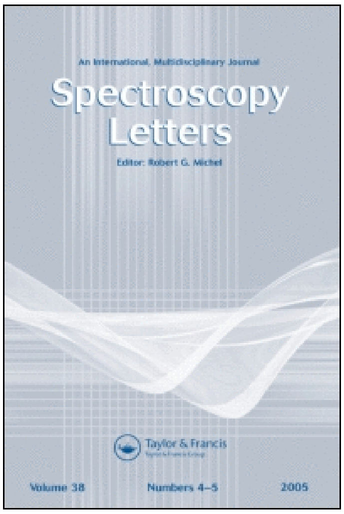

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DETERMINATION OF FIRING TEMPERATURE OF ANCIENT POTTERIES BY MEANS OF INFRARED AND MOSSBAUER STUDIES

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ABSTRACT

FT-IR, XRD and Mossbauer spectra of recently excavated archaeological potteries from Theriruveli, Tamilnadu, India were studied with as received state and refried at different temperatures in laboratory. The type of clay minerals associated with the potteries, their origin, the oxidation state of iron bearing minerals and the art of firing adopted during manufacturing were established. An attempt has also been made to correlate the colour of the potteries with the iron compounds.

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INTRODUCTION

Recently, ancient human ruins were excavated (2000) in Theriruveli village (9°19′ Lat.N; 78°38′ Long.E), located in Southern Tamilnadu, India. There are different types of potteries, bones and bricks have been found at the time of excavation. They belongs to 700–800 AD. The transformation of clay into pottery was an important step in the development of artisans. The technology of production of archaeological materials reveals the level of the technical background of the people and can be used as an index of ancient civilizations and their interactions.[1] In the present investigation potteries have been studied by using FT-IR, X-ray diffraction and Mossbauer spectroscopy. Usually all clays contains 1 to 10 weight percent of iron.[2] This is sufficient for measuring a good Mossbauer spectra of clay-based materials like potteries, bricks and tiles etc.

DESCRIPTION OF THE MATERIAL

For the present investigation black and red wares have been subjected to FTIR, XRD and Mossbauer studies. The X-ray diffraction yields the information about the major minerals present in the material, while FTIR technique has been used to study the type of clay mineral, their structural characteristic and lower limit of firing temperature during manufacturing. The Mossbauer spectroscopy provides the clue about the iron-bearing minerals and their oxidation state in clays and clay-based materials like potteries, bricks and tiles. These iron oxides tend to escape detection by XRD because of their small particle size and low concentrations.[3]

EXPERIMENTAL TECHNIQUES

The infrared absorption spectra were recorded in the wavelength 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 $\pm 4\,\mathrm{cm}^{-1}$ in 4000 to 2000 cm^{-1} region and $\pm 2\,\mathrm{cm}^{-1}$ in 2000 to 400 cm^{-1} region. The X-ray powder diffraction spectra were recorded on X'pert MPD from Philips using CuK_α radiation at a wavelength of 1.54056 A°. The spectra were recorded in the 2 theta (2θ) range from 20° to 80°. The Mossbauer measurements were preformed in conventional constant acceleration spectrometer. A 54 $\mathrm{mC_i}$ $^{57}\mathrm{Co}$ in Rh matrix was used as radioactive source. The spectra were calibrated using a standard 25 mm thick natural iron foil and the Lorentzian curve has been fitted for the Mossbauer experimental data of the pottery samples.

INFRARED ANALYSIS

The IR spectra of pottery samples TIV-1, TIV-2 in the as received state and refired at laboratory in steps of 250°, 450° and 750°C are shown in Fig. 1 and the probable assignments are given in Tables 1 and 2. The spectra of both the samples in as received state shows a broad band centered about 3400 cm^{-1} and 1640 cm^{-1}, which are attributed to stretching and bending of absorbed water molecules present in the samples. The water molecules are absorbed by the potteries during burial under the earth. These bands are sensitive to temperature effect. After refiring the samples to 250°C these bands gets diminished which reflects the evaporation of absorbed water molecules. The OH-stretching of crystalline water band around 3700 cm^{-1} is completely absent which reflects the destruction of clay structure and the samples were subjected to temperature of above

