Application of FTIR and Mössbauer spectroscopy in analysis of some South Indian archaeological potteries

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FTIR, XRD and room temperature Mössbauer spectra have been recorded for the recently excavated archaeological potteries from Sriperumbudur, Ellichanur (Tamil Nadu) and Thiruvanchikulam (Kerala). When firing the clay based materials like potteries, bricks and tiles etc., the presence of a few per cent of iron undergoes characteristic changes in its physical and chemical states depending upon the maximum firing temperature reached and kiln atmosphere, which can be followed by using FTIR and Mössbauer spectroscopic techniques. From the above techniques, the lower limit of firing temperature, firing atmosphere and type of clay used for the production of archaeological potteries were well established.

[Keywords: Archeological potteries, Archeo-magnetic dating, Clay materials]

1 Introduction

The recently excavated South Indian archaeological potteries collected from Sriperumbudur (SPR) (Lat 12°58’ N; Long 79°57’E), Ellichanur (ECR) (Lat 10°09’N; Long 79°36’E) and Thiruvanchikulam (TVM) (Lat 10°12’N; Long 76°12’E), were subjected to spectroscopic studies.

Representative pottery samples SPR-1 (red ware), SPR-2 (black ware), ECR (black ware) and TVM (red ware) were studied by using FTIR, XRD and Mössbauer spectroscopy. The archaeo-magnetic dating of the above samples was established which belongs to 610 AD (SPR), 910 AD (ECR) and 100 AD (TVM), respectively. Initially, the artisans were using sun-dried potteries for different purposes like, storing food materials, water and cooking purposes. After the development of technology, they used to make good quality potteries, by subjecting them to firing methods. The technology of production of archaeological materials reveal the level of the technical background of the people and can be used as an index of ancient civilizations and their interactions.

On firing the clay materials, the thermal transformation takes place and these can be followed by FTIR technique. Usually, clay is a mixture of minerals. Major minerals can be identified by using the X-ray diffraction technique. The microscopic analysis of the iron (state-of-iron i.e. Fe° and Fe⁺, 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.

2 Experimental Details

The FTIR absorption spectra were recorded in the frequency region 4000-400 cm⁻¹, using model Paragon 500, Perkin-Elmer spectrophotometer with 16 scan mode by using standard KBr pellet technique. The accuracy of the measurement is ± 4 cm⁻¹ in 4000 to 2000 cm⁻¹ region and ± 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 CuKα radiation, at a wavelength of 1.5405 Å. 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 analysis

The FTIR spectra of pottery samples SPR-1, SPR-2, ECR and TVM in the as-received state and re-fired at laboratory, in steps of 300, 500 and 800 °C are shown in Figs 1-4. The spectra of all the above samples in the as-received state shows a broad band centered around 3450 and 1640 cm\(^{-1}\) attributed to O-H stretching and H-O-H bending of absorbed water molecules, respectively. These bands are sensitive to temperature effect. On re-firing the samples, these bands get diminished and disappear at higher temperature which reflect the evaporation of absorbed water molecules. The absence of O-H stretching of inter-layer water and inner O-H group of adsorbed water bands around 3700 and 3620 cm\(^{-1}\) indicate that, the destruction of clay structure has taken place. The above bands are sensitive up to 450 °C. The absence of above bands indicate that, the samples were fired above 450 °C. The bands at 1100 and 915 cm\(^{-1}\) along with weak shoulder at 935 cm\(^{-1}\) are also sensitive to temperature effect up to 450 °C. The absence of these bands indicates that, the samples were fired above 450 °C. When clay is fired to 600 °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. In all the samples, a broad band was observed at 1030 cm\(^{-1}\) which indicates that the above samples were subjected to a firing temperature of above 600 °C during manufacturing.
500 °C along with the bands at 915 cm$^{-1}$ with the appearance of band at 540 cm$^{-1}$ due to hematite. The presence of the bands at 580 and 540 cm$^{-1}$ is attributed to the presence of iron oxides. By the presence of the bands at 540 and 580 cm$^{-1}$, the firing atmosphere and maximum firing temperature of the archaeological artifacts like potteries, bricks and tiles can be established.

