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# Application of $^{57}$Fe Mössbauer Spectroscopy for the Characterization of Archaeological Pottery of Tamilnadu, India

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**Abstract**: This paper report on a study of recently excavated archeological potteries of Tamilnadu using $^{57}$Fe Mössbauer spectroscopy and XRD. The Mössbauer spectra were measured at room temperature (RT) of archaeological potteries. During firing, the iron-bearing compounds in clays undergo characteristic changes which depend on kiln temperature and atmosphere. These changes can be observed in the Mossbauer spectra. The recorded Mössbauer spectra were used to derive information about the firing temperatures and the kiln atmosphere on oxidizing/ reducing conditions during firing of potteries was established. The XRD study supports the determination of firing temperature and atmospheric condition prevailed at the time of manufacturing the potteries. The combined method of XRD and Mössbauer spectroscopic techniques revealed the artisan's skill in manufacturing different colour of the pottery with atmospheric conditions.

**Keywords**: Archaeological Potteries, Mössbauer spectroscopy, XRD, Firing Temperature, Firing conditions.

## 1 Introduction

Mössbauer spectroscopy has now established itself as a technique which can provide valuable information in many areas of science. In the last thirty years, Mössbauer spectroscopy has gradually become a well established method for the characterization of materials of interest in the field of archaeology. Mössbauer spectroscopic study of archaeological artefacts such as potteries, bricks and tiles have been used extensively to estimate the firing conditions, firing temperature and state of oxidation present in the samples. Mössbauer spectral studies on archaeological artefacts were briefly carried out by many authors to establish the presence of magnetic components and their transformation due to fire, firing conditions and colouring mechanism [1-8].

The Mössbauer effect proved to be an excellent method for studying iron positions in layer silicate minerals and has been used to establish the presence of $Fe^{2+}$ and $Fe^{3+}$in clay minerals [9]. Presence of Fe (III) containing hematite and Fe (II) containing magnetite suggests that the artefacts were manufactured by firing in an oxidizing/reducing atmosphere. The most important primary information to be gleaned from Mössbauer spectra is on the hyperfine interactions between the Mössbauer nuclei and their electronic environment in solids through its parameters, i.e., (i) The isomer shift (IS), (ii) The electric quadrupole splitting (QS) and (iii) The magnetic hyperfine splitting of the Mössbauer pattern. These provide information (i) on the chemical state of the iron, mainly on its valence state ($Fe^{2+}$ or $Fe^{3+}$), (ii) on the symmetry of the environment of the iron in the sense that the distortion of the environment influences the electric field gradient at the iron nuclei and hence the quadrupole splitting, and (iii) on the magnetic properties of the iron bearing compounds. This enables one to determine which iron bearing compounds or minerals are present in a composite material [10].

The interest of the present work focuses on the production technology and firing temperature of the recently excavated archaeological pottery from Tamilnadu using Mössbauer spectroscopy and XRD analysis.

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## 2 Materials and Methods

### *2.1 Sample Collections*

The excavation had been carried out by the Department of History, School of Social Sciences & International Studies, Pondicherry University, Puducherry, India at different archaeological sites in various places of Tamilnadu such as Thoppur, Veeranam, (Thandrampet), Kottapalayam, Kavalapatti, Thamaraikulam, Porunthal, Alagapuri and Nattapurakki etc. Potsherd types are the bottom and the rim of the wares. Body layers have buff color with fine and medium grains in the texture. Almost all the slip layers have been nearly worn-out. They are in color Red ware; Red slipped ware and Black and Red ware. The samples were taken at a depth of 6 mts. Samples were taken from the body of the pottery fragments, avoiding 1 mm surface layer. The hole of the samples is fine powdered using an agate mortar in order to be analyzed by different analytical techniques. Description of Pottery samples of Tamilnadu are given in Table 1.

### *2.2 Archaeological Sites*

The investigated archaeological pottery samples were collected at the excavation sites, Thoppur, (Tiruvannamalai District) (Long: 12˚29′32”N; Lat: 78˚77′53”E), Veeranam, (Tiruvannamalai District) (Long: 12˚14′26”N; Lat: 78˚94′48”E), Kottapalayam, (Karur District) (Long: 10˚78′24′′N; Lat: 77˚58′23′′E), Kavalapatti (Dindigal District)(Long: 10˚25′40′′N; Lat: 77˚26′13′′E), Thamaraikulam, (Dindigul District) (Long: 10˚36′25′′N; Lat: 77˚53′40′′E). Porunthal, (Dindigul District) (Long: 10˚34′58′′N; Lat: 77˚52′59′′E), Alagapuri (Sivaganga District) (Long: 9˚82′31′′N; Lat: 78˚26′37′′E) and Nattapurakki, (Sivaganga District) (Long: 9˚68′45′′N; Lat: 78˚45′59′′E). The pottery samples excavated from above locations dates back to5th (Iron Age grave) century.

