Received: 05-04-2014
Accepted: 10-05-2014

ISSN: 2321-4902
Volume 2 Issue 1

Online Available at www.chemijournal.com

International Journal of Chemical Studies

Characteristic Analysis of Archaeological Pottery Recently Excavated from the Site Mayiladumparai, Krishnagiri District, Tamil Nadu, India by Analytical Techniques.

K.Veeramuthu [1], S. Chandra Sekar [2], D.Saravanan [3]

1. Department of Physics, Thiru Kolanjiappar Government Arts College, Virudhachalam- 606001, Tamil Nadu, India.
2. Department of Physics, Shri Krishnaa College of Engineering & Technology, Mannadipet, Puducherry-605501, India.
3. Department of Physics, A.R. Engineering College, Villupuram- 605601, Tamil Nadu, India.

Corresponding Author: S. Chandra Sekar, Department of Physics, Shri Krishnaa College of Engineering & Technology, Mannadipet, Puducherry-605501, India.

Archaeology has been called 'the science of the artefact' and nothing demonstrates this point better than the current interest displayed in provenance studies of archaeological objects. From the Fourier transform infrared spectra (FT-IR) of the pottery samples of firing temperature and chemical composition have been determined. XRD study has been attempted on the shreds to characterize the mineral composition of the pottery artefacts. In the present work, some of the ancient pottery samples were collected from recently excavated site at Mayiladumparai, Krishnagiri District, Tamil Nadu, India to estimate the firing temperature of the pottery samples and atmosphere prevailed at the time of manufacturing those potteries by the ancient artisans. The results obtained from different analytical techniques on pottery shreds provide information of the firing temperature of the pottery greater than 650 °C in the oxidizing atmosphere.

Keyword: Ancient Pottery, FT-IR, XRD.

1. Introduction

Analysis of ancient remains can provide information of the civilization's culture, trade and technology of that time. Different types of objects belonging to old civilizations, i.e. glasses, coins, paintings, pottery, tiles, paper and inks, and human remains such as femurs and mummy hairs etc., are attractive targets of investigation [1-2]. Especially, Cooking pots are likely to have rounded shapes to avoid thermal damage and for greater exposure to heat. They also have relatively thin walls for better heat conduction and reduction of the thermal gradient between the surfaces. Moreover, cooking pots are usually coarse textured, porous, and tempered with material having low thermal expansion coefficients, all this to reduce thermal stresses [3]. The mineralogical composition of archaeological potsherds must be assessed to answer technological issues [4-5] like the production processes of antique ceramics or the changes in the manufacturing techniques; in this respect, maximum heating temperature, duration of firing and kiln reducing/oxidizing atmosphere are important factors that help in understanding the relevant transformations. Many analytical techniques, based on different theories and giving complementary information, are usually employed in the study of artistic objects. In particular, FT-IR spectroscopy is a common and well-established tool for the ceramic body identification. The X-ray powder diffraction (XRPD), commonly coupled to other techniques [6] is the analytical tool often used. SEM analysis is used to study the morphology of the pottery section and to obtain some information about the temperatures, cooking clay process and pottery fabrication.

In the present paper, we report and discuss the experimental results obtained through FT-IR measurements performed on a set of four shards of different varieties of pottery found during archaeological excavation in Mayiladumparai of Krishnagiri District (Tamilnadu, India). FT-IR study also shows how this spectroscopy to assess the mineral transformations occurring during firing. Also XRD was used as a complementary technique in order to confirm the reliability of assignments made on the basis of the FT-IR results.

2. Materials and Methods

The pottery shreds were recently excavated from the site Mayiladumparai (12˚32´26”N; 78˚16´32”E) of Krishnagiri district, Tamilnadu, India. The pottery shreds of Mayiladumparai belonging to 5^{th} century BC. Black and Red ware, Black ware and Red ware were collected in the site. The samples are labeled as MP1, MP2, MP3 and MP4. After removal of surface layers, the pottery shreds were grounded into fine powder using agate mortar. They were sieved using an 85 sµm mesh.

The infrared spectra were recorded in the mid IR region 400–4000 cm^{-1} using PERKIN ELMER FTIR interferometer equipped with Glober source. The KBr pressed pellet technique was used to record the spectrum. The crushed samples were grounded before making the KBr pellet. The samples were mixed with KBr in the proportion of 1: 20 and pressed to 5 tons for one minute in preparing the disc. The accuracy of the measurement is ±5 in 4000 to 400 cm–1 region.

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 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 10º to 70º. Qualitative mineralogy of the studied samples is determined with the standard interpretation procedures of XRD.