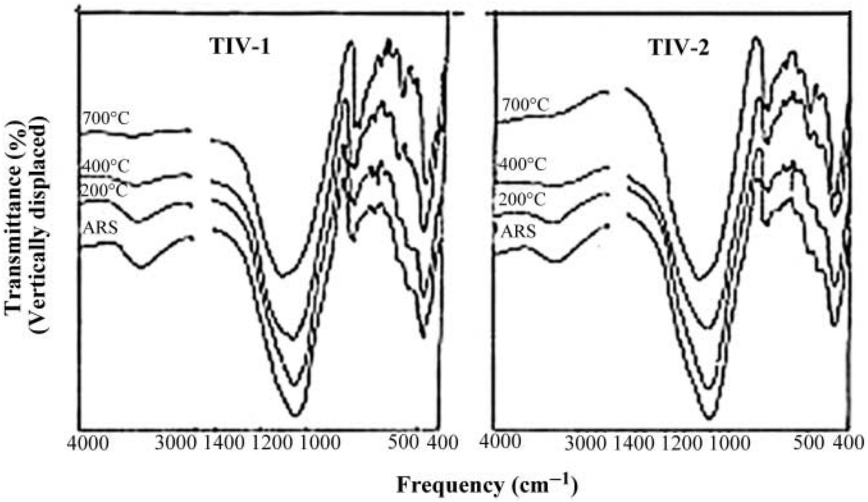

Figure 1. Infrared absorption spectra of TIV-1 and TIV-2 pottery samples at different temperatures.

Table 1. Infrared Absorption Frequencies, Relative Intensity Estimate, and Probable Assignments of Theriruveli Pottery (TIV-1) at Different Temperatures

	Intensities				
Frequency cm^{-1}	As Received State	250°C	450°C	750°C	Tentative Assignments
3700	—	—	—	—	O-H stretching of inter layer water
3669	—	—	—	—	Inplane degenerated vibration of water molecule
3652	—	—	—	—	O-H stretching of inner hydroxyl group
3620	—	—	—	—	Inner O-H group of adsorbed water
3450	VW	VW	VW	VW	O-H stretching of absorbed water molecule
1640	VW	VW	VW	VW	H-O-H bending vibration of absorbed water molecule
1100	—	—	—	—	$[A1\text{-}O\text{-}(OH)]_6$
1080	—	—	—	VS	Si-O-Si
1030	VS	VS	VS	—	Si-O-Si
935	—	—	—	—	O-H deformation
915	—	—	—	—	A1-OH
875	—	—	—	—	Fe^{3+} (A1-OH)
795	VW	W	W	M	Si-O of quartz
775	W	W	W	M	Si-O of quartz
725	WS	WS	—	—	—
695	VW	VW	VW	VW	Si-O of quartz
670	VW	VW	VW	VW	—
640	VW	VW	VW	VW	Al-O co-ordination vibration
580	WS	WS	W	W	Fe-O of Fe_3O_4
540	WS	WS	W	VW	$Si\text{-}O\text{-}Al^{IV}$ or Fe_2O_3
515	WS	WS	WS	—	$Si\text{-}O\text{-}M^{VI}$
465	M	M	M	S	Si-O-Si bending
430	—	—	—	—	Si-O of mixed vibrations

W = weak; VW = very weak; WS = weak shoulder; M = medium; S = strong.

Table 2. Infrared Absorption Frequencies, Relative Intensity Estimate, and Probable Assignments of Theriruveli Pottery (TIV-2) at Different Temperatures

Frequency cm^{-1}	Intensities: As Received State	250°C	450°C	750°C	Tentative Assignments
3700	—	—	—	—	O-H stretching of inter layer water
3669	—	—	—	—	Inplane degenerated vibration of water molecule
3652	—	—	—	—	O-H stretching of inner hydroxyl group
3620	—	—	—	—	Inner O-H group of adsorbed water
3450	VW	VW	VW	VW	O-H stretching of absorbed water molecule
1640	VW	VW	VW	VW	H-O-H bending vibration of absorbed water molecule
1100	—	—	—	—	$[Al\text{-}O\text{-}(OH)]_6$
1080	—	—	—	VS	Si-O-Si
1030	VS	VS	VS	—	Si-O-Si
935	—	—	—	—	O-H deformation
915	—	—	—	—	A1-OH
875	—	—	—	—	Fe^{3+} (A1-OH)
795	VW	VW	W	W	Si-O of quartz
775	VW	VW	W	W	Si-O of quartz
725	WS	WS	—	—	—
695	VW	VW	VW	VW	Si-O of quartz
670	VW	VW	VW	VW	—
640	VW	VW	VW	VW	Al-O co-ordination vibration
580	VW	VW	VW	W	Fe-O of Fe_3O_4
540	W	W	W	W	$Si\text{-}O\text{-}Al^{IV}$ or Fe_2O_3
515	—	—	—	—	$Si\text{-}O\text{-}M^{VI}$
465	M	M	M	M	Si-O-Si bending
430	—	—	—	—	Si-O of mixed vibrations