### *2.3 Sample Analysis*

The Mössbauer measurements have been carried out with a conventional constant acceleration spectrometer (M /s WISSEL, Germany) equipped with a room temperature Rh matrix $^{57}$Co source. The hyperfine parameter isomer shift (IS), quadrupole splitting (QS), full line width at half maximum (W), expressed in mm /s, and the internal magnetic field $H_{int,}$ expressed in tesla, have been obtained by means of a standard least-squares minimization technique. The spectra are fitted to Lorentzian line shapes using a minimum number of doublets and sextets. The spectra recorded at room temperature, are fitted to a PC with a least squares minimization procedure assuming Lorentzian line shapes. All the Mössbauer spectra are fitted first to Lorentzian profiles by a least-squares method using the ISO fit program [11]. For the pottery, generally one or more broad doublets (Fig.4.) are used, characterized by an isomer shift ($IS_D$) and a quadrupole splitting ($QS_D$) [12-13].

Room temperature of Mössbauer spectrum and XRD was recorded for the selected samples TPP3, TP1, KMP3, KPP1, TKP4, PP1, PP4, AP1 & NP4. A typical Mossbauer spectrum is depicted in Fig.1-5. A typical XRD spectrum is shown in Fig.6. Samples for X-ray powder diffraction (XRD) studies were packed in shallow cavities in glass slides to minimize preferred orientation. The X-ray patterns of powdered pottery samples were recorded at room temperature by using X-ray diffractometer (D500, Siemens) having a curved graphite crystal diffracted monochromator, with a source of CuKα radiation and NaI(Tl) scintillation detector. Diffraction patterns were obtained by continuous scanning from 10to70°. Qualitative mineralogy of the studied samples is determined with the standard interpretation procedures of XRD. A typical XRD spectrum of Thoppur potsherds is shown in Fig.6.

## 3 Results and Discussions

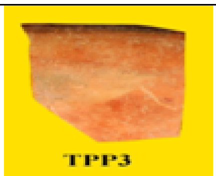
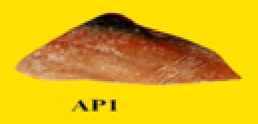
### *3.1 Mössbauer Analysis*

The Mössbauer studies on archaeological artefacts is based on the iron bearing clay minerals as well as associated minerals, including iron oxides undergo characteristic chemical and physical changes depending on the firing temperature and kiln atmosphere [3]. The Mossbauer parameters of the samples were derived from the peak position of the spectrum. The Mossbauer parameter of selected samples is reported in Table 2. From presence or absence of $Fe^{2+}$ and $Fe^{3+}$, firing temperature, firing atmosphere and colouring technique of ancient potteries have been determined. In the sample TPP3, the value of isomer shift (δ) of 0.31 mm/s and the value quadrupole splitting of 1.02 mm/s observed in the sample is attributed to $Fe^{3+}$. Tominga et al., (1978) have extensively studied Japanese roofing tiles and reported the value of isomer shift 0.205 mm/s and quadrupole splitting -0.21 ± 0.03 for pure hematite [14].

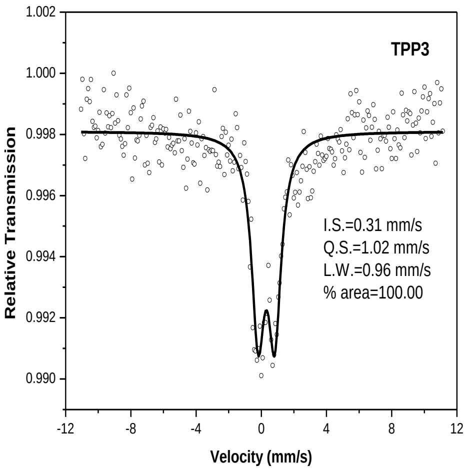
Coey, (1980) reported that the isomer shift (δ) value range from 0.2 to 0.6 mm/s and quadrupole splitting (Δ) value from 0 to 1.8 mm/s are attributed to $Fe^{3+}$ [15]. Wagner et al., (1999) reported that the isomer shift (δ) value ranges from 0.3 to 0.4 mm/s and quadruple splitting (Δ) value from 1.6 to 1.8 mm/s are attributed to $Fe^{3+}$ [4]. The above results compared with our sample (TPP3) which indicated that $Fe^{3+}$ ion in the samples.

