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## FT-IR X-RAY DIFFRACTION AND THERMAL ANALYSIS TO ESTIMATE THE FIRING TEMPERATURE OF THE ARCHAEOLOGICAL SAMPLES EXCAVATED RECENTLY AT BANAHALLI IN KARNATAKA, SOUTH INDIA

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### ABSTRACT

The firing temperature of the archaeological pottery shreds, collected from the recently excavated site Banahalli, Karnataka, South India, is estimated from the composition of the potteries, using FT-IR spectroscopic analysis, X-ray diffraction and Thermal analysis by TGA-DTA. The pottery shreds were subjected to analysis as in the received state for estimation of firing temperature, at the time of manufacturing the potteries. The characterization studies reveal the skill and style of the artisan lived in the ancient time.

**KEY WORDS:** FT-IR, XRD, Thermal analysis, Pottery shreds.

### 1. INTRODUCTION

Potteries are made up of clay materials, which include primary, secondary and accessory minerals and amorphous materials. Clay minerals are made up of chains of SiO<sub>4</sub> tetrahedral and AlO<sub>6</sub> octahedral, which are the basic structural units of silicates. The silicon atoms are tetrahedrally surrounded by oxygen atoms and the hydroxyl groups to form a hexagonal network which is repeated infinitely. The tetrahedral are arranged so that all their apexes (O or OH) point in the same direction and their bases are in the same plane. The oxygen atoms and hydroxyls on the free apexes are coordinated to Al ions forming octahedral sheets. Accessory minerals generally are the various iron oxides and oxo hydroxides. These are often found dispersed as finely divided particles or as surface coatings. Minute quantities of these minerals, can influence the morphological and mineralogical properties of the clay minerals (Janaki and Velraj,2011). The purpose of the present study is to estimate the firing temperature of the pottery shreds belonging to the Neolithic site, Banahalli (12°58'N 78°6'E) near Bangalore, Kolar district, Karnataka. The site was excavated by Archaeological Survey of India (ASI).

### 2. EXPERIMENTAL

**2.1 Sample:** Archaeological pottery samples collected from the Site Banahalli have been coded as BNH1, BNH2 and BNH3 respectively and arranged in depth wise BNH1 from the highest depth, BNH3 from the lowest depth and BNH2 from the middle layer are the representative samples from the available samples of potteries. The nature of the faces of the shreds is distinct from one another in appearance.

**2.2 Fourier Transform Infrared Spectrometry (FT-IR):** The pottery samples were analyzed from the FT-IR absorption spectra in transmittance mode to characterize their mineralogical composition from the specific transmittance peak observed. The spectra were recorded in the region 4000–400 cm<sup>-1</sup> at room temperature using Perkin Elmer FT-IR Spectrometer with 1cm<sup>-1</sup> resolution in its 100 scan mode using KBr pellet technique.

**2.3 X-Ray Diffraction Analysis (XRD):** The representative samples for this study was subjected to X-ray diffraction patterns of potteries (Powdered samples) were recorded in room temperature by using Jeol – JDX 8030, X-ray computer controlled diffractometer system, having a curved graphite crystal diffracted monochromator, with a source of CuK $\alpha$  radiation of wavelength  $\lambda=1.5418\text{\AA}$  and NaI (T1) scintillation detector. The diffractograms were recorded with run between 20°-80° as the 2 $\theta$  angle with proportional counter 1600V, scanning speed of 1° per minute.

**2.4 Thermo Gravimetric Analysis and Differential Thermal Analysis (TGA - DTA):** TGA and DTA were carried out in SDT Q 600 V.8.3 thermal analyzer. The experiment was carried out by heating the samples from room temperature to 1200°C in step of 20°C min<sup>-1</sup> in a static nitrogen atmosphere.

