FT-IR Spectroscopy and X-Ray Diffraction Studies to Determine the Firing Temperature of Ancient Potteries Excavated at Gudnapur in Karnataka, South India

R.Ramya, G.Velraj*
Department of Physics, Periyar University, Salem – 636011, Tamilnadu, India

In the present study, fragmented pottery samples were collected from the recently excavated archaeological site Gudnapur in Karnataka state, India. An attempt has been made to estimate the mineral compositions, firing conditions and firing temperature achieved by the artisans at the time of manufacturing the potteries by using FT-IR analysis in mid frequency region 4000-400 cm\(^{-1}\) and XRD studies in 2θ range from 20º to 60º. The results from these non destructive analyses provided the information about the mineral compositions such as Quartz, Magnetite, Hematite, Calcite, Orthoclase, Kaolinite, Albite, Biotite, Dickite were detected in the samples. The lower limit of the firing temperature of potteries well evidenced from the FT-IR spectra recorded as received state. The band at 915 cm\(^{-1}\) is due to Al (OH) vibrations in the octahedral sheet structure which starts to disappear with increasing temperature. At 500°C the band is absent due to the complete destruction of octahedral sheet structure in clay of the pottery samples. In the present study all the samples were no absorption band at 915cm\(^{-1}\), so all the samples might have been fired above 500°C at the time of manufacture. If the amount of the magnetite present in the sample is larger than hematite, it may be fired at reducing atmosphere or else it may be at oxidizing atmosphere. From the ratio of magnetite to hematite present in the samples the artisans in this site may aware of firing the potteries in both oxidizing and reducing atmosphere.

**Keywords:** Archaeological pottery, Firing temperature, FT-IR, XRD.

**INTRODUCTION**

The provenance, manufacturing techniques and trade of pottery in the ancient world are a subject of great archaeological interest as indices of the artistic and technological level of various cultures and their influence [1]. One of the important areas of archaeology is the identification of the source and the origin of ancient artifacts. Knowing the origin is imperative for tracking correctly the ancient civilization and history. Pottery shreds are the most common artifacts which reflect the ancient people life style, mainly the skills utilized during the time of manufacture of pottery. Archaeological understanding of pottery material has largely been based on the graphical representation of findings. The compositional analysis of ceramic artifacts contributes to our understanding of past cultural practices beyond provenance. Due to the relationship between paste preparation and chemical composition of ceramics, similarities may signify shared resource procurement patterns. Continuity of composition over time may indicate the intergenerational transmission of knowledge required to make pottery with the desired mechanical performance characteristics.

Pottery is not usually formed from raw clay; prior to vessel manufacture, the clay is subjected to purification, tempering, and/or mixing processes. These procedures may alter the chemical composition of clay and make it difficult to match the paste of a ceramic vessel to the raw clays from which it was formed [2]. In these cases, it is often more useful to compare the paste compositions of vessels recovered from different archaeological sites. Raw clay is purified through the process known as slaking, which involves adding excess water to create thin slurry and allowing coarser grained sand and silt to settle out while the fine-grained clay particles remain suspended [3]. Tempering agents are minerals or organic materials intentionally added to clay.

The identification of minerals is an important to elucidation of firing temperature of potteries. The knowledge of firing temperature and conditions of firing give us better understanding of civilization that created potteries [4]. In the present work the spectroscopic measurement performed by FT-IR and X-ray diffraction studies on potteries shreds collected from Gudnapur in Karnataka, attributed to historical periods were reported. The experimental results allowed us to identify the different components of the ceramic body and the main crystalline phases as well.

**Gudnapur (lat. 14º 53´ N; long. 75º20´S)**

In this study the archaeological pottery shreds were collected from the recently excavated archaeological site Gudnapur in the Karnataka state, India. This site was excavated by the Archaeological Survey of India, Karnataka. Gudnapur is a historical place, associated with Kadamba rulers – the founder of Kannada kingdom at Banavasi district. The site is at a distance of 19 kilometers from Sirsi on Banavasi Road. Gudnapur is located 4 kms away from Banavasi. Banavasi used to be the capital of the Kadamba rulers. Relics of that period are found in ample here even today [5]. The site map of the Archaeological site is shown in Fig. 1.

