

## X-RAY DIFFRACTION AND TG-DTA STUDIES OF ARCHAEOLOGICAL ARTIFACTS RECENTLY EXCAVATED IN SALAMANKUPPAM TAMILNADU

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### Abstract

The present study deals with the characterization of pottery samples which were recently excavated in Salamankuppam, Tamilnadu. The samples were subjected to X-ray diffraction and thermal studies. The mineralogical composition of the potteries were found using XRD. By noting the difference in the mineral composition of the samples the firing temperature is interpreted. TG-DTA is used as the complementary technique to find the firing temperature.

**Keywords:** Artifacts, XRD, TG-DTA, Firing temperature

### Introduction

Clays are the basic materials for the production of ceramics [1]. Clay minerals as main raw material for production of potteries show some characteristic transformation effects in the course of their decomposition [2]. Pottery analysis reveals the important information about the daily life of ancient people and their ethnical and cultural aspects of the period. Therefore pottery studies are very important for the reconstruction of life-style of society during the period under construction [3]. The physical and chemical characterization of the potteries used in ancient periods gives the historical and the technological information regarding their manufacture [4-6]. X-Ray diffraction analysis is one of the most suitable analytical tools for mineral characterization of potteries [7-9]. Thermal analysis (TG-DTA) is a very important characterization method used for the control of the reaction process and of the properties of the materials obtained. This paper intends to show how X-Ray diffraction is used in mineralogical characterization and TG-DTA for the determination of firing temperature.

### Excavation site

The site excavated for the present study is Salamankuppam in Tamilnadu. It is about 1.5 km north of the famous shore temple of Mahabalipuram and 150 m from the sea. Mahabalipuram is a natural heritage of a fine seacoast together with abundant man-made historical and archaeological monuments. Excavations at this site revealed multiple cultural settlements with clear-cut working levels and associated sedimentary horizons. Artifacts found at the site include broken hard portion with a bangle of beads, roofing tiles made of terracotta figurine, hop-scotches and different varieties of potteries. For the present

study five pottery samples excavated from Salamankuppam namely SMP1, SMP2, SMP3, SMP4 and SMP5 are considered. The location of the site is given in figure.1 and the photograph of the samples is shown in figure. 2.

Fig. 1. Geological map showing the recently excavated archaeological site Salamankuppam



Fig. 2. Pottery samples of Salamankuppam (SMP1-SMP5)



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## Experimental details

### X-Ray Diffraction

All the pottery samples (powdered samples) of Salamankuppam were subjected to X-Ray diffraction at room temperature using PANALYTICAL XPERT-PRO diffractometer available in Indian Institute of Science (IISc), Bangalore. It was operated at 40 kV and 30 mA with a source of  $\text{CuK}_\alpha$  radiation of wavelength  $\lambda=1.5405 \text{ \AA}$ . It has an X-ray computer controlled diffractometer system, having a fixed tube Cu target, secondary graphite monochromator, flat plate horizontal sample holder and X-Celerator for the faster acquisition of data. The diffractogram patterns were obtained by continuous scanning from  $20^\circ - 80^\circ$  as  $2\theta$  angle.

### Thermal analysis (TG-DTA)

The TG-DTA analysis was carried out using NETZSCH STA 409 which runs under PROTEUS Software available in Indian Institute of Science (IISc), Bangalore. The TG sample carriers exchanged with

TG-DSC or TG-DTA modes operation with top-loaded samples ensure total protection of the balance. The experiment was carried out by heating the samples from room temperature to  $1200^\circ\text{C}$ .

## Results and Discussion

### XRD analysis

XRD analysis was carried out in all the five samples of Salmankuppam to find the mineralogical composition of all the pottery samples. The diffractograms of all the samples SMP1, SMP2, SMP3, SMP4 and SMP5 are given in figure 3. and their mineral composition is given in Table 1. X-ray diffraction (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 a mixture of clay minerals, additive minerals and their transformation products yields information on the mineral composition of objects[10].