### 3. RESULTS AND DISCUSSION

**3.1 FT- IR analysis:** The FT - IR spectra of BNH1, BNH2 and BNH3 are shown in Figure 1. The peak positions of various bands of varied intensity observed in these spectra along with their tentative assignments are given in Table 1. According to Velraj (2009), the appearance and disappearance of a very weak absorption band around 3626 cm<sup>-1</sup> due to O-H stretching of crystalline hydroxyl which is present in the sample BNH3. It has been stated earlier on the

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IR analysis of archeological artifacts that the absorption band at  $1639\text{ cm}^{-1}$  is due to the H-O-H bending of water molecule (Palanivel and Velraj,2007). A medium absorption band appearing at  $1635\text{ cm}^{-1}$  is due to H-O-H bending of water exists in all samples owing to the absorption of moisture present in the sample. According to Maritan (2005) a strong band at  $1447\text{ cm}^{-1}$  in BNH3 is assigned to Calcite. Palanivel and Meyvel (2009), Dowty (1987), Rutestein and White (1971) and Shoval (1994) have stated that the absorption band at  $1085\text{ cm}^{-1}$  in the samples is due to the presence of Wollastonite. BNH1 and BNH2 show a band at  $1083\text{ cm}^{-1}$  and  $1080\text{ cm}^{-1}$  is due to wollastonite, but the absence of corresponding band in the shred BNH3 is reveals that the shred has no wollastonite in its composition (Dowty,1987; Rutestein and White,1971). The peak around  $1034\text{ cm}^{-1}$  is the result of the red clay origin of kaolinite. The spectrum of BNH3 has a peak centered at  $1030\text{ cm}^{-1}$  with strong intensity. It indicates the red clay origin of kaolinite present in the clay of the pottery shred BNH3. The absence of corresponding band in BNH1 and BNH2 determines that these shreds are of different origin referring the BNH3. The appearance of absorption at  $795\text{ cm}^{-1}$  and  $695\text{ cm}^{-1}$  indicates the quartz presence in accordance with the results of earlier researchers in the similar studies (Palanivel and Velraj,2007). The presence of CaO in all the samples below 6%, by the chemical analysis indicate all the samples are non-calcareous clay type in nature (Velraj,2009). The absorption band appearing at  $668\text{ cm}^{-1}$  is due to the presence of anorthite (Kieffer,1979). The shred BNH3 exhibited a weak intensity peak at  $668\text{ cm}^{-1}$  due to clay mineral anorthite and the absence of corresponding peak in BNH1 and BNH2 affirms that the BNH1 and BNH2 are not having anorthite and have different composition with respect to BNH3. The absorptions around  $580\text{ cm}^{-1}$  and  $540\text{ cm}^{-1}$  are due to magnetite and hematite respectively (Velraj,2009). The absorptions observed at  $585\text{ cm}^{-1}$  in BNH3 and  $535\text{ cm}^{-1}$  in BNH1 and BNH2 are attributed to the magnetite and hematite present in the samples respectively. But the band present at  $535\text{ cm}^{-1}$  in BNH1 and BNH2 does not appear in BNH3. Therefore it is understood that BNH3 has no hematite in its composition. The formations of magnetite and hematite depend on the firing atmosphere prevalent at the time of manufacture. The presence of weak intensity peak due to magnetite refers the transformation of  $\text{Fe}_3\text{O}_4$  to  $\text{Fe}_2\text{O}_3$  during the firing process. The hematite peak at  $535\text{ cm}^{-1}$  in the samples BNH1 and BNH2 implies that the potteries were fired in an oxidizing condition (Velraj,2009). The absence of hematite band in BNH3 indicates that the firing condition achieved may be a reduced atmosphere or in closed kiln, in the sample. So it is inferred that the artisans of Banahalli were well aware of technique of firing the potteries in both oxidizing and reducing atmosphere. The absorption band in BNH2 and BNH3 the sample at  $465\text{ cm}^{-1}$  is assigned to the presence of clay mineral microcline, referring the studies on fired clay artifacts (Rutestein and White,1971; Palanivel and Rajesh kumar,2011; Farmer,1974). The absorption bands around  $779,773$  and  $774\text{ cm}^{-1}$  indicating the presence of quartz and feldspar as secondary minerals in the samples. The doublet occurring at  $779$  and  $731\text{ cm}^{-1}$  is characteristic of Feldspar minerals (Velraj,2009). Other characteristic bands of the Feldspar mineral (orthoclase) are  $645\text{ cm}^{-1}$ ,  $647\text{ cm}^{-1}$ .