Hematite is one of the most colouring materials in potteries. The presence of hematite gives reddish color to the pottery. Eissa and Sallam, (1988) reported that the red color of the pottery to $Fe^{3+}$ ion which is attributed to hematite whose formation in favour of oxidizing firing

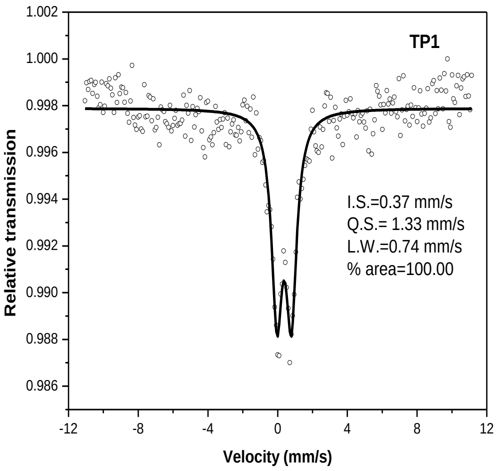
**Table 1** Description of Pottery samples of Tamilnadu.

| S.No | Sample Location | ID | Inner color | Outer color | Period | Figure |
|---|---|---|---|---|---|---|
| 1 | Thoppur | TPP3 | Red | Red | 500 BC |  |
| 2 | Veeranam | TP1 | Red | Red | Between 100BC and 300AD |  |
| 3 | Kottapalayam | KMP3 | Black | Red | 500 BC |  |
| 4 | Kavalapatti | KPP1 | Black | Red | 500 BC |  |
| 5 | Thamaraikulam | TKP4 | Black | Black | 500 BC |  |
| 6 | Porunthal | PP1 | Red | Red | 500 BC |  |
| 7 | Porunthal | PP4 | Black | Black | 500 BC |  |
| 8 | Alagapuri | AP1 | Black | Red | 500 BC |  |
| 9 | Nattapurakki | NP4 | Black | Red | 500 BC |  |