W = weak; VW = very weak; WS = weak shoulder; M = medium; S = strong.

450°C during manufacturing because this band is sensitive up to 450°C.[4] A very strong symmetry band observed at 1080 cm^{-1} shows the complete destruction of octahedral sheet structure of clay minerals. In pure clays there are three prominent bands observed at 1100 cm^{-1}, 1080 cm^{-1} and 915 cm^{-1} with weak shoulder at 935 cm^{-1}. These bands are sensitive to temperature effect when clay mineral are fired to 650°C the complete destruction takes place and a symmetry band observed at 1030 cm^{-1} for red clay and at 1080 cm^{-1} for white clay type.[5–7] From the above observations, it is concluded that the pottery samples TIV-1 and TIV-2 are made up of red clay type (disordered clay) and subjected to firing temperature of about 650°C during manufacturing. The sharp bands appeared at 795 cm^{-1} and 775 cm^{-1} along with 695 cm^{-1} in both the samples are due to Quartz.[7,8] The band at 640 cm^{-1} is attributed to Al-O coordination vibration. The presence of the bands at 580 cm^{-1} and 540 cm^{-1} are attributed to the presence of magnetite and haematite in both the samples. In case of pure clays a sharp band at 540 cm^{-1} is appeared due to Si-O-Al^{IV} octahedral sheet structures and is also sensitive to temperature effect. This band disappears by heating the clay minerals to 470°C along with the bands at 915 cm^{-1} [9]. The disappearance of the band at 540 cm^{-1} and appearance of the bands at 580 cm^{-1} and 540 cm^{-1} are due to the replacement of Al- by Fe^{2+}, Fe^{3+} or Mg^{2+}. These bands are also sensitive to atmospheric conditions under which the samples fired during manufacturing. The IR spectra of TIV-1 sample shows weak shoulder at 580 cm^{-1} and 540 cm^{-1} in as received state and at 250°C while it is obvious and equal in intensity at 450°C. At 750°C, the intensity of the band at 580 cm^{-1} gets increased than that of 540 cm^{-1} band indicating that the oxidation taking place during refiring the sample in laboratory under open atmosphere which converts the haematite into magnetite.

From the above observations it is evident that the presence of symmetry band at 1030 cm^{-1} coupled with weak bands at 580 cm^{-1} and 540 cm^{-1} indicate that the pottery sample TIV-1 was subjected to firing temperature of around 650°C under oxidizing conditions. In TIV-2 sample very weak band at 580 cm^{-1} persists upto 450°C with weak band at 540 cm^{-1}. At 750°C, the intensity of the band at 540 cm^{-1} gets decreased with the increase of 580 cm^{-1} indicating the oxidation of Fe occurs during refiring. The presence of symmetry band at 1030 cm^{-1} along with very weak band at 580 cm^{-1}, weak band at 540 cm^{-1} indicates that the pottery might have been heated around 650°C to 700°C under reduced atmosphere. It is also evident from the black colour of the pottery, while TIV-1 is red in colour. The presence of 470 cm^{-1} in both the samples is attributed to Si-O-Si bending of silicate mode and is free from any temperature effects.

X-RAY DIFFRACTION

Often, X-ray diffraction technique has been considered as a supplement to Mossbauer spectroscopy because of analyzing the complete picture of iron bearing minerals in archaeological materials. XRD provides the information about the major minerals present in the material while Mossbauer spectroscopy provides the form of iron present in the material, which cannot be detected by XRD because of small particle size and low concentrations. X-ray diffraction spectra have been recorded for the powdered pottery samples of TIV-1 and TIV-2. The presence of mineral phases has been identified by comparing the JCPDS file.[10] The spectra of TIV-1 and TIV-2 are shown in Fig. 2.