**3.2 The Firing Temperature of Potteries:** FT-IR spectroscopy has been shown to be extremely helpful in the characterization of the samples and hence to estimate the firing temperature of the potteries, as given in Table 3. The IR band around  $3630\text{ cm}^{-1}$  is due to crystalline hydroxyl group which will continue to persist up to  $800\text{ }^\circ\text{C}$ . The FT-IR spectra of the shred BNH3 show the absorption band at  $3626\text{ cm}^{-1}$ . Thus the samples BNH3 may be fired around  $800^\circ\text{C}$ . Hence the firing temperature of the sample during manufacturing may be around  $800^\circ\text{C}$ , from the very strong band which occurs at  $1030\text{ cm}^{-1}$  in the received state, which is due to Si-O stretching of kaolinite clay mineral. Among the three samples BNH3 show a strong band around  $1032\text{ cm}^{-1}$ . Claret (2003) have suggested that the bands at  $2921\text{ cm}^{-1}$  and  $2852\text{ cm}^{-1}$  are due to organic matter and assigned to C-H stretching band. The bands present in the BNH samples around at  $2923\text{ cm}^{-1}$  in BNH1, at  $2923\text{ cm}^{-1}$ , in BNH2 and around at  $2918\text{ cm}^{-1}$  in BNH3 confirms the presence of organic matter in the potteries. According to Maritan (2005) the C-H stretching bands due to organic matter which are appearing in the samples were not combusted during firing. The high temperature Ca - Silicates was observed at around  $850^\circ\text{C}$  their amount increases with rise in temperature. Presence of gehlenite and anorthite in the pottery samples BNH1 and BNH2 indicates that the firing temperature is above  $800\text{ }^\circ\text{C}$ . Calcite is particularly reflective and can serve as a useful diagnostic mineral to estimate the maximum firing temperature (Murray,2000). Legodi and Waal (2007) have stated that the presence of Calcite confirms the processing temperature below  $800^\circ\text{C}$ . Calcite is present in the sample BNH3 and presence of anorthite in the pottery indicates the firing temperature of the samples may be below  $800^\circ\text{C}$ . In the samples BNH1 and BNH2 hematite is prominent this again affirms that the samples may be fired above  $800^\circ\text{C}$ .

**3.3 XRD analysis:** X-ray diffraction analysis was carried out in all the three samples of Banahalli to find the mineralogical composition of all the pottery samples. The X-ray diffraction patterns of the samples BNH1, BNH2 and BNH3 are given in figure 2 (a, b and c), their mineral composition is given in Table 2.

XRD is an important tool in mineralogy, for identifying and characterizing minerals in complex mineral assemblages. The application of XRD to ancient ceramics, which are the mixture of clay minerals, additive minerals and their transformation products they yield information on the mineral composition of objects (Stanjek and

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Hausler,2004). Schwertmann (1993) reported that hematite is one of the most intense coloring materials in potteries. The presence of hematite make the shreds reddish, the reddish color observed in samples BNH1 and BNH2 might be due to presence of hematite, BNH3 is having both hematite and magnetite but the magnetite ratio is more, black colour of the pottery is due to this mineral inclusion. The minerals quartz and feldspar were present in all the samples of Banahalli. The diffraction peaks of Quartz were the most intense in all the samples. Iordonidir (2009) and Velraj (2010) reported in their studies that the mineral feldspar decomposes completely at around 900-950 °C. The presence of feldspar in all the samples indicates that all the samples were fired at around 900°C (Joachim,1991). Calcite is present in the sample BNH3 in XRD also confirms that the sample may be fired below 800°C. The presence of kaolinite, feldspar, muscovite, quartz, calcite and hematite in the pottery fragments were also evidenced by FT-IR analysis and serves as a complimentary tool to compare the characteristics of the shreds.