![Fig.1. The archaeological site map of recent excavation in Gudnapur (•) in Karnataka (South India)](image-url)
MATERIALS AND METHODS

The potteries from Archaeological site Gudnapur were examined using FT-IR, XRD with a view to acquire information on the techniques employed on the samples to fire them and to estimate the firing temperature attained by the artisan at the time of manufacturing the potteries. The pottery samples of interest were collected at different depths and are named as GDP1, GDP2, GDP3, GDP4 and GDP5 serially.

FT-IR Spectrometry
FTIR spectroscopy is considered to be an important tool to analyze the clay minerals and mineral transformation due to thermal effects. The typical collection of the representative pottery samples is shown in Fig.2. After removal of surface layers, the pottery shreds were ground into fine powder using agate mortar. The Fourier transform infrared spectra of the pottery samples were recorded in the mid frequency region 4000 - 400cm\(^{-1}\) using Bruker Tensor 27 FT-IR spectrophotometer by KBr pellet technique. The samples were pelletedized 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 1cm\(^{-1}\) resolution, which is commonly used for standard laboratory investigations as it covers almost all the vibrational and rotational transitions [6].

X-ray diffraction measurements
The phase analysis of the mineral structure of the powdered pottery samples were carried with the use of Mini Flex II XRD at the operating voltage 30 KV and the current 15 mA on X-ray tube with CuK\(_\alpha\) radiation of \(\lambda = 1.5405\). Diffractogram patterns were obtained by continuous scanning in 2\(\theta\) range from 20\(^{\circ}\) to 60\(^{\circ}\). The data were compared with the JCPDS (Joint Committee on Powder Diffraction Standards, 2011) database. Alternately, the comparison was done with the Match (Crystal Impact) program.

RESULTS AND DISCUSSION

Estimation of lower limit of Firing temperature using FT-IR
Infrared (IR) spectroscopy provides information about firing temperature because minerals exist between finite ranges of temperatures [7]. The mineralogical compositions of the archaeological potteries are mainly depending on the nature of relevant raw materials, firing atmosphere, process of firing and depositional changes. The mineral present in the shreds can be identified by the FT-IR analysis and thereby the range of firing temperature can also be estimated. The FT-IR spectra of the samples GDP1, GDP2, GDP3, GDP4 and GDP5 respectively are shown in Fig.3. The tentative vibrational assignments of IR peak as received state of samples are given in Table.1. Analysis targets oxides present in the ceramic material as carbonates, chain and framework silicates, iron oxides, aluminum oxides, and silica (SiO\(_2\)). If firing temperatures exceed 800\(^{\circ}\)C, calcite (CaCO\(_3\)) decomposes into lime (CaO) and carbon dioxide (CO\(_2\)). The presence of vitreous material indicates high-temperature firing; in addition, clay minerals progress through a series of transformations at different temperatures. For example, as firing temperatures increases, kaolinite dehydrates to metakaolin, then to a SiO\(_2\) and spinel phase, and finally to mullite at about 1075\(^{\circ}\)C [8].

![Fig.2. Photograph of the samples](image)

![Fig.3. FT-IR spectra of the samples (GDP1-GDP5)](image)

![Fig.4. X-Ray Diffractogram of the samples (GDP1-GDP5)](image)

The composition in the ceramic materials are the ‘finger print’ of the stable or meta stable solid phase formed during firing, the production processes of ceramics and pottery can be derived from their assemblage [14]. The recognizable phases of minerals and their association are mainly depend on the raw materials, maximum heating temperature, heating ratio, firing and kiln atmosphere. These factors would help in understanding the course of reactions. The IR absorption band at 915cm$^{-1}$ is due to Al(OH) vibrations in octahedral sheet structure which begins to disappear at the temperature 500°C [15-17]. All the shreds in the present study have no band at 915cm$^{-1}$. So it is viable to understand that all the samples might have been fired above 500°C. According to Velraj et al, the decomposition of kaolinite occurs around 800°C [18].