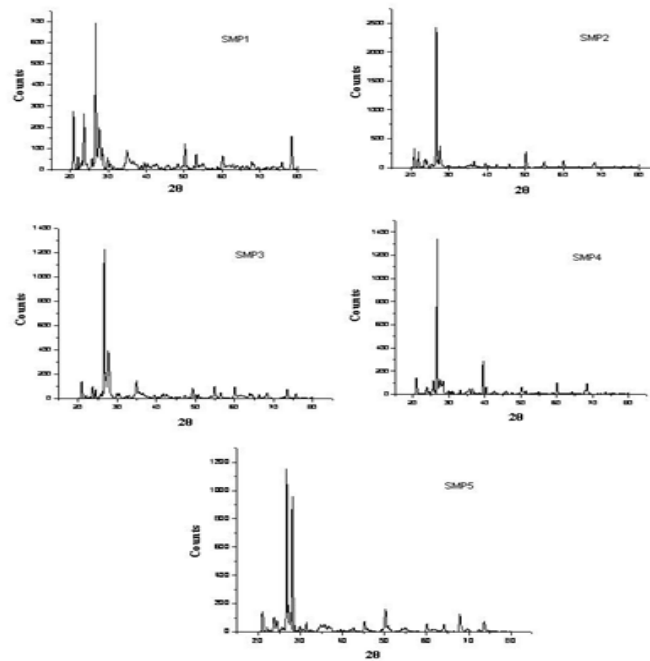
Table 1. Mineral phases obtained by XRD analysis

Minerals	SMP1	SMP2	SMP3	SMP4	SMP5
Quartz	+	+	+	+	+
Hematite	+	+	+	-	+
Kaolinite	-	-	+	-	-
Feldspar	+	+	+	+	+
Anorthoclase	+	+	-	-	-
Magnetite	-	+	+	+	+
Sepiolite	-	+	-	-	+
Orthopyroxene	-	-	-	-	+
+ - Present      — - Absent					

Hematite is present in all the samples except SMP4. Schwertmann et al [11] reported that hematite is one of the most intense coloring materials in potteries. The presence of Hematite gives reddish color to the pottery and in the present investigation, the reddish color observed in samples SMP1, SMP2, SMP3 and SMP5 might be due to the presence of

hematite. The presence of only 1-1.5% of hematite is enough to give the reddish colour. The minerals quartz and feldspar were present in all the samples of Salamankuppam. The diffraction peaks of Quartz were the most intense in all the samples. Iordondir et al [12] reported in his study that the mineral feldspar decomposes completely around  $900-950^\circ\text{C}$ .

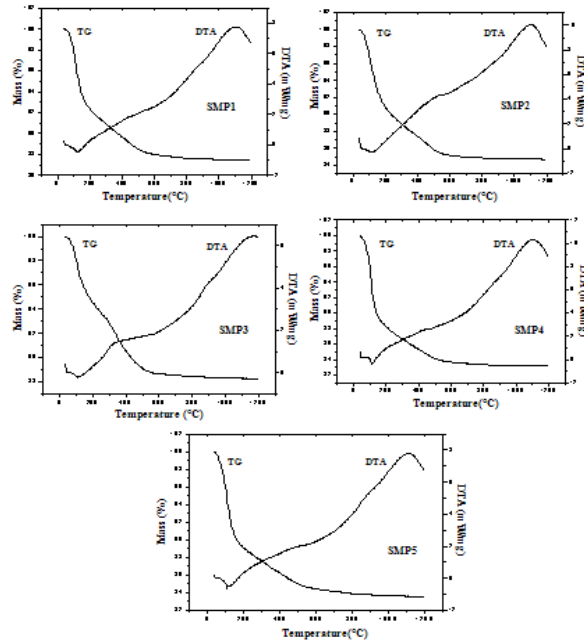
Fig. 3. Diffractogram of the samples SMP1, SMP2, SMP3, SMP4 and SMP5



The presence of feldspar in all the samples indicates that all the samples were fired below 900°C [2]. The samples SMP2, SMP3, SMP4 and SMP5 show the presence of magnetite. Kaolinite peak was

observed only in the sample SMP3. Anorthoclase is present in SMP1 and SMP2 whereas sepiolite is present in SMP2 and SMP5. Only the sample SMP5 shows the presence of orthopyroxene.