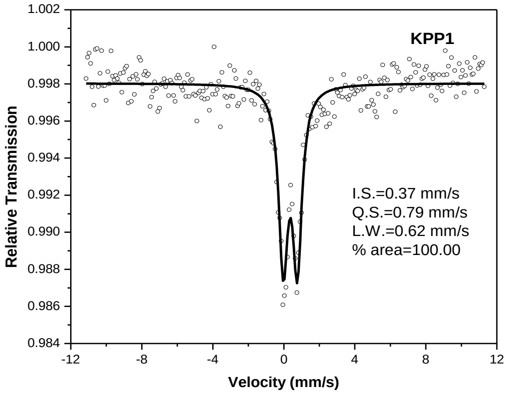
1



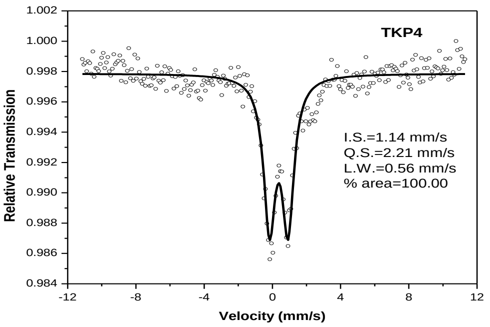
2



3



4



5

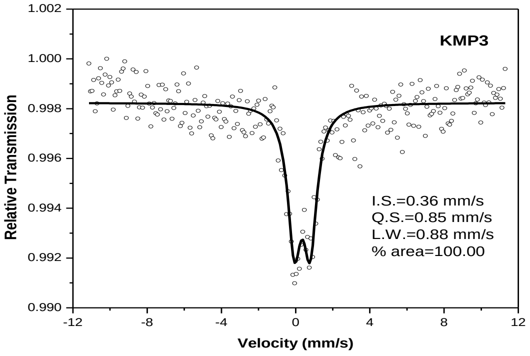


**Figure 1-5** shows Mossbauer spectrum of selected samples

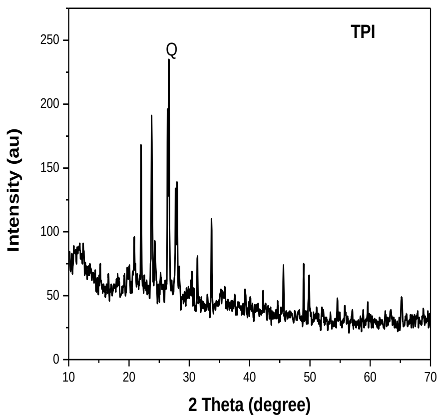


**Figure .6**.A typical XRD spectrum of Thoppur potsherd

while the black color to $Fe^{2+}$ phase and magnetite present in the sample and the firing conditions is reduced atmosphere [16]. From the above discussions, the sample TPP3 is fire d under oxidizing atmospheric conditions during manufacturing. It is well established from the red color of the pottery. The absence of $Fe^{2+}$ in receiving state indicating that the firing will form around 680˚C. Wagner et al., (2000) has reported that on fire clay in between 700–900˚C, the structure of the class will break down together [5]. The structural clays then mainly form hematite. The formation of hematite is seen in the Mössbauer spectrum as an increase of the magnetic, or conversely, is a decrease of the non magnetic areas of the Mössbauer spectrum. This indicated that this sample has been fired above 700˚C. Further, there is no magnetic six line pattern observed in the samples clearly indicating that there are no well crystallized or magnetically ordered iron ions or compounds in the samples.

**Table.2** Mössbauer parameters of Tamilnadu pottery samples in as- received state

| **S.No:** | **Sample ID** | **I.S. (mm/s)** | **Q.S. (mm/s)** | **Line-width** | **% Area** | **Result** |
|---|---|---|---|---|---|---|
| 1 | TPP3 | 0.31 | 1.02 | 0.96 | 100 | $Fe^{3+}$ (Hematite) |
| 2 | TP1 | 0.37 | 1.33 | 0.74 | 100 | $Fe^{3+}$ (Hematite) |
| 3 | KMP3 | 0.36 | 0.85 | 0.88 | 100 | $Fe^{3+}$ (Hematite) |
| 4 | KPP1 | 0.37 | 0.79 | 0.62 | 100 | $Fe^{3+}$ (Hematite) |
| 5 | TKP4 | 1.14 | 2.21 | 0.56 | 100 | $Fe^{2+}$ (Magnetite) |
| 6 | PP1 | 0.35 | 1.04 | 0.83 | 100 | $Fe^{3+}$ (Hematite) |
| 7 | PP4 | 1.22 | 2.51 | 0.85 | 100 | $Fe^{2+}$ (Magnetite) |
| 8 | AP1 | 1.17 | 2.26 | 0.61 | 100 | $Fe^{2+}$ (Magnetite) |
| 9 | NP4 | 0.43 | 0.90 | 0.84 | 100 | $Fe^{3+}$ (Hematite) |

The value of isomer shift (δ) of 0.37 mm/s and the value quadrupole splitting of 1.33 mm/s is present in the sample TP1. This may be attributed to the presence of Fe$^{3+}$. Wagner et al., (1999) reported that quadrupole splitting 0.66 to 1.05 mm/s is attributed to Fe$^{3+}$ species on fire at 400˚C and the splitting reaches a maximum of 1.35 mm/s on fire at 700˚C [4]. In the present work, the value of 1.43 mm/s obtained in the received state indicating that the sample has been fired above 700˚C under oxidizing atmosphere. It is well established from the red color of the pottery.

In the sample KMP3, the value of isomer shift (δ) of 0.36 mm/s and the value quadrupole splitting of 0.85 mm/s is identified in the sample indicate that the presence of hematite. The absence of Fe$^{2+}$ indicates that the sample was not fired in strong oxidizing atmosphere. The larger percentage of non magnetic Fe$^{3+}$ reveals that the sample was not fired above 900˚C, at which entire structural iron forms hematite. The quadrupole value of 0.85 mm/s for Fe$^{3+}$ is in agreement with clay fired at higher temperature reported by Wagner et al.,(2000) [5]. For the above reason, it may be concluded that the sample was fired above 750˚C in oxidizing atmosphere, the same is also revealed from the black and red ware. Wagner et al., (1999) reported that black inner reveals that sufficient air is not allowed to the inner surface of the pottery is dense, so oxidation have not taken place and another reason is artisans used to fire the pottery in the inverted position, so enough air is not admitted, which is reason for the black surface of inner portion [4]. The estimated firing temperature of the sample is well comparable with infrared results.

