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Advances in Applied Science Research, 2012, 3 (2):776-779

ISSN: 0976-8610
CODEN (USA): AASRFC

Fourier transform infrared spectroscopic study of ancient brick samples from Salavankuppam Region, Tamilnadu, India

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ABSTRACT

Infrared spectroscopy can be a very useful technique for analysis of ceramic materials. It allows in assessing basic molecular and mineralogical composition as well as the firing temperature of the ceramics. In this paper, FT-IR spectra of recently excavated archaeological bricks from salavankuppam, Tamilnadu, India were studied with as received state to establish the type of clay minerals associated with the bricks, their origin and the art of firing adopted during manufacturing. From the tentative infrared vibrational assignments with relative intensity the mineralogical composition of the ancient bricks were evaluated and by studying the differences in mineral composition in the representative samples the firing temperature and conditions were interpreted. The results showed that all the samples have been fired above 600^{0}C.

Key words: Archaeological bricks; FTIR; Mineralogical composition and firing temperature.

INTRODUCTION

Archaeology is a scientific process of analyzing the material remains of sites and artefacts of cultures from the past [1]. Archaeological artifacts like potteries, bricks and tiles are the source of information about the ancient civilization, their technological skills and cultural trade links between continents [2]. Thousands of archives have been discovered, but an enormous amount of material has been lost. Only a fraction of available archaeological sites have been surveyed, and only a fraction of surveyed sites have been excavated. It is important to understand that remain as the primary source of authority [3].

Clay is widely available easily worked raw material that serves very well in its fired form. Among, bricks are the most popular building materials of human societies have ever put to use. From the first villages settled before the invention of pottery to many modern towns and cities, bricks have kept people warm in the winter and cool in the summer for thousands of years. Just bricks have provided human societies with an invaluable foundation [4]. The identification of these archaeological artifacts can be aided enormously by judiciary application of analytical techniques borrowed from a wide range of scientific disciplines.

For the present FT-IR analytical study it is being attempted to evaluate the sourcing clays, firing temperature and temper of the brick samples (artifacts) used by the ancient bricks at the time of manufacture. From the data and interpretation derived from the scientific approach using the infrared spectroscopic technique can help us to know the skill, technology and cultural sequence of the ancient people.

MATERIALS AND METHODS

Three ancient bricks (SLKB-1, SLKB-2 and SLKB-3) belongs to 3rd century AD were excavated from the archaeological site salavankuppam, Tamilnadu, India by Archaeological Survey of India (ASI), Chennai. Small fragments of the each brick sample (around 1mg) were powdered and pressed in KBr pallets. The infrared spectra of the brick samples were recorded in the mid frequency region 4000-400 cm $^{-1}$ using model Paragon 500, Perkin.Elmer spectrophotometer with 16 scan mode. The accuracy of the measurement is 4 cm^{-1}.

RESULTS AND DISCUSSION

Infrared spectroscopy provides data for assessing the firing temperature as well as the basic mineralogical composition of the brick under investigation. The infrared spectra of salavankuppam brick samples are shown in Figure 1. The tentative vibrational assignments have been made as listed in the Table 1. The relative intensities of the peak were determined after the baseline correction and the characteristic absorption peak values were noted.

(i) Mineralogical composition

From the infrared spectra an absorption band around 3440 cm^{-1} is an indicative of hydroxyl group present in the ceramic samples. This is always accompanied by a band around 1640 cm^{-1} assigned to H-O-H bending of adsorbed water molecules. Hence, the FT-IR spectra of the samples SLKB-1, SLKB-2 and SLKB-3 which show very weak, medium and strong absorption bands in the region 3441-3453 cm^{-1} along with the weak and medium absorption bands in the region 1627-1632 cm^{-1} are typical absorbance bands of water [5,6].

Continuing our spectroscopic study of the bricks collected from Salavankuppam locality in South India, our attention was focused on the specimen SLKB-2 containing calcite, one of the most widely spread mineral in the nature. It is well known that the vibrational spectra of carbonate minerals contain modes caused by symmetric stretching (ν_1), out-of-plane bending (ν_2), asymmetric stretching (ν_3), in-plane-bending (ν_4). The band corresponding to the vibrational mode ν_1 is theoretically IR inactive. In pure calcite, the bands of ν_2, ν_3, ν_4 appeared to be centered at 876, 1427, and 725 cm^{-1} respectively [7, 8]. Hence in the present work, the strong and weak bands due to the v_3 and v_4 modes in the spectra of SLKB-2 samples registered at 1435 and 727 cm^{-1}, respectively indicates the mineral calcite.