Fig.4. TG-DTA curves for the samples SMP1, SMP2, SMP3, SMP4 and SMP5



### Thermal analysis

The TG-DTA curves of the Salamankuppam samples SMP1, SMP2, SMP3, SMP4 and SMP5 are given in figure 4. It is well known that thermal analysis is a very important characterization method which is

used for the control of the reaction process and of the properties of the materials obtained [3].

Based on the work done by Drebuschat et al [17], the weight loss of the pottery in thermogravimetric can be explained in three steps. The thermal loss from temperature ranging from room temperature to 100 °C

is due to dehydration, from 400-500 °C is due to decomposition of hydroxyls and from 700-800 °C is due to the decomposition of carbonates, mainly calcite. All the samples show larger mass loss on dehydration and less at dehydroxylation. All the samples showed nearly the same amount of weight loss due to decomposition of hydroxyls except SMP3. In SMP3 the weight loss due to the decomposition of hydroxyls is comparatively higher than the other samples. None of the samples showed the weight loss due to the decomposition of calcite, which occurs in the range of 700-800 °C indicating that the mineral calcite is absent in all the samples. This result coincided with XRD also.

In all the samples of Salamankuppam endothermic peak was observed in the range of 100-200 °C. A broad endothermic peak was observed in samples SMP1, SMP2 and SMP3 whereas the endothermic peak is sharp in SMP4 and more sharper around 106 °C in SMP5. According to Franquelo et al, Clark et al and Moropoulou et al the endothermic peak around 100-200 °C is due to the presence of absorbed water [13, 14, 15]. Exothermic peak was found in the sample SMP4 in the temperature range of 43-108 °C. The presence of endothermic peak in the samples SMP1, SMP2, SMP3 and SMP5 around the temperature range of 100-200 °C shows the presence of hygroscopic water.

The presence of exothermic peak in the range of 200-500 °C is due to the combustion of organic material present in the sample [14]. A broad exothermic peak is observed around the temperature range of 250-420 °C in SMP3. This indicates the presence of organic material in sample SMP3. The absence of exothermic peak in this region for all the other samples shows the absence of organic material in SMP1, SMP2, SMP4 and SMP5. The presence of organic material in SMP3 indicates that it might have been present in the raw material even or it might have been added intentionally by the ancient artisans as a binder [15].

A very slight endothermic peak is seen in SMP3 in the temperature range of 450-680 °C. From the previous studies it is well evident that the presence of endothermic peak around 450-650 °C indicates the presence of kaolinite and it is due to its dehydroxylation [16]. This peak shows that the kaolinitic mineral has survived the process of firing and shows that the sample SMP3 has not been fired above 650 °C. Therefore the sample SMP3 would have been fired around 450-650 °C and the absence of this endothermic peak in all the other samples indicates that the other samples have been fired above this temperature.

The samples SMP1, SMP2, SMP3, SMP4 and SMP5 showed no exothermic peak in 900-1000°C region, indicating that all the samples were fired at 900°C or below this temperature. The absence of

exothermic peak at 900°C and the dehydroxylation of kaolinite peak in samples SMP1, SMP2, SMP4 and SMP5 indicate that the firing temperature of these four samples might be between 650 to 900 °C.

## Conclusion

The X-ray diffraction and Thermal analysis techniques were applied on the archaeological samples collected from the recent excavations at Salamankuppam to know the firing temperature achieved by the ancient artisans in that particular archaeological site during the manufacture of the potteries. Quartz and feldspar are present in almost all the samples with Quartz recording the intense peak in all the samples. The presence of Kaolinite in the sample SMP3 indicates that it might have been fired below 650 °C. From the presence of the exo and endothermic peak in the TG-DTA analysis it is found that the firing temperature of the samples SMP1, SMP2, SMP4 and SMP5 were found to lie between 650 - 900°C whereas SMP3 would have been fired around 450-650°C. Thermal analysis results showed larger mass loss at dehydration than dehydroxylation and the organic material is used in the making of the pottery SMP3.

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