3. Results and Discussions

The potteries from Archaeological site Mayiladumparai have been examined using FT-IR to acquire information on the techniques employed on the samples during manufacturing and also to estimate the firing temperature. FT-IR Spectra of pottery shred excavated in Mayiladumparai in received state is shown in Fig-1. The tentative mineralogical assignments of IR peaks in as received state of the samples are given in Table-1. It has been stated earlier on the IR analysis of archaeological artefacts that the absorption band at 1639 cm-1 is due to the H-O-H bending of water molecule [7]. The absorption band appearing at 1640 along with around 3440 cm-1 is due to H-O-H bending of water exists in all samples owing to the absorption of moisture present in the sample. The peak around 1035 cm-1 is the result of the red clay origin of kaolinite [7]. The spectrum of all the samples has a peak centred at 1040 cm-1 with strong intensity. It indicates the red clay origin of kaolinite present in the clay of the pottery shreds. The appearance of absorption at 1080, 795, 695 and 460 cm-1 indicates the quartz presence in accordance with the results of earlier researchers [8-9]. The absorption band appearing at 590 cm-1 is due to the presence of microcline [9]. The peak around at 470, 645 and 730 are due to presence of feldspar mineral orthoclase. The presence of band centred at 720 cm-1 is due to another feldspar mineral albite. The presence of bands around 580 and 540 cm-1 are due to magnetite and hematite respectively (iron oxides) [10]. The band around at 540 cm-1 was observed in all the samples, but the band was observed in the samples MP3 and MP4.

According to Mendelovici *et al.* [11] the absorption band around 3630 cm−1 is due to crystalline hydroxyl groups which persist only octahedral sheet structure which begins to disappear with increasing temperature and at 500 ◦C the band disappears completely [12]. None of the samples taken for the present study showed the sharp shoulder band at 915 cm−1. This implies that all the samples were fired to the temperature above 500 ◦C. According to Yariv and Mendelovici [13] a shoulder band at 875 cm^{-1} indicates dehydroxylation of Kaolinite minerals which are completed at 800 ◦C and octahedral sheet structure in the clay mineral disappeared. The shoulder band of 540 and 580 cm^{-1} appear in Mayiladumparai samples due to presence of iron content in the samples were fired above 650 ◦C. The amount of Magnetite and Hematite decides the reducing or oxidizing atmosphere for firing the artefacts [14]. The FT-IR spectra of all the samples

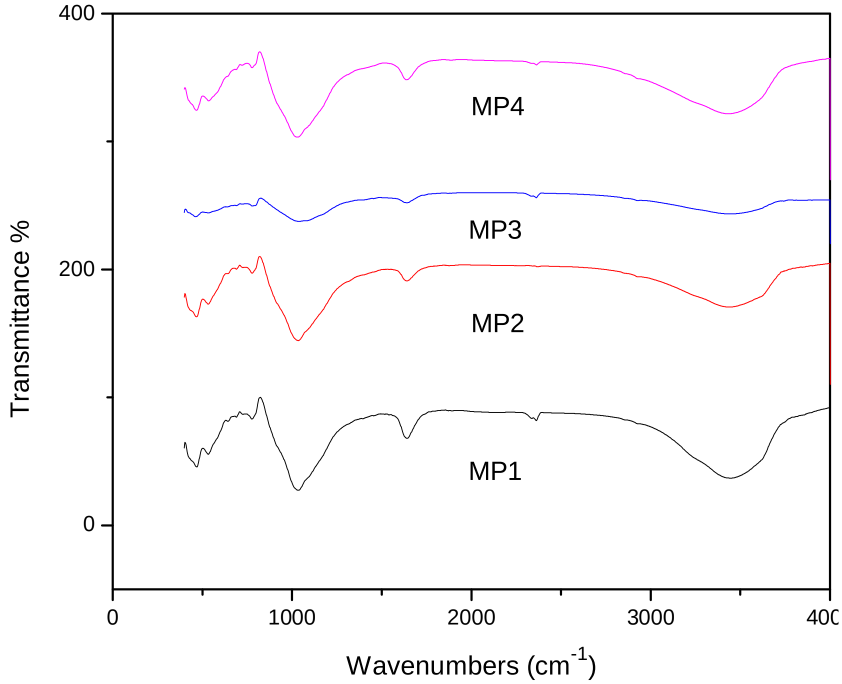

Fig 1: A typical FT-IR spectrums of received state potsherds of Mayiladumparai.