Ghosh had suggested that the position of the silicate band with intense absorption at 1080 cm^{-1} is due to white clay origin of kaolinite and that around 1025 cm^{-1} refers red clay origin [9]. If the absorption band around 1040 cm^{-1} probably due to the mixture of both red and white clay origin. Therefore very strong intensity band for the samples SLKB-2 and SLKB-3 observed at 1041 cm^{-1} and 1047 cm^{-1} respectively have been assigned to both red and white clay mixed origins and the appearance of very strong peak at 1082 cm^{-1} confirms the white clay origin in the briquettes coded SLKB-1.

The presence of sharp band around 790 along with 695 cm^{-1} in the IR spectra of the sample is due to the presence of quartz (Si-O) [5]. In addition, it is also specified by the presence of weak absorption band centered at 777 (cm^{-1}) [10]. Quartz and feldspar are often present in clays either because they are present already in the raw clay, or because they are added as temper. Hence, for the present investigation, each brick sample taken shows the presence of secondary mineral Quartz denoted by medium absorption band centered around 778 cm^{-1} for SLKB-1, 2 and strong absorption band at 794 cm^{-1} associated with weak band at 690 cm^{-1} for SLKB-3.

The accessory minerals magnetite and hematite is identified by the absorption bands around 580 cm^{-1} and 540 cm^{-1} respectively. These iron oxides are of low abundance in clay minerals and sometimes it may be difficult to identify in the infrared spectra due to the overlap of absorption bands of silicates [5]. Here, the iron rich compounds, magnetite and hematite is present in SLKB-1 and SLKB-2 which are evident from the weak absorption bands around 585 cm^{-1} and 535 cm^{-1} respectively except SLKB-3. The absence of the corresponding band in SLKB-3 may be due to the low abundance of magnetite and hematite and the overlap of silicate absorption bands.

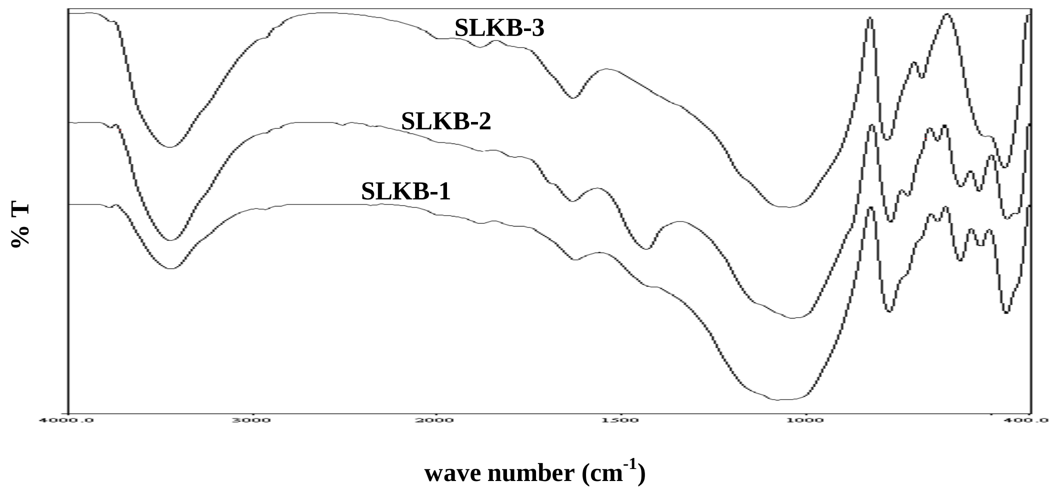

Figure. 1 FTIR spectra of the brick samples taken from salavankuppam site

Table. 1 Band components wave number revealed by the infrared spectra and their tentative vibrational assignments

