FTIR and Mössbauer spectroscopy applied to study of archaeological artefacts from Maligaimedu, Tamil Nadu, India

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Archaeological potteries belonging to 300 BC collected from Maligaimedu (11°48’Lat.N; 79°35’Long.E) Tamil Nadu, India were subjected to FTIR, XRD and Mössbauer spectroscopic studies in order to characterise the clay minerals associated, their origin and technology of firing adopted by artisans. To determine the firing temperature of the potteries and to find any phase change in magnetic minerals, the pottery samples were refired to different temperatures. From FTIR studies, it is observed that these pottery samples were made up of disordered kaolinite type clay with appreciable amount of iron with a firing temperature of about 800°C. The minerals like quartz, anorthite, orthoclase and hematite were identified using XRD. No change in the Mössbauer parameters are observed in the case of sample MGM-2 during laboratory firing up to 800°C, which indicates that original firing temperature is above 800°C. Changes in the Mössbauer spectra of sample MGM-5 during laboratory firing reveal that the laboratory firing atmosphere differs from original firing atmosphere. The presence of Fe$^{2+}$ ion in as-received state spectra of black pottery (MGM-5) indicates that the sample was fired under reduced atmospheric condition during manufacturing. The colour of the potteries also reflects the above results.

Keywords: FTIR, Mössbauer spectroscopy, Archaeological potteries, Firing temperature

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1 Introduction

The transformation of clay into pottery by firing was an important step in the development of prehistoric man$^1$. The availability of clay based materials especially pottery is plenty in many of the archaeological excavations. Various spectroscopic techniques have been adopted by researchers to establish the firing temperature of the archaeological materials like Fourier Transform Infrared (FTIR), X-ray diffraction (XRD), Mössbauer spectroscopy$^1$ etc.

FTIR spectroscopy has been for decades, a frequently used method to investigate the structure, bonding and chemical properties of clay minerals$^5$. On firing the pottery to higher temperatures in order to get final products, thermal changes are taking place mainly on structure and bonding of clay minerals, which can be studied by using FTIR spectroscopy$^6$. When clay products are fired to maximum firing temperature, the presence or absence of certain minerals plays an important role in the determination of firing temperature$^7$. Usually, clay is a mixture of minerals, which can be identified by using the XRD technique. The microscopic analysis of the iron (state of iron i.e. Fe$^{2+}$/Fe$^{3+}$, and iron oxides) bearing minerals can be carried out by Mössbauer spectroscopy, which is used in determining the oxidation state of Fe-content, firing temperature, firing conditions and colouring mechanism$^4$.

The authors made extensive studies on clay minerals and archaeological artefacts by subjecting them to FTIR, XRD and Mössbauer spectroscopic studies$^2,3,8-12$. For the present investigation, representative archaeological potteries (MGM-2 red ware and MGM-5 black ware) belonging to 300 BC, excavated from Maligaimedu, Villupuram District, Tamil Nadu were subjected to the above methods. To compare the results local clay were collected from the site and subjected to FTIR studies by heating it to different temperatures in laboratory condition.

2 Experimental Details

The FTIR absorption spectra were recorded in the frequency region 4000-400 cm$^{-1}$, using model Paragon 500, Perkin-Elmer spectro-photometer with 16 scan mode by using standard potassium bromide tablet (KBr pellet) technique. The accuracy of the measurement is $\pm 4$ cm$^{-1}$ in 4000 to 2000 cm$^{-1}$ region and $\pm 2$ cm$^{-1}$ in 2000 to 400 cm$^{-1}$ region. The X-ray powder diffraction spectra were recorded on X’ pert MPD from Philips using CuK$_\alpha$ radiation, at a wavelength of 1.5405Å. The spectra were recorded
in the two-theta (2θ) range from 20 to 80°. The Mössbauer measurements were performed in conventional constant acceleration spectrometer. Spectra were recorded at room temperature and fitted on a PC with a least square minimization procedure, assuming Lorentzian line shapes.

3 Results and Discussion

(i) FTIR studies — The FTIR spectroscopy was used to analyse the local clay (MGM-clay) and archaeological potteries MGM-2 (red ware) and MGM-5 (black ware). The FTIR spectra recorded for the local clay in as-received state and fired to different temperatures under laboratory conditions are shown in Fig. 1.