**3.4 TGA-DTA analysis:** It is evident that thermal analysis TGA-DTA is a relevant characterization method to understand the reaction process and properties of the raw materials used in the manufacture of the pottery (Dowty,1987). In order to estimate the firing temperature of the archaeological potteries, the composition of the potteries, the mineral assemblage, weight loss due to firing, by TGA. TGA - DTA curves of pottery samples BNH1-BNH3 are shown in figure 3 (a, b and c). In TGA curves the mass loss between room temperature to 200 °C due to dehydration of water. The mass losses between room temperature to 200 °C attributed to dehydration of water, the weight losses due to dehydration are given in the table for all three samples. Moropoulou (1995) and Franquelo (2008) stated that the endothermic peak around 100°C to 200°C is due to the adsorbed water. An endothermic peak appeared in the range of temperature 100°C to 200°C in the DTA curves of the samples. Appearance of an exothermic peak from 250°C–500°C is due to combustion of organic material in the pottery shreds as reported by Shoval (1994) and Clark (2008). A small exothermic peak appearing in the temperature region 250°C-500 °C is due to the partial combustion of organic material in the samples BNH1, BNH2 and BNH3. Mackenzie has stated that the endothermic peak appearing from 550°C–650°C is due to the decomposition of kaolinite (Mackenzie and Cardile,1990). From the present investigation; the decomposition of kaolinite is evident from the endothermic peak in the range 575°C-665°C in the samples BNH3. According to Planivel and Meyvel (2009) Moropoulou (1995) the decomposition of kaolinite peak is the indicating of that the pottery is not fired above 800°C. According to the references, the samples BNH3 might have been fired around 800°C as evident from the FT- IR and X-ray diffraction analysis. The absence of exothermic peak in the range 900°C-1000°C in the pottery samples is an indicating that the potteries were not fired above 900°C-1000°C (Mackenzie and Cardile,1990). The absence of the exothermic peak in the samples BNH1 and BNH2 in the range between 900°C to 1000°C indicating the pottery shreds were not fired above 900°C - 1000°C which coincides much with FT-IR and XRD studies. In the TGA curve the mass loss between room temperature (30°C to 200°C) is due to dehydration of water. Weight losses due to dehydration are in the range of 2.6% to 2.9% for the samples. In the region 400°C -600°C the weight loss is due to de-hydroxylation is less than 2% (Shoval,1994). According to Drebushckak (2005) that the weight loss between 700°C to 800°C, is indicative of the absence of calcite in the samples. The pottery samples BNH1 and BNH2 show no mass loss in the temperature range 700°C to 800°C. A broad endothermic peak in the range 250°C to 500°C is due to the combustion of organic material are 3.55%, 3.53% and 1.54% respectively, in BNH1, BNH2 and BNH3. It is evident that there may be the intentional addition of some organic matter in the raw materials of the potteries at the time of manufacture.

### 4. CONCLUSION

The Pottery shreds excavated from Banahalli were characterized by FT-IR, XRD and TGA-DTA analysis; the components of pottery ceramic materials are the solid phase formed during firing of pottery. From the investigations, the range of firing temperature of the pottery shreds was estimated. It may be confirmed that the samples BNH1 and BNH2 were fired above 850°C and BNH3 was fired below 800°C by the artisans at the time of manufacture. The results obtained from the techniques FT-IR, XRD and TGA-DTA are in good agreement with reported results. The artisans of Banahalli were aware of making good quality pottery for house hold utilities. Hence it may be concluded from the results obtained that they are very much informed about the oxidizing and reducing atmosphere for making both red and black potteries.

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Table 1 FT-IR Vibrational assignments of the coded pottery samples

Pottery sherd code			Tentative Vibrational Assignment
BNH1	BNH2	BNH3	
-	-	3626 VW VW	O - H Str. Crystalline hydroxyl
3442 VS	3416 M	3480 VS	O - H Str. adsorbed water
2923 VW	2923 VW	2918 W	C - H Stretching
1637 VS	1624 W	1635 VS	H - O - H bending of water
-	-	1447 S	CaCO <sub>3</sub> - Calcite
1083 VS	1080 VS	-	C - O Stretching Wollasonite
-	-	1030 VS	Kaolinite Si - O Stretching
779 VS	773 S	774 VS	Si - O of quartz
731 S	731 S	732 S	Feldspar (orthoclase)
692 S	694 M	694 W	Si - O of quartz
-	-	668 M	Anorthite
645 VW	647 VW	647 VW	Feldspar (orthoclase)
-	-	585 VS	Fe - O of Magnetite
536 W	535 W	536 W	Fe - O of Hematite
464 VS	468 VS	466 VS	Si - O Microcline

VS-Very Strong, S-Strong, M-Medium, VW-Very Weak, W-Weak

Table 2 Mineral phases obtained by XRD analysis

Minerals	BNH1	BNH2	BNH3
Quartz	+	+	+
Muscovite	+	+	-
Anorthite	-	-	+
Hematite	+	+	+
Feldspar	+	+	+
Kaolinite	-	-	+
Calicite	-	-	+

