Journal of Experimental Sciences Vol. 2, Issue 5, Pages 04-06 [2011]

Regular Article

FTIR spectroscopic and X-ray diffraction analysis of archaeological grey potteries excavated in Alagankulam, Tamil nadu, India

P. Sathya[1*] and G. Velraj[2]

[1]Department of Physics, Muthayammal College of Arts & Science, Rasipuram-637408;
[2]Department of Physics, Periyar University, Salem – 636 011 Tamil nadu

Abstract

Archaic potteries are the representative tool for material culture that results the interaction between man and his territory. They also allow us to reconstruct the whole manufacturing process from the preparation of the paste to the firing of artifacts. Each of the pottery production reveals us the potter's technical skills, their artistic sense and their practical necessities. In this regard, scientific analyses applied to pottery give the possibility of evaluating the ceramic raw materials and of the clay type. X-ray diffraction and Fourier Transform Infrared Spectroscopic analysis of grey pottery fragments from an intensively studied Alagankulam archaeological site, Ramanathapuram district, Tamilnadu, India belonging to first century BCE is detailed in this work. By knowing the crystalline phase and chemical composition of minerals present in the pottery sherds through the XRD and FT-IR respectively we tried to determine the materials used by the potters, and the clay origin. We also examined the changes of phases produced by the heating which could furnish information on the manufacturing conditions. Hence, both of these methods enables us to reveal differences in the mineralogy of a components, and characteristic minerals as "fingerprints" which may allow distinguishing potteries of different provenance and origin.

Keywords: Ancient pottery sherds, XRD and FT-IR

Introduction

Archaeology studies the story of man's past through his material remains. It is essentially a method of reconstructing the past from the surviving traces of former societies. Of various remnants, pottery vessels and sherds are often the most tangible evidence of trade relations and exchange systems of ancient societies, and the study of their distribution forms the basis of any analysis of these systems (Sharon Zuckermana et al., 2010). In addition, the technical and artistic quality of pottery indicates the achievements of prehistoric societies, which have left no written records, but nevertheless often had highly developed handicrafts (Wagner et al., 1998). Potteries are made of clays which consist of a mixture of different minerals mainly of hydrous aluminium silicates, iron oxides and oxyhydroxides. During firing, these minerals change their structure, they decompose and finally new minerals are formed (Venkatachalapathy et al., 2008). The clay mixtures of pottery are significant because they are economical raw materials which have been used since the earliest times (Bertelle et al., 2001). Hence, the knowledge of chemical and mineralogical compositions is mandatory in characterization studies of pottery since the former depends on the raw materials used to produce the wares, processing and depositional changes and latter on both the initial composition and the processing, as minerals are the "fingerprints" of the stable and also the metastable solid phases formed during firing (Rice, 1987). In the present paper, we report spectroscopic measurement performed by FT-IR and XRD on grey potteries collected from Alagankulam (Tamilnadu), attributed to historical periods. The experimental results allowed us to identify the different components of the ceramic body and the main crystalline phases as well.

Materials and Methods

The analyzed samples are fragments of grey pottery coming from Alagankulam archaeological site and dated back to first century BCE. Alagankulam is a village situated on the east coast of Ramanathapuram district in Tamilnadu. It is situated on the banks of the river Vaigai and is about three kilometers away from the seashore. The excavation in this site was carried out by the Department of Archaeology, Government of Tamil Nadu, Egmore, Chennai.

Spectroscopic techniques are very useful in the field of cultural heritage because they provide a direct and accurate analysis of the samples and usually require only a small amount of material. The samples were analyzed by FT-IR and XRD measurements in order to characterize their analytical composition.

X-ray diffraction analysis was performed by using a Philips X'Pert Pro X-Ray diffractometer, with the following working conditions: CuKα Ni-filtered radiation; 40 kV, 30 mA; divergence slit 0.47°. The analyses have been carried out with the powder specimen directly inserted into the sample-rack of the instrument, with the X ray beam pointing directly on the specimen surface.

FT-IR analyses were performed by using a Perkin-Elmer spectrometer, equipped with a Globar source and a DTGS (deuterated tryglycine sulphate) detector. Pellets were prepared by gently grounding pottery sample with KBr in the 1:20 ratio. Spectra were recorded in the 400 - 4000 cm^{-1} range with a resolution of 4 cm^{-1}, averaging 100 scans.