Brick samples Frequency (cm^{-1}) with relative intensities			Tentative vibrational assignments
SLKB-1	**SLKB-2**	**SLKB-3**	
3446 VW	3441 M	3453 S	ν(OH) stretching of water
1627 W	1632 W	1632 M	δ(OH) bending of water
-	1435 S	-	C-O antisymmetric stretching of calcite
1082 VS	-	-	ν(Si-O) normal to the plane str. of clay minerals
-	1041 VS	1047 VS	ν(Si-O) planar str. of clay minerals
-	-	794 S	Si-O str.of quartz
778 M	774 M	-	Si-O-Si str. of quartz
-	727 W	-	C-O In plane bending of calcite
-	-	690 W	Si-O bend of quartz
647 VW	648 VW	-	Si-O-Si bending of silicates
586 W	584 W	-	Fe-O bend of magnetite
533 W	535 W	-	Fe-O bend of hematite
461 M	460 W	466 S	Si-O-Si bending

VW-very weak; W-weak; M-medium; S-strong; VS-very strong

(ii) Assessment of firing temperature and kiln atmosphere

Clay firing is one of the earliest technological operations of mankind. The clay minerals as well as associated minerals including iron oxides undergo characteristic chemical and physical changes during firing [11]. Hence, the firing temperature of the brick fragments can be determined with the help of the study of thermal transformation of the clay minerals present in them.

When clay is fired between 300–500 °C, dehydroxylation of octahedral layers of most clay minerals takes place [12]. At 600 °C, the silicate structure collapses and a broad symmetry band is observed at 1030 cm^{-1} for red clay and 1080 cm^{-1} for white clay type [9]. The absence of hydroxyl bands and the presence of broad symmetry band centered around 1080 cm^{-1} and 1040 cm^{-1} in the as received state spectra indicate that the brick samples SLKB-1, SLKB-2 and SLKB-3 have been fired above 600°C. The well resolved and distinct peaks at 540 and 580 cm^{-1} in the spectra of as received state in SLKB-1 and SLKB-2 reveal the presence of iron oxides. It also confirms the firing temperature as above 600 °C [13].

The most prominent band in all FT-IR spectra is the band due to the stretching Si-O mode. The position of this band is temperature dependent and thus influenced by the firing temperature of the objects [14] and appears at different frequencies in the spectra of the analyzed objects. In the IR spectra of the Salavankuppam brick finds, two different wave number ranges due to ν(Si-O) bands can be distinguished (~1050 cm^{-1} and ~1080 cm^{-1}) and consequently two different firing temperatures were estimated: between 700–800°C for SLKB-2 & 3, and between 800–900°C for

SLKB-1 [14]. The above result can also be confirmed with Calcite band. Calcite can serve as a diagnostic mineral to estimate the maximum firing temperature [15]. *Legodi and Waal* have stated that the presence of calcite at ARS confirms the processing temperature below 800^0C and above this temperature calcite decomposes to CaO and CO_2 [16]. Hence, in this investigation the brick sample SLKB-2 which contains calcite may be considered to be fired below the temperature 800^oC.

The presence of iron oxides in the region of 700-400 cm^{-1} formed during the firing process of clay is due to the replacement of aluminium by iron. Some iron oxides that do not normally occur in natural clays may form during firing of pottery. Magnetite may form during firing under reducing condition and hematite during oxidizing condition [17]. The prominent peak around 540 and 580 cm^{-1} in sample SLKB-1 and SLKB-2 reveals that the sample is fired under reduced atmosphere. At the same time, air has been allowed at a higher temperature during cooling which has enabled the oxidation of iron components formed during reduced atmosphere, the reason for the red colour of the brick. Allowing air during cooling is a common practice for coloration of the baked clays [9].

CONCLUSION

The infrared spectra of the studied brick samples showed that white clay material was used for preparing the SLKB-1. On the other hand, mixed red and white clay was used for manufacturing of the SLKB-2 and SLKB-3. From the FTIR studies, it is also concluded that all the samples have been fired above 600^oC under different atmosphere (reducing followed by oxidizing at higher temperature). Hence, the artisans belongs to Salavankuppam site have the ability to adopt two different atmosphere conditions while manufacturing process.

Acknowledgements
The authors wish to thank the Archaeological Survey of India (ASI), Chennai, Tamilnadu, for providing the archaeological samples for this research work. They also want to extend their heartfelt thanks to the staff-in-charge of CSIL (Centralized Sophisticated Instrumentation Lab), Annamalai University, Annamalainagar for recording the FT-IR spectra of the samples.

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