The Mössbauer spectrum of the pottery sample KPP1 shows the presence of paramagnetic Fe$^{3+}$ ion. Tominga et al., (1978) reported that the isomer shift of 0.25 to 0.35 mm/s and the quadrupole splitting of 0.7 to 0.9 mm/s attributed to paramagnetic Fe$^{3+}$ ion [14]. The value of isomer shift (δ) of 0.37 mm/s and the quadrupole splitting of 0.79 mm/s is due to presence of Fe$^{3+}$ in the sample KPP1 from the above value. Maniatis et al., (1981) reported that the red color of the pottery is attributed to hematite whose formation in the favoured oxidizing firing while the black color to Fe$^{2+}$ phase and magnetite present in the sample and the firing condition of reducing atmosphere [17]. The absence of Fe$^{2+}$ indicates that the sample was fired under oxidizing atmosphere and the sample might have been fired above 750˚C.

The received spectra of TKP4 & PP4, the value of isomer shift (δ) of 1.14 & 1.22 mm/s and quadrupole splitting of 2.21 & 2.51 mm/sis attributed to Fe$^{2+}$. Tominga et al., (1978) reported that the isomer shift 1.19 &1.2 mm/s and the quadrupole splitting of 2.30&2.57 mm/s attributed to Fe$^{2+}$ ion [14]. The above statement is compared with our results of TKP4 showed the presence of Fe$^{2+}$ ion in the sample. Further, there is no magnetic six line pattern observed in the received state indicates that there is no well crystallized or magnetically ordered iron or ion compounds present in the sample. Eissa and Sallam, (1988) reported that the red color of the pottery is attributed to hematite whose formation in favor of oxidizing firing while the black color to Fe$^{2+}$ phase and magnetite present in the sample and the firing conditions is reduced atmosphere [16]. The presence of Fe$^{2+}$ in the sample is well correlated with the black color of the pottery and this sample was fired in reducing atmosphere above 700˚C.

The Mössbauer spectra of the sample PP1 shows the value of isomer shift (δ) of 0.35 mm/s and the value quadrupole splitting of 1.04 mm/s are identified in the sample indicate that the presence of Fe$^{3+}$. The absence of Fe$^{2+}$ ions indicative of oxygen rich in original firing atmosphere and also red colour surface is due to conversion of Fe$^{2+}$ to Fe$^{3+}$. The quadrupole splitting of 1.04 mm/s indicates that the sample might have been fired above 750˚C. The presence of Fe$^{3+}$in the received state indicates that the sample is fired open atmosphere and it is well established the red color of the pottery.

The observed value of isomer shift (δ) of 1.17 mm/s and the value quadrupole splitting of 2.26 mm/s indicated the presence of Fe$^{2+}$ ion in the sample of AP1. The presence of Fe$^{2+}$ indicated magnetite in the sample. The interior black color of the pottery may be due to the presence of magnetite [18]. From the above information, one can identify that this pottery might have been fired under reducing conditions and air was not allowed during the firing cycle. The firing temperature of this sample might have been fired around 700˚C during manufacture.

The obtained Mossbauer spectrum of the sample NP4 shows the presence of paramagnetic Fe$^{3+}$ ion from the values of the value of isomer shift (δ) of 0.43 mm/s and the value quadrupole splitting of 0.90 mm/s. The low value of quadrupole splitting of 0.90 mm/s for Fe$^{3+}$ shows that the sample might be fired above 750˚C under oxidizing atmosphere during manufacturing. It is also well established from the red color of the pottery.

According to Ramaswamy et al (1989) and Venkatachalapathy et al (2008), the presence of higher percentage of Fe$^{2+}$ reveals the reduced atmosphere and is the reason for black colour of the pottery, whereas higher percentage of Fe$^{3+}$ is due to the strong oxidizing atmosphere which reflects reddish colour of the pottery [19, 20]. Based on the above statement, the black colour pottery sherds of TKP4 & PP4 have shown the presence of higher amount of ferrous compounds attributed to the reducing conditions in the kiln during firing. These ferrous compounds together with carbon from dense smoke are the causes for the black colour.