![Fig.1 — FTIR absorption spectra of local clay (MGM-clay) in the as-received state to 800°C](image)

The absorption bands at 3700 and 3620 cm\(^{-1}\) in the local clay reveal that the type of clay is disordered kaolinite and the same is also established by the weak shoulder at 915 cm\(^{-1}\) which is due to the substitution of aluminium in octahedral sheet\(^{13}\). The bands at 3700 and 3620 cm\(^{-1}\) are assigned to O-H stretching of interlayer and inner O-H group of adsorbed water, respectively. On firing the clay in steps of 100°C, all the above bands exist with decrease in intensity around 300°C, and disappear at 500°C. Venkatachalapathy et al.\(^{8}\) reported that the firing temperature of archaeological potteries as above 450°C during manufacturing from the absence of the bands at 3700, 3620 and 915 cm\(^{-1}\). The presence of weak broad bands at 3440 and 1640 cm\(^{-1}\) indicate the presence of absorbed water molecules. For the present samples, these bands persist up to 800°C, which is due to the water molecules absorbed from the atmospheric air while recording the spectra. A broad band centered at 1030 cm\(^{-1}\) with asymmetry around 1100, 935 and 915 cm\(^{-1}\) are attributed to Si-O-Si, \([\text{Al-O-(OH)}]\)\(_6\), O-H deformation and Al-OH, respectively\(^{10,13}\). A broad symmetry band centered around 1030 cm\(^{-1}\) at 700°C indicates that the destruction of octahedral sheet structure have taken place around 650°C. Maniatis and Tite\(^{4}\), Ghosh\(^{14}\) reported that when clay was fired to 650°C, the silicate structure collapsed and a broad symmetry band is observed at 1030 cm\(^{-1}\) for red clay and at 1080 cm\(^{-1}\) for white clay type.

The presence of the bands at 795 and 775 cm\(^{-1}\) along with 695 cm\(^{-1}\) in the sample is due to quartz\(^{15}\). The weak band at 640 cm\(^{-1}\) is attributed to Al-O co-ordination vibration. The Si-O-Al bending vibration observed at 530 cm\(^{-1}\) is the most sensitive band to the presence of residual Al in the octahedral sheet\(^{16}\). Maniatis et al.\(^{17}\) reported that during firing, no perceptible changes are observed in this region up to 450°C; above this temperature as iron replaces aluminium, the intensity of the band at 530 cm\(^{-1}\) decreases with the appearance of the band at 540 cm\(^{-1}\) along with weak shoulder at 580 cm\(^{-1}\) attributed to iron oxides. At 800°C, the increase in intensity of the band at 580 cm\(^{-1}\) indicates that it is due to oxidation and crystallization of hematite. The band at 470 cm\(^{-1}\) due to Si-O-Si bending is free from any temperature effects.

Hence, the local clay is of disordered kaolinite type. The structural changes in clays due to temperature effects are identified from the FTIR
studies. Further, it is noticed that the intense band at 580 and 540 cm\(^{-1}\) indicate that the presence of iron oxide is rich in the clay.

The results obtained from the FTIR studies of local clay were compared with that of the potteries in order to conclude the type of clay, firing temperature and firing condition used for the production of archaeological potteries. The FTIR absorption spectra of pottery samples MGM-2 and MGM-5 in the as-received state and refired in laboratory condition at 300, 500 and 800ºC are shown in Figs 2 and 3. In both samples, the absence of the bands at 3700 and 3620 cm\(^{-1}\) indicates that they have been fired above 450ºC. The broad symmetry band observed at 1030 cm\(^{-1}\) in MGM-2 and MGM-5, indicates that the samples were made of red clay and subjected to a firing temperature of above 600ºC during manufacturing.

In the case of sample MGM-2, the intensity of the band at 580 cm\(^{-1}\) is more than that of 540 cm\(^{-1}\), and the intensity remains same up to 800ºC. From the observation, it is evident that the sample might have been fired under oxidizing atmospheric condition with firing temperature of above 800ºC. The red colour of the pottery also reflects the oxidizing atmosphere followed during manufacturing. In the case of sample MGM-5, the increase in intensity of the band 580 cm\(^{-1}\) at 500º and 800ºC might be due to re-oxidation in laboratory condition. It is confirmed that, the pottery sample MGM-5 might have been fired above 600ºC under reduced atmosphere. The black colour of the sample reflects the reduced firing condition adopted by the artisans.

(ii) XRD studies — X-ray diffraction spectra have been recorded for the powdered pottery samples MGM-2 and MGM-5. The presence of major minerals is identified by comparing the JCPDS (Joint Committee on Powder Diffraction Standards) file\(^{18}\). The spectra of all the above samples are shown in Fig. 4.

From XRD pattern of MGM-2 and MGM-5, the following minerals were identified: quartz (4.2515, 3.3406, 2.2332, 1.9777, 1.8159 and 1.5416 Å), anorthite (4.0346, 3.7271, 3.2073, 3.1745, 3.0292, 2.9338 and 2.8301 Å), orthoclase (3.4406 and 1.5975 Å) and hematite (2.5246, 1.8365 and 1.2558 Å). Quartz is predominant and makes the clay self-tempered.