Fig. 3 — FTIR absorption spectra of Elichur pottery ECR

The FTIR spectra of pottery sample SPR-1 shows weak shoulders in the band position 540 and 580 cm$^{-1}$ and might have been due to dissolved iron oxide particles in water during its long burial. When the sample was re-fired at 300 °C in the laboratory, the form of iron oxide becomes obvious at the band position 580 cm$^{-1}$, attributed to hematite and the intensity of the band remains the same at 500 °C. When the sample was re-fired at 800 °C, the intensity of the band 580 cm$^{-1}$ increases due to the re-oxidation process, that is, the laboratory firing temperature exceeds the original firing temperature of the pottery sample. It is evident that, the pottery sample SPR-1 might have been fired around 650-700 °C, under oxidizing atmospheric conditions, which is also reflected from the red colour of the pottery. The FTIR spectra of pottery sample SPR-2 show the presence of both 540 and 580 cm$^{-1}$ bands in the as-received state and the intensity remains the same when the sample was re-fired at 300 °C.

Fig. 4 — FTIR absorption spectra of Thiruvanchikulam pottery TVM

At 500 °C, the intensity of the band 580 cm$^{-1}$ increases than that of 540 cm$^{-1}$ band, which means that, re-oxidation might have taken place. Ursel Wagner et al. reported that, the sample manufactured under reduced atmosphere gives black colour. When re-firing the sample in laboratory atmosphere, the oxidation process takes place between 450 and 600 °C. This concept is well correlated with our pottery sample SPR-2. At 800
°C, the intensity of the band 580 cm⁻¹ increases than that of the intensity observed at 500 °C. It is confirmed that, the pottery sample SPR-2 might have been fired around 600-650 °C under reducing atmosphere, which reflects the black colour of the sample.

concluded that, the pottery sample ECR might have been fired around 650-700 °C, under strong reduced atmosphere, which is also reflected from black colour of the pottery. The spectra of the pottery sample TVM show weak shoulders at 580 and 540 cm⁻¹ in the as-received state, while its presence is obvious at 300 °C. Similar observations were obtained at 500 °C. While at 800 °C, the increase in intensity of 580 cm⁻¹ indicates that re-oxidation takes place. The pottery sample TVM might have been fired around 650-700 °C, under oxidizing atmospheric conditions, which is also reflected from the red colour.

The FTIR spectra of pottery sample ECR show weak shoulder in the band position 540 and 580 cm⁻¹ in the as-received state and remains the same in intensity by re-firing it up to 500 °C. This clearly indicates that, the pottery sample ECR was subjected to strong reduced atmosphere during its manufacturing. But, at 800 °C, the intensity of 580 cm⁻¹ is more than that of 540 cm⁻¹ which means that the oxidation process takes place. Hence, it is

Fig. 5 — XRD spectra of pottery samples (a) SPR-1, (b) SPR-2 (c) ECR, (d) TVM. Minerals peaks identified are quartz (Q), anorthite (A), albite (AL), orthoclase (O) and oligoclase (OL).

(i) XRD Analysis

X-ray diffraction spectra have been recorded for the powdered pottery samples SPR-1, SPR-2, ECR and TVM. The presence of major minerals was identified by comparing the JCPDS (Joint committee on powder diffraction standards) file. The spectra of all the above samples are shown in Fig. 5.

In SPR-1, the identified minerals are quartz (3.3416, 4.2582, 1.8173, 1.5415, 2.2803, 2.2978, 2.4520, 1.3711, 2.1259, 1.9783, 1.2511, 1.4484 and
1.6674 Å) and anorthite (3.1876 and 3.2454 Å). In SPR-2 similar minerals are identified like, quartz (3.3421, 4.2910, 1.3539, 2.2796, 2.4510, 1.3754, 2.1244, 1.6692, 1.9785 and 1.2558 Å) and anorthite (3.1833, 3.6534 and 4.0219 Å).