show absorption due to hematite indicating that these samples were fired in the open air or perfectly oxidizing atmosphere at the time of manufacture. The less amount of magnetite is due to the transformation of Fe_3O_4 to Fe_2O_3 during the process of firing [15]. The red colour of the potteries is due to presence of hematite, black and gray colours are due to higher amount of magnetite [16] from this, the relative amount of hematite and magnetite is responsible for the colour of the potteries. The variation in the amount of these oxides gives important information regarding the nature of the environment in which the potteries were made [17]. The amount of Magnetite and Hematite decides the atmosphere whether reducing or oxidizing for firing the artefacts. All the Mayiladumparai samples contains more amount of hematite and visually red in colour, which indicates that the oxidizing atmosphere was prevailed by the artisans at the time of manufacture. The samples are red in colour implies that the oxidizing atmosphere was adopted by the artisans. The absorption at 540 cm−1 appeared for all the samples indicate that these samples were fired in the oxidizing atmosphere.

From the above discussions one can conclude that the samples was subjected to firing temperature around 650 **°**C under oxidizing atmospheric condition.

XRD spectrums are recorded for the as received state samples and minerals present in the samples identified by comparing the JCPDS file [18]. Fig-2 shows representative XRD spectrum of Mayiladumparai pottery samples. The XRD semi-quantitative analysis indicates that the main mineralogical phase of the pottery quartz, orthoclase, albite and hematite. The minerals quartz and feldspar were virtually present in all samples. Quartz diffraction peaks are intense in all the samples may indicate a temperature of at least 750 °C. Quartz may be an indigenous mineral in natural clay or may be an intentionally added temper [19]. This gives a clear indication that all the samples were fired above 650 °C. It has been reported by Schwertmann *et al.* that hematite is one of the most intense colouring material and only 1–1.5% of hematite is enough to give reddish colour to the pottery [20]. The reddish colour observed in all the samples might be due to the presence of hematite. The results of XRD analysis are in good agreement with the analysis of FT-IR study of the received state samples.

Table 1: Observed Absorption Frequency in the region of 400 – 4000 cm^{-1} of the ancient potteries of Mayiladumparai together with minerals identification.

S. No	Observed wave numbers (cm^{-1})	Mineral Name	Sample ID			
			MP1	MP2	MP3	MP4
1.	458, 777, 695,1080	Quartz	+	+	+	+
2.	466, 590, 645, 723, 728	Feldspar	+	+	+	+
3.	1033, 1642, 3441	Clay Minerals	+	+	+	+
4.	540	Hematite	+	+	+	+
5.	580	Magnetite	-	-	+	+
6.	2925, 2855	Organic matter	+	+	+	+

+ = Present, - = Absent

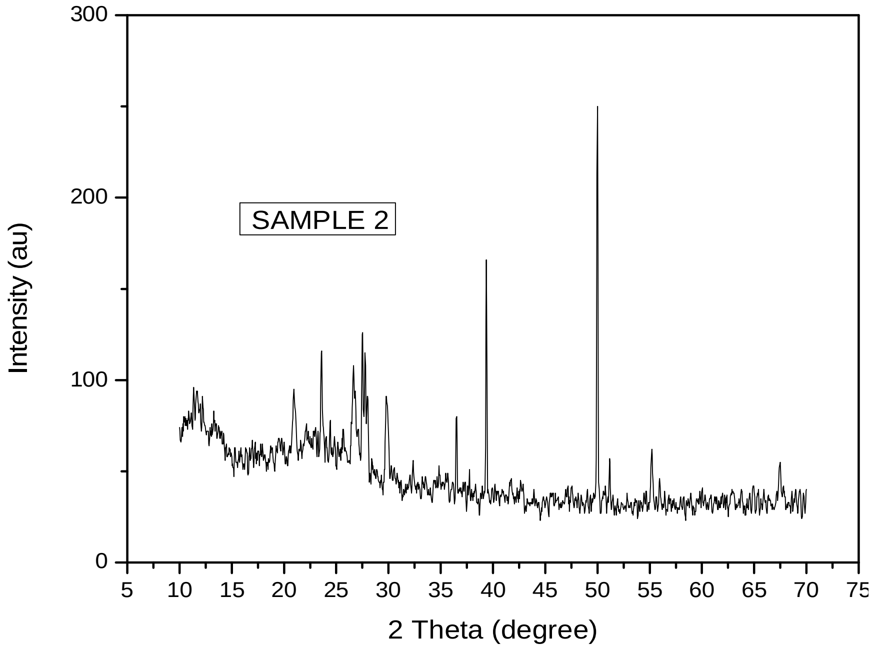

Fig 2: A typical XRD Spectrum of Mayiladumparai potsherds.