In TIV-1, the identified minerals are quartz (4.2507 A°, 3.3418 A°, 2.4520 A°, 2.2761 A°, 2.1257 A°, 1.8144 A°, 1.6679 A°, 1.5365 A° and 1.3710 A°) as predominant and the minor minerals of oligoclase (4.0369 A°, 3.4750 A° and 3.1744 A°), orthoclase (3.9365 A°, 3.7549 A° and 2.1659 A°) and hematite (2.5183 A° and 1.8429 A°) while in TIV-2, the identified minerals are quartz (4.2484 A° and 3.3420 A°), oligoclase (3.1808 A° and 1.3599 A°), orthoclase (3.2317 A°) and biotite (2.6108 A° and 1.9873 A°). Quartz is predominant and makes the clay self-tempered.[11] The presence or absence of certain minerals can serve as a thermometer for determining the temperature of firing of the potteries[12] and they have been described in the following sections.

MOSSBAUER MEASUREMENTS

^{57}Fe room temperature Mossbauer spectra in transmission geometry were recorded for as received state of the pottery sherds and refired to 450°C

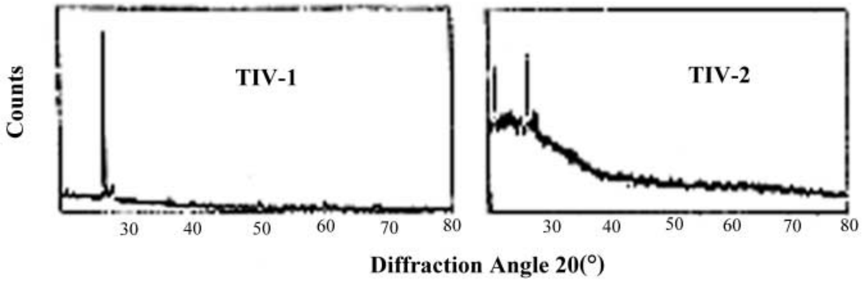

Figure 2. X-ray diffraction diagrams measured with CuKα radiation for pottery samples TIV-1 and TIV-2.

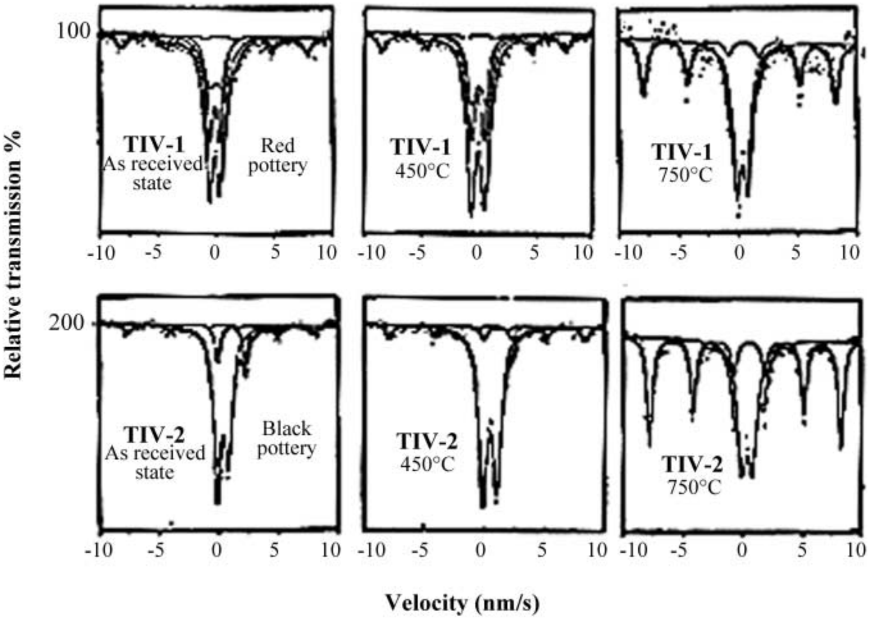

Figure 3. Room temperature Mossbauer spectra of TIV-1 and TIV-2 pottery sherds in the as received and refired at different temperatures.

and 750°C and the data were obtained. Typical Mossbauer spectra of TIV-1 and TIV-2, of as received state and refired at laboratory to 450°C and 750°C are shown in Fig. 3 and the Mossbauer parameters are given in Table 3.