The minerals identified in ECR are quartz (3.3424, 4.2475, 1.8169, 1.8120, 1.5406, 1.3710, 2.1203 and 1.6748 Å) albite (3.1913, 2.9318 and 3.8329 Å) and orthoclase (3.2388, 3.2839, 2.1575 and 1.4588 Å). In TVM, the identified minerals are quartz (3.3398, 4.2491, 1.8166, 1.5319, 2.2719, 2.4533 and 1.3747 Å), oligoclase (3.1890, 3.6975, 2.0160 and 1.2495 Å) and orthoclase (3.7741 and 1.9184 Å). Quartz is predominant and makes the clay self-tempered.

(iii) Mössbauer Analysis

Room temperature Mössbauer spectra were recorded for the samples SPR-1, SPR-2, ECR and TVM in the as-received state and are shown in Fig.6. The Mössbauer parameters were derived from the peak positions of the spectra.

From the presence or 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 or disappearance of Fe$^{3+}$ ion indicative of oxygen rich in original firing atmosphere. Coey$^{12}$ 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$^{3+}$. The isomer shift value from 0.2 to 0.6 mm/s and quadrupole splitting value from 0 to 1.8 mm/s are attributed to Fe$^{2+}$. The Mössbauer spectrum of pottery sample SPR-1 shows the presence of paramagnetic Fe$^{2+}$ ion. The observed Mössbauer parameters ($\delta=0.446$ mm/s and $\Delta=1.200$ mm/s) are attributed to the presence of Fe$^{2+}$ ion. The pottery fired in oxidizing atmosphere, at temperatures above 500 °C, shows no Fe$^{2+}$ in its Mössbauer spectra. Murad et al.$^{11,12}$ reported that, usually the quadrupole splitting of Fe$^{2+}$ exhibits a typical increase of 0.7 to 1.35 mm/s on firing at 300-700 °C and decrease above 800 °C. From the above information and from the quadrupole splitting value (1.200 mm/s) of the sample SPR-1 indicates that, the sample might have been fired around 650 to 700 °C, under oxidizing atmosphere. It is also well established from the red colour of the pottery. The observed Mössbauer spectrum of pottery sample SPR-2 shows the presence of both paramagnetic Fe$^{2+}$ and Fe$^{3+}$ ions. The observed Mössbauer parameters ($\delta=0.412$ mm/s and $\Delta=1.090$ mm/s) are attributed to Fe$^{2+}$ ion, while ($\delta=1.162$ mm/s and $\Delta=2.590$ mm/s) are attributed to Fe$^{3+}$ ion. The presence of both Fe$^{2+}$ and Fe$^{3+}$ ions in the as-received state indicates that, the sample was fired under reducing atmosphere and gives the black colour.

The Mössbauer spectrum of pottery in the as-received state indicates the presence of paramagnetic Fe$^{2+}$ and Fe$^{3+}$ ions. The observed Mössbauer parameters ($\delta=1.083$ mm/s and $\Delta=2.433$ mm/s) are attributed to the presence of Fe$^{2+}$ ions, while ($\delta=0.361$ mm/s and $\Delta=0.988$ mm/s) are attributed to the presence of Fe$^{3+}$ ion. As seen in the previous case, the presence of both Fe$^{2+}$ and Fe$^{3+}$ ions in the as-received state indicates that, the sample was fired under reducing condition. It is also well established from the black colour of the pottery. The obtained Mössbauer spectrum of pottery sample TVM shows the presence of paramagnetic Fe$^{2+}$ ion. The observed Mössbauer parameters ($\delta=0.429$ mm/s and $\Delta=1.225$ mm/s) are attributed to the presence of Fe$^{3+}$ ion. From the observed quadrupole splitting value of 1.225 mm/s, it is concluded that the TVM pottery might have been fired around 650-700 °C, under oxidizing atmosphere during manufacturing. It is also well established from the red colour of the sample.

The results obtained from Mössbauer techniques are in good agreement with the result obtained from FTIR technique.

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References