The pottery shreds KMP3, KPP1, AP1 & NP4 are in black and red colours might be fired in between 700ºC to 800˚C. The presence of black and red colours on these shreds may be attributed to the blow of air in the closed kiln during the firing process at reduced atmosphere and also adoption of changing atmosphere during heating and cooling the potteries in the kiln at the time of manufacture. The pottery sherds TPP3, TP1 & PP1 might be fired above 700˚C under oxidizing atmosphere. It is well established from the red color of the pottery. This may be due to the presence of $Fe_2O_3$ and the adoption of oxidizing atmospheric firing are the reasons for the reddish colour of the pottery sherds.

From the analysis the important findings are (i) The strong oxidizing atmosphere results red ware of samples (ii) The strong reducing atmosphere results black ware of the samples (iii) The strong reducing atmosphere with admission of air at lower temperature results the brown and black ware (iv) The strong reducing atmosphere with admission of air at higher temperature results in the red and black ware. The firing temperature and firing conditions derived from Mossbauer Technique are given in Table 3. The results obtained from the Mössbauer spectroscopy is confirmed from the XRD analysis.

**Table 3** Site name, sample I, nature of the sample color, firing temperature and firing conditions derived from Mossbauer Technique

| Site Name | Sample ID | Nature of the Sample colour | | Mossbauer Technique | |
|---|---|---|---|---|---|
| | | Interior | Outer | Probable firing Temperature | Firing Conditions |
| Thoppur | TPP3 | Red | Red | > 700ºC | Oxidizing |
| Veeranam | TP1 | Red | Red | > 700ºC | Oxidizing |
| Kottapalayam | KMP3 | Black | Red | > 750ºC | Oxidizing |
| Kavalapatti | KPP1 | Black | Red | > 750ºC | Oxidizing |
| Thamaraikulam | TKP4 | Black | Black | around 700ºC | Reducing |
| Porunthal | PP1 | Red | Red | > 750ºC | Oxidizing |
| Porunthal | PP4 | Black | Black | around 700ºC | Reducing |
| Alagapuri | AP1 | Black | Red | around 700ºC | Reducing |
| Nattapurakki | NP4 | Black | Red | > 750ºC | Oxidizing |

### *3.2 X-Ray Diffraction Analysis*

The Mössbauer study indicating the chemical state of iron ($Fe^{2+}$/ $Fe^{3+}$) in the samples and the firing temperature adopted by the ancient artisans at the time of manufacturing the artefact is well established. The color of the pottery and different firing atmosphere adopted by artisans during manufacturing of the artefacts is also revealed from the Mössbauer study. The XRD analysis revealed the mineralogical composition of potsherds and gives a clue for determining the firing temperature and atmospheric condition prevailed at the time of manufacturing the potteries. The whole set of data showed the firing temperature in the range of 700-900°C. The combined method of XRD and Mössbauer spectroscopic techniques revealed the artisan's skill in manufacturing different color of the pottery with atmospheric conditions.

reactions: gehlenite is obtained from decomposition products of illite and calcite at 800–850°C [25] and diopside is formed from illite, calcite and quartz at 850–900°C [26]. Hence it may be inferred that the samples of TP1, TKP4 & PP4 was subjected to firing temperature around 850°C and the samples of KPP1 & NP4 was fired around 800°C. The remaining samples may be heated around 750°C. The absence of kaolinite in all the samples may be due to the dehydroxylation during heating. The XRD data analysis also provides some insight into the production processes and firing temperature and also in good agreement with the Mössbauer spectroscopy. The results of the Mössbauer spectroscopy and XRD analysis well support FT-IR finding of our earlier works [21, 27-29].

## 4 Conclusions

The Mössbauer study indicating the chemical state of iron ($Fe^{2+}$/ $Fe^{3+}$) in the samples and the firing temperature adopted by the ancient artisans at the time of manufacturing the artefact is well established. The color of the pottery and different firing atmosphere adopted by artisans during manufacturing of the artefacts is also revealed from the Mössbauer study. The XRD analysis revealed the mineralogical composition of potsherds and gives a clue for determining the firing temperature and atmospheric condition prevailed at the time of manufacturing the potteries. The whole set of data showed the firing temperature in the range of 700-900°C. The combined method of XRD and Mössbauer spectroscopic techniques revealed the artisan's skill in manufacturing different color of the pottery with atmospheric conditions.

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