When refiring the ancient pottery sherds in laboratory, no changes will arise in the Mossbauer parameters until the refiring temperature exceeds original firing temperature during manufacturing. In this manner the maximum original firing temperature of the archaeological materials can be determined.[13] The Mossbauer spectra of TIV-1 of received and at 450°C are identical which exhibits the characteristics of doublet. This may be attributed to the presence of Fe^{3+} ion in the sample having an isomer shift of 0.44 mm/s to 0.60 mm/s and a quadrapole splitting of -0.49 mm/s, 1.32 mm/s and 0.86 mm/s with the field of 496 kOe. At 750°C, changes have been observed in Mossbauer parameters, so one can confirm that the material was fired below 750°C. The presence of quadrapole splitting 0.86 mm/s exhibits the Fe^{3+} ions in oxides or silicates. Also the presence of quadrapole splitting 1.32 mm/s exhibits the material might have been fired around 650°C. At 750°C, the sample exhibit a characteristic of six-line magnetic pattern associated with magnetic Fe^{3+} doublet having an isomer

Table 3. Mossbauer Parameters of Pottery Samples TIV-1 and TIV-2 at Different Temperatures (Refired)

			As Received State					450°C					750°C			
Sample Pottery	Colour of the Pottery	Magnetic Field kOe	δ mm/s		Δ mm/s		Magnetic Field kOe	δ mm/s		Δ mm/s		Magnetic Field kOe	δ mm/s		Δ mm/s	
			Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}		Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}		Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}
TIV-1	Red	496	—	0.6053	—	−0.49	494	—	0.4052	—	0.45	500	—	0.4435	—	−0.28
			—	0.5937	—	1.32		—	0.5437	—	1.30		—	0.3921	—	0.91
			—	0.4412	—	0.86		—	0.4279	—	0.84		—	—	—	—
TIV-2	Black	476	—	0.4305	—	−0.36	474	—	0.4640	—	0.30	497	—	0.4432	—	−0.25
			—	0.4406	—	0.90		—	0.4440	—	1.15		—	0.4165	—	0.98
			1.1885	—	2.30	—		1.1140	—	2.30	—		—	—	—	—

δ – Isomer shift.

Δ – Quadrupole splitting.

shift of 0.44 and 0.39 mm/s and quadruple splitting of −0.28 and 0.91 mm/s with the field of 500 kOe. The presence of quadruple splitting −0.28 mm/s with the field of 500 kOe attributed to Fe^{3+} ion both in haematite and in tetrahedral sites of magnetite.[14] The observed quadruple splitting 0.91 exhibits the formation of Fe^{3+} species by reoxidation of Fe^{2+}. From the above informations it is confirmed that the material has been subjected to firing of around 650°C during manufacturing. The above results are in good agreement with the FTIR results. The presence of Fe^{3+} ion in as received state and exists up to 450°C during refiring of TIV-1 sample indicating that it was subjected to firing under oxidizing atmosphere during manufacturing. It is also well reflected from the red colour of the pottery. In TIV-2 sample, the presence of both Fe^{2+} ($\delta = 1.1885$ mm/s and $\Delta = 2.30$ mm/s) and Fe^{3+} ($\delta = 0.4305, 0.4406$ mm/s and $\Delta = -0.36, 0.90$ mm/s) ions observed at as received state with the field of 476 kOe. The same mossbauer parameter values are observed at 450°C with very slight variations, but Fe^{2+} ion peak intensity decreased and it might be due to reoxidation process takes place in laboratory reheating or by weathering during burial of the shreds in the ground may change the chemical and physical state of the iron. So, in such cases, the changes will arise below the original firing temperature. If the firing atmosphere differs in the original and the laboratory can affect the Mossbauer spectra.[13] The above conclusions are agreed well with our results of TIV-2 sample. At 750°C, the sample exhibits a characteristic of six-line magnetic pattern with the effective field of 497 kOe may be attributed to haematite.[11] Usually haematite will form at this temperature. From the above results one can confirm that TIV-2 sample was fired around 650–700°C under reducing condition deduced from the presence of Fe^{2+} with Fe^{3+} at as received and 450°C. It is well evidenced from the black colour of the sample.

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