(iii) Mössbauer studies — Mössbauer spectra at room temperature were recorded for the samples MGM-2 and MGM-5 in the as-received state and refired in laboratory

![Fig. 2 — FTIR absorption spectra of Maligaimedu pottery sample (MGM-2)](image)

![Fig. 3 — FTIR absorption spectra of Maligaimedu pottery sample (MGM-5)](image)
Fig. 4 — XRD spectra of pottery samples (a) MGM-2 and (b) MGM-5. Minerals peaks identified are quartz (Q), anorthite (A), orthoclase (O) and hematite (H).

Fig. 5 — Mössbauer spectra at room temperature of MGM-2 in the as-received state and refired at different temperature at 500 and 800°C are shown in Figs 5 and 6. The Mössbauer parameters were derived from the peak positions of the spectra and are presented in Table 1.

From the presence/absence of paramagnetic Fe\(^{2+}\) and Fe\(^{3+}\), the firing condition, firing temperature and colouring mechanisms of the archaeological potteries have been deduced. The decrease/disappearance of Fe\(^{2+}\) ion is indicative of oxygen-rich in original firing atmosphere. Coey\(^{19}\) pointed out that, the isomer shift (\(\delta\)) value range from 0.8 to 1.5 mm/s and quadrupole splitting (\(\Delta\)) value from 1 to 3.5 mm/s are attributed to Fe\(^{2+}\). The isomer shift value from 0.2 to 6.0 mm/s and quadrupole splitting value from 0 to 1.8 mm/s are attributed to Fe\(^{3+}\). Venkatachalapathy et al.\(^{8}\) reported values of isomer shift of 0.388 m/s, quadrupole splitting of 0.21 ± 0.03 mm/s and hyperfine field value of 514± 6 kOe for hematite (\(\alpha\)-Fe\(_2\)O\(_3\)) present in archaeological potteries.
Wagner and Wagner\textsuperscript{20,21} reported that the different clay minerals basically appear to exhibit essentially the same behaviour up to firing temperatures of about 900°C. At firing temperatures up to about 200°C first the pore and surface water and then the water that may be contained in the interlayer spaces of the layer silicates will be driven off. These processes usually do not cause noticeable changes in the Mössbauer spectra of the clay. At about 200°C, the structural Fe\textsuperscript{2+} in the clay begins to be oxidized to Fe\textsuperscript{3+}, a process that is concluded at about 450°C in most cases. Between about 300 and 500°C dehydroxylation of the octahedral layers of most clay minerals takes place. As a consequence, the number of ligands of the octahedral iron is reduced from six to five in some of the octahedral in the clay structure, and other octahedral become severely distorted, which increase the quadrupole splitting of Fe\textsuperscript{3+} from 0.7 mm/s to 1.4 and 1.6 mm/s. The quadrupole splitting of Fe\textsuperscript{3+}, reaches a plateau that is usually several 100°C and extends up to 800°C. Above 800°C, the environment of the structural iron becomes more symmetrical by the concomitant decrease of quadrupole splitting of Fe\textsuperscript{3+}.

Wagner \textit{et al.}\textsuperscript{22} suggested that refiring the archaeological artefacts in the laboratory may be of help in the assessment of the original firing conditions. No changes in the Mössbauer parameters and spectra occur during laboratory firing of archaeological artefacts until the refiring temperature exceeds the original firing temperature. In this manner, the maximum original firing temperature can be determined as the lowest refiring temperature at which the Mössbauer parameters begin to change. However, the changes in the Mössbauer spectra occur below the original firing temperature, when the composition of the atmosphere differs in the original and the laboratory firing, e.g., when artefacts originally fired under reducing condition are refired in an oxidizing atmosphere or vice versa.

The Mössbauer spectra of MGM-2 pottery sample in as-received state exhibits a doublet due to paramagnetic Fe\textsuperscript{3+} ion along with formation of sextet is attributed to well-crystallized and magnetically-ordered hematite (α-Fe\textsubscript{2}O\textsubscript{3}) present in the sample. The absence of Fe\textsuperscript{2+} in the spectra indicates that the sample was fired under oxidizing atmosphere, and the presence of hematite indicates that the sample was fired to higher temperature. No perceptible changes have been observed in Mössbauer parameters at 500 and 800°C which confirms the firing temperature of the sample was above 800°C, fired under oxidizing atmosphere. It is also well established from the red colour of the pottery.

The Mössbauer spectra of MGM-5 in as-received state shows two doublets corresponding to paramagnetic Fe\textsuperscript{3+} and Fe\textsuperscript{2+} ions along with a sextet attributed to hematite present in the sample. While refiring the sample in laboratory to 500°C the intensity of the peak for Fe\textsuperscript{3+} increases, which indicates that the re-oxidation of Fe\textsuperscript{2+} takes place and it completes at 800°C. From the above observation, the presence of Fe\textsuperscript{3+} along with Fe\textsuperscript{2+} in as-received state indicates that this pottery might have been fired under reducing atmospheric condition and air was not allowed during the entire firing cycle. It is also well established from the black colour of the pottery. The results obtained from Mössbauer techniques are in agreement with FTIR results.

**References**


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