Table 3 Firing temperature estimation of the Banahalli potteries

Sample Code	Particle Nature	Clay Type	Weight Loss % (TGA)	XRD	FT-IR	TGA
BNH1	Coarse	NC	3.55	>850°C	>850°C	>1000°C
BNH2	Coarse	NC	3.53	>850°C	>900°C	>1000°C
BNH3	Coarse	NC	1.54	<800°C	<900°C	<900°C

[+ present - Absent]

Figure 1 FT-IR Spectrum of BNH samples Figure 2(a) &amp; 2(b) X-Ray Diffractogram of BNH1 &amp; BNH2

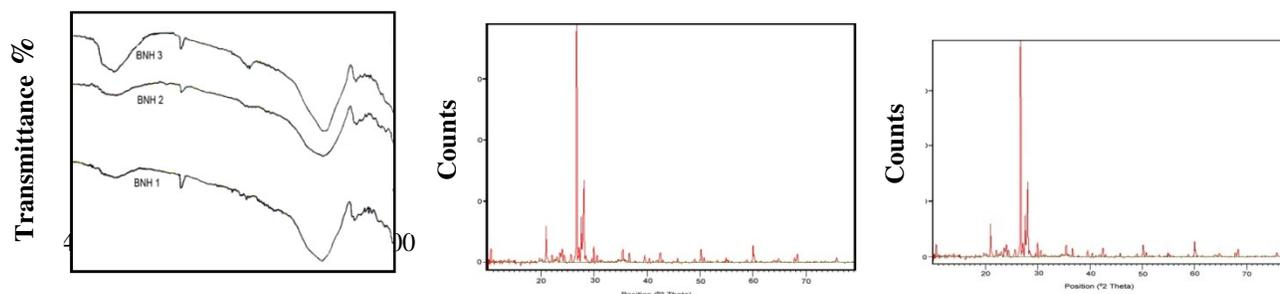


Figure 2(c) X-Ray Diffractogram of BNH3

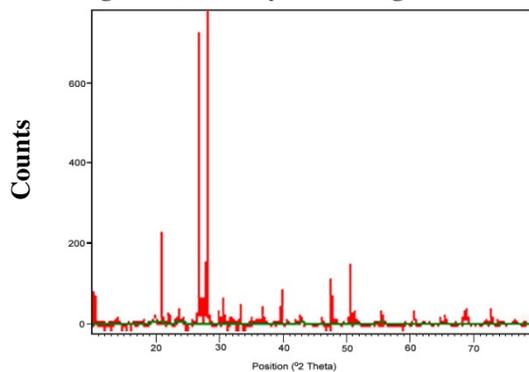


Figure 3(a) TGA-DTA of BNH1

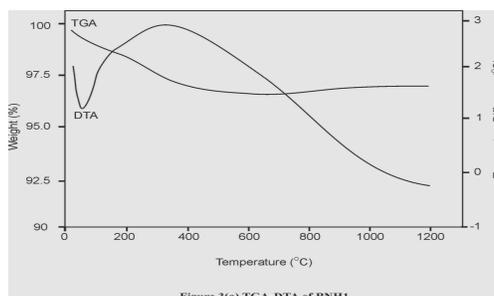


Figure 3(b) TGA-DTA of BNH2

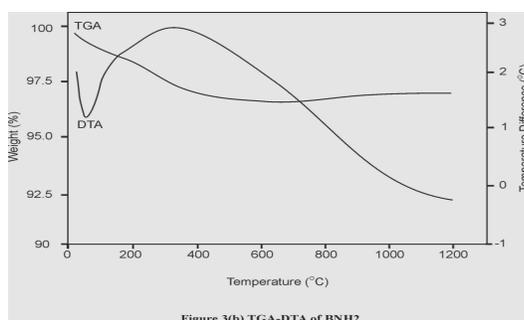
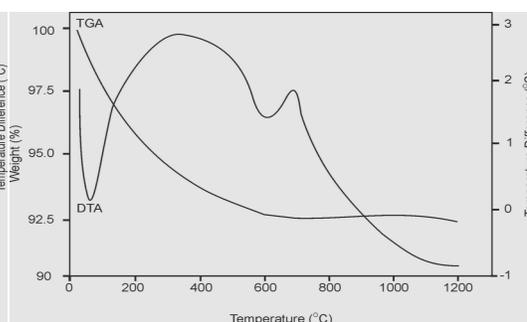


Figure 3(c) TGA-DTA of BNH3



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