**Table 1:** Infrared absorption frequencies (cm$^{-1}$) of Gudnapur pottery samples with tentative vibrational assignments

<table>
<thead>
<tr>
<th>GDP 1</th>
<th>GDP 2</th>
<th>GDP 3</th>
<th>GDP 4</th>
<th>GDP 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency (cm$^{-1}$) &amp; Relative intensity</td>
<td>Frequency (cm$^{-1}$) &amp; Relative intensity</td>
<td>Frequency (cm$^{-1}$) &amp; Relative intensity</td>
<td>Frequency (cm$^{-1}$) &amp; Relative intensity</td>
<td>Tentative Vibrational Assignments</td>
</tr>
<tr>
<td>3450</td>
<td>S</td>
<td>3465</td>
<td>S</td>
<td>3438</td>
</tr>
<tr>
<td>2923</td>
<td>S bd</td>
<td>2928</td>
<td>W</td>
<td>1869</td>
</tr>
<tr>
<td>2837</td>
<td>-</td>
<td>2869</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1887</td>
<td>S Sp</td>
<td>1630</td>
<td>S</td>
<td>1438</td>
</tr>
<tr>
<td>1480</td>
<td>S</td>
<td>1387</td>
<td>S vs</td>
<td>-</td>
</tr>
<tr>
<td>1040</td>
<td>S</td>
<td>1059</td>
<td>S bd</td>
<td>1053</td>
</tr>
<tr>
<td>845</td>
<td>S Sp</td>
<td>824</td>
<td>S</td>
<td>821</td>
</tr>
<tr>
<td>791</td>
<td>S Sp</td>
<td>796</td>
<td>S</td>
<td>796</td>
</tr>
<tr>
<td>690</td>
<td>S Sp</td>
<td>691</td>
<td>S</td>
<td>715</td>
</tr>
<tr>
<td>615</td>
<td>S sp</td>
<td>658</td>
<td>S</td>
<td>673</td>
</tr>
<tr>
<td>588</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>S</td>
</tr>
<tr>
<td>460</td>
<td>S</td>
<td>476</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>399</td>
<td>S</td>
<td>475</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>399</td>
<td>S</td>
<td>447</td>
<td>S</td>
<td>S</td>
</tr>
</tbody>
</table>

V.S – Very Strong; S – Strong; M – Medium; W – Weak; V.W – Very Weak; bd – broad; Sp – Sharp

According to Shoval, the firing temperature 800°C is sufficient to decompose the calcite [19]. The presence of calcite in the samples may occur essentially for two reasons; a low firing temperature or a post burial deposition processes [20]. From the absorption peaks in FTIR, the presence of calcite and kaolinite in the all the samples from GDP1 to GDP5 denoted that these samples might have been fired below 800°C. The presence of quartz gives information about the origin of the potteries. The presence of quartz in largest part of the samples confirms the common origin of these samples.

**X-ray diffraction analysis**

X-ray diffraction (XRD) is an important tool in mineralogy for identifying and characterizing minerals in complex mineral assemblages and thereby finding the firing temperature of clay minerals. The application of XRD to ancient ceramics which are a mixture of clay minerals, additive minerals and their transformation products yields information on the mineral composition of objects [21]. XRD analysis was carried out to complement the FT-IR vibrational assignment in order to elucidate the mineralogical characterization of the pottery shreds and thereby to find the firing temperature achieved by the
We can reveal that the firing temperature ranges between 600-
the firing temperature as above 600
samples were fired below 900
presence of feldspar in all the samples indicates that all the
concentrations of the Magnetite and Hematite present in the
at oxidizing atmosphere [29 - 33]. To determine the
it may be fired at reducing atmosphere or else it may be fired
If the amount of magnetite present in the sample is large then
iron oxides (Magnetite and Hematite) present in the sample.
fired at the time of manufacture is identified by the ratio of
In the present study the atmospheric condition of the sample
during the firing process which decides the atmosphere
to magnetite refers the transformation of Fe
Magneto and Hematite [26]. From this, the relative amount of hematite and magnetite
is responsible for the colour of the potteries. The variation in the
amount of these oxides gives important information regarding the nature of the environment in which the potteries were made [27]. The formations of these two minerals depend on the firing atmosphere prevalent at the time of manufacture. The presence of low intensity peak due to magnetite refers the transformation of FeO to Fe2O3 during the firing process which decides the atmosphere whether reducing or oxidizing for firing the artifacts [28].

