorillonite	O-H- Stretching of absorbed water molecule
1645	Kaolinte	H-O-H bending vibration of absorbed water molecules
1035	Kaolinte	Si-O-Stretching of clay mineral
935	Kaolinte	O-H deformation
875	Calcite	Fe^{3+} (Al-OH)
795	Quartz	Si-O Symmetrical stretching vibration
775	Quartz	Si-O symmetrical stretching vibration
715	Calcite	-
695	Quartz	Si-O symmetrical bending vibration
635	Orthoclase	Al-O coordination vibration
585	Magnetite	Fe-O of Fe_3O_4
545	Orthoclase	Fe-O of Fe_3O_4
535	Hematite	Si-O asymmetrical bending vibration
475	Hematite	-
455	Quartz	Si-O asymmetrical bending vibration
435	Albite	Si-O of mixed vibration
405	Albite	-

cm^{-1} from all the samples taken at different depths. The bands in this region are due to crystalline hydroxyl present in the clay mineral structure. According to Prost *et al.* (1989), the absorption band around 3630 cm^{-1} persists after heating to 500°C. From the point of view of Prost *et al.* (1989), the samples might have been fired to 500°C as its lower limit. The absence of the absorption band at 915 cm^{-1} indicates the firing temperature is above 500°C. To narrow the gap between the two limits for firing temperature a refiring study is conducted. It is known that once clay is fired at a certain temperature and then cooled down, it freezes at a stage which cannot be further altered by subsequent refiring unless the initial temperature is exceeded. This property of clays provide a mean for estimating the firing temperature reached by a pottery in antiquity and this determination can have a possible small error only due to the fact that the original firing schedule and atmosphere cannot be replicated exactly. For the purpose, the samples were fired in the laboratory to temperature 250°C, 500°C and 750°C for one hour using muffle furnace. The spectra are then recorded with these refired samples. A comparison of the spectra of refired samples with that of the 'as received state' samples reveal the following. The absence of inner hydroxyl bands at 3700 cm^{-1} and Si-O-Al band (915 cm^{-1}) indicates that all the samples were fired above 450°C during manufacturing (Prost *et al.,* 1989; Elass & Oliver, 1978; Miller, 1961). The presence of weak broad band at 3445 cm^{-1} coupled with 1645 cm^{-1} in all the samples indicate the presence of absorbed water molecules which are due to long burial (Wolf, 1963; 1965; Ramasamy & Kamalakannan, 1987; Ramasamy & Venkatachalapathy, 1992). A broad symmetry band centered around 1030 cm^{-1} in all the samples indicates that the destruction of octahedral sheet structure have taken place around 650°C. In all above the samples the absorption band at 475 & 535 cm^{-1} and 585 cm^{-1} attributed to hematite and magnetite respectively are of in varying intensity and also it indicates the iron components are dissolved in water due to long burial of the samples. The band at 475 cm^{-1} due to Si-O band remains unchanged during heating, which reflects that this band is free from any temperature effects. In all the refired samples, the presence of band at 535 cm^{-1} and 585 cm^{-1} at 750°C indicates the completion of reoxidation of iron compounds. At 750°C, the lattice iron is liberated and more iron oxides are formed which are established from the sharp bands at 535 cm^{-1} and 585cm^{-1}. Firing at 700°C results in the appearance of magnetic components either poorly crystallized or substituted hematite (Kanchan *et al.,* 1986; Maniatis *et al.,* 1981, 1983). In all the refired samples, sharp bands observed at 535 $cm^{-1}$and 585 cm^{-1} exist even up to 750°C indicates the complete oxidation of iron compounds which reveals the oxidizing atmospheric condition with firing temperature of above 750°C during manufacturing. From the above discussion one can say that the samples might have been fired around 750°C in reduced atmosphere.

The presence or absence of the IR absorption peaks in all the received state as well as refired samples indicates that they may be belonging to the same state of origin and also it gives an information about they are not belonging to different origin. This may be due to the raw materials used for the production of potteries of same materials in the same place of the origin. The presence of quartz gives information about the origin of the potteries; quartz was used in piedmont for covering of engobed pottery, while kaolin was used elsewhere for the same purpose. The presence of quartz is then a confirmation that the samples come from piedmont; on the contrary it is not possible to state that the findings not showing quartz inclusions do not belong to the piedmont area: the performed samplings cannot account for the complete absence of quartz inclusions in the whole pottery. The presence of quartz in the largest part of the samples confirms thus the common origin of these samples.

Conclusion

The mineral characterization of ancient potteries of Tamil Nadu was carried out by FT-IR technique. The performed analysis revealed the presence of mineral in potteries. Quartz, orthoclase and kaolinte were detected in all the samples. The presence of quartz gives information about the origin of the potteries. The major clay mineral used in making potteries is kaolinte. The study of thermal transformations of the clay minerals can thus help in determining the firing temperatures of the potteries. The samples were fired at different temperatures and the spectra are then recorded with these refired samples. A comparison of the spectra of refired samples with that of the 'as received state' samples reveal the firing temperature of the potteries. Spectroscopic results indicate that all the potteries were fired to a temperature less than 800°C in oxidizing atmosphere. The advantages of the proposal of FT-IR approach with respect to the traditional one are tremendous and preparation (no acidic dissolution is necessary), experimental procedure, cleanliness and simplicity) and analysis time. It was possible to infer the fundamental information like technological condition implemented for production of pottery and found to give useful information about firing temperature of the potteries.

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