4. Conclusion

Ancient pottery samples excavated from Mayiladumparai, Krishnagiri District in Tamilnadu were analyzed by FT-IR and XRD techniques. From the FT-IR measurements it was inferred that mineral composition of the pottery samples was determined and all the samples were fired above 650 °C in an oxidizing atmosphere. From the XRD study also concluded that the firing temperature of the samples at the time of manufacturing is above 650 °C. The artisans lived at that time of manufacturing the potteries in Mayiladumparai archaeological site knew the influence of iron oxides and aware of oxidizing kiln method during firing the potteries.

5. References

1. Mommsen H, Beier T, Diehl U, Podsuweit CH. Provenance determination of Mycenaean sherds found in Tell el Amarna by Neutron Activation Analysis. Journal of Archaeological Science 1992; 19:295-302.
2. Weber J, Beier TH, Diehl U, Lambrecht DL, Mommsen H, Pantenburg FJ. A PIXE minibeam setup at the Bonn cyclotron for archaeometric metal analyses. Nucl instrum Methods B 1990; 50:221-225.
3. Rice P. Pottery Analysis. A Sourcebook, The University of Chicago Press, Chicago, 1987.
4. Maggetti M. Composition of Roman pottery from Lousonna (Switzerland). Br Museum Occasional Paper 1981; 19:33–49.
5. Heimann RB, Maggetti M. Experiments on simulated burial of calcareous terra sigillata (mineralogical change). Preliminary results Br Museum Occasional Paper 1981; 19:163–177.

6. Dominuco P, Messiga B, Riccardi MP. Firing process of natural clay some microtexture and related phase composition. Termochim Acta 1998; 321:185-190.
7. Palanivel R, Velraj G. FTIR and FT-Raman spectroscopic studies of fired clay artifacts recently excavated in Tamilnadu, India. Ind J Pure & Appl Phys 2007; 45:501-508.
8. Ravisankar R, Raja AG, Naseerutheen A, Chandrasekaran A, Prasad MVR, Satpathy KK *et al.* Analytical characterization of recently excavated megalithic sarcophagi potsherds in Veeranam village, Tiruvannamalai dist, Tamilnadu, India. Spectrochimica Acta Part A 2013; 115:845-853.
9. Ravisankar R, Raja AG, Rajan K, Naseerutheen A, Senthilkumar G. Mineral Analysis in Archaeological Pottery from Porunthal, Dindigal Dist, Tamil Nadu, India by FT-IR spectroscopic Technique. International Journal of Science Innovations and Discoveries 2012; 2(1):53-60.
10. Velraj G, Janaki K, Mohamed MA, Palanivel R. Spectroscopic and porosimetry studies to estimate the firing temperature of some archaeological pottery shreds from India. Appl Clay Sci 2009; 43:303-307.
11. Mendelovici E, Yariv SH, Villalba R. Iron-Bearing Kaolinite in Venezuelan Laterites: I. Infrared Spectroscopy and Chemical Dissolution Evidence. Clay Miner 1979; 14:323-331.
12. Hlavay J, Jonas K, Elek S, Inczedy J. Characterization of the Particle Size and the Crystallinity of Certain Minerals by Infrared Spectrophotometry and Other Instrumental Methods—I. Investigations on Clay Minerals Clays and Clay Miner 1977; 25:451–456.
13. Yariv SH, Mendelovici E. The Effect of Degree of Crystallinity on the Infrared Spectrum of Hematite. Appl Spectrosc 1979; 33(4):410-411.
14. Barilaro D, Barone G, Crupi V, Donato MG, Majolino D, Messina G *et al.* Spectroscopic techniques applied to the characterization of decorated potteries from Caltagirone (Sicily, Italy). J Mol Struct 2005; 744-747:827-831.
15. Harrell GO, Russell RR. Influence of Ambient Atmosphere in Maturation of structural products, Bulletin 204, Engineering Experiment station, Chio state University, Columbus, 1967.
16. Mirti P, Davit P. New developments in the study of ancient pottery by colour measurement. J Arch Sci 2004; 31:741-751.
17. Mirti P, Perardi A, Gulmini M. A Scientific investigation on the provenance and technology of a black-figure amphora attributed to the priam group. Archaeometry 2006; 48:31-43.
18. Mineral Powder Diffraction File. Joint Committee on Powder Diffraction Standards (JCPDS) 1999.
19. Ravisankar R, Chandrasekara A, Kiruba S, Senthilkumar G, Maheswaran C. Analysis of ancient potteries of Tamilnadu, India by spectroscopic techniques. Indian Journal of Science and Technology. 2010; 3:858-862.
20. Schwertmann U, Bigham JM, Ciokosz EJ. (Eds) Soil Color, Soil Society of American Special Publication, Madison, Wiscons, 1993; 31:51.