In the present study the atmospheric condition of the sample fired at the time of manufacture is identified by the ratio of iron oxides (Magnetite and Hematite) present in the sample. If the amount of magnetite present in the sample is large then it may be fired at reducing atmosphere or else it may be fired at oxidizing atmosphere [29 - 33]. To determine the concentrations of the Magnetite and Hematite present in the

Feldspar decomposes completely at around 900-950°C. The presence of feldspar in all the samples indicates that all the samples were fired below 900°C [22, 23]. Hematite shows the firing temperature as above 600 °C [24]. Kaolinite shows the firing temperature of 800 °C [25]. From the above statements we can reveal that the firing temperature ranges between 600-
800 °C. The firing temperature ranges of both FTIR and XRD are same for the present Gudnapur pottery samples.

**Identification of firing atmosphere from FT-IR**

The red colour of the potteries is due to presence of hematite, black and grey colours are due to higher amount of magnetite [26]. From this, the relative amount of hematite and magnetite is responsible for the colour of the potteries. The variation in the amount of these oxides gives important information regarding the nature of the environment in which the potteries were made [27]. The formations of these two minerals depend on the firing atmosphere prevalent at the time of manufacture. The presence of low intensity peak due to magnetite refers the transformation of FeO to Fe2O3 during the firing process which decides the atmosphere whether reducing or oxidizing for firing the artifacts [28].

In the present study the atmospheric condition of the sample fired at the time of manufacture is identified by the ratio of iron oxides (Magnetite and Hematite) present in the sample. If the amount of magnetite present in the sample is large then it may be fired at reducing atmosphere or else it may be fired at oxidizing atmosphere [29 - 33]. To determine the concentrations of the Magnetite and Hematite present in the

### Table.2: Mineral phases identified by XRD

<table>
<thead>
<tr>
<th>Minerals</th>
<th>GDP1</th>
<th>GDP2</th>
<th>GDP3</th>
<th>GDP4</th>
<th>GDP5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hematite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Feldspar</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Magnetite</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Biotite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Dickite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Calcite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Illite</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

* + = Present, - = Absent

### Table. 3: Estimation of Lower limit of firing temperature of the pottery samples using FT-IR technique

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Colour of sample</th>
<th>Ratio of Magnetite and Hematite</th>
<th>Atmosphere</th>
<th>Firing temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDP 1</td>
<td>Black ware</td>
<td>0.40</td>
<td>Oxidizing</td>
<td>&lt; 800°C</td>
</tr>
<tr>
<td>GDP 2</td>
<td>Black ware</td>
<td>1.01</td>
<td>Oxidizing</td>
<td>&lt; 800°C</td>
</tr>
<tr>
<td>GDP 3</td>
<td>Red ware</td>
<td>2.47</td>
<td>Reducing</td>
<td>&lt; 800°C</td>
</tr>
<tr>
<td>GDP 4</td>
<td>Black and red ware</td>
<td>3.61</td>
<td>Reducing</td>
<td>&lt; 800°C</td>
</tr>
<tr>
<td>GDP 5</td>
<td>Red ware</td>
<td>1.00</td>
<td>Oxidizing</td>
<td>&lt; 800°C</td>
</tr>
</tbody>
</table>

Feldspar decomposes completely at around 900-950°C. The presence of feldspar in all the samples indicates that all the samples were fired below 900°C [22, 23]. Hematite shows the firing temperature as above 600 °C [24]. Kaolinite shows the firing temperature of 800 °C [25]. From the above statements we can reveal that the firing temperature ranges between 600-
800 °C. The firing temperature ranges of both FTIR and XRD are same for the present Gudnapur pottery samples.

**CONCLUSION**

Application of FTIR spectroscopy together with XRD for the study of samples recently excavated at Gudnapur shows great potential for understanding technological conditions implemented for the production and found to give useful information about mineralogical composition of the pottery fragments. The presence of clay minerals such as Quartz, kaolinite, and Feldspar were detected in all the samples from GDP1 to GDP5 allows us to draw a conclusion that the samples might have been fired below 800°C. From the XRD studies it is estimated that the range of firing temperature of the Gudnapur potteries lies between 600-800°C. The results indicate that the red coloration was due to hematite and
black coloration was due to magnetite. Since the samples contain both hematite and magnetite the artisans in this site may have been firing the potteries both oxidizing and reducing atmosphere.

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