Results and Discussion

The investigation proceeded with (i) FT-IR analyses to provide detailed compositions of the clay mineral components and clay type of the sherds in order to allow more reliable comparison between them and (ii) XRD analysis of the powered specimens to assess the crystalline phases in potsherds compared with others.

Fourier Transform Infrared analysis

The infrared spectra of three pot sherds coded as AGMP-1, AGMP-5 and AGMP-7 are shown in Fig. 1. Band assignments with relative intensities are listed in Table 1. From the FTIR spectra recorded the absorption bands at 3648 cm^{-1} and 3620 cm^{-1} in AGMP-2 sherd reveal that the type of clay disordered Kaolinite (Bantiguies et al., 1997). The bands at 3648 cm^{-1} and 3620 cm^{-1} are assigned to O-H stretching of inter layer and inner O-H group of adsorbed water, respectively (Manoharan et al., 2007). The presence of weak broad band around 3440 cm^{-1} and less intensive absorption at 1635 cm^{-1} in all the representative pot sherds can be attributed to the adsorbed water (or water of crystallization) and O-H vibrations (Nakamoto, 1986 and Schrader, 1995). Lara Maritan et al and Colombini et al have reported that the two weak peaks observed at 2852 cm^{-1} and 2922 cm^{-1} are due to C-H stretching mode and reveal the presence of some organic contribution (Lara Maritan et al., 2005 and Colombini et al., 2005). Thus, in the present study, a very weak band in the region 2926-2929 cm^{-1} and 2854 cm^{-1} in all the samples can be assigned to C-H stretching of organic matter.

* *Corresponding Author, Email: sathya_physics @ yahoo.com*

Fig.1. FT-IR spectra of typical pottery samples belonging to Alagankulam site

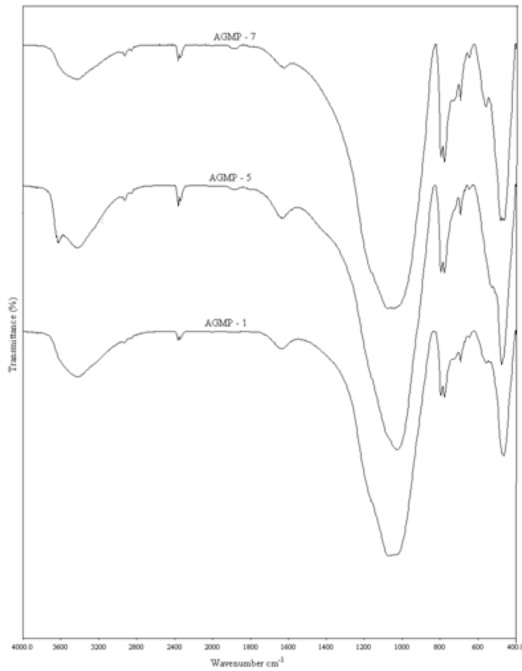


Table 1. The characteristic infrared frequencies for the minerals possibly present in a ceramic pot sherd

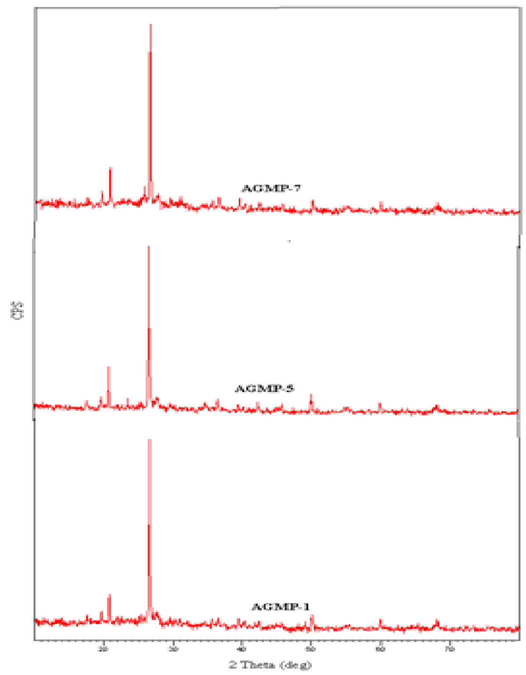
Pottery samples			
Frequency with relative intensity (cm^{-1})	**Frequency with relative intensity (cm^{-1})**	**Frequency with relative intensity (cm^{-1})**	**Tentative vibrational Assignments**
AGMP-1	**AGMP-5**	**AGMP-7**	
-	3648 w	-	O-H str. of Kaolin
-	3629 w	-	O-H str. of Kaolin
3421 vw	3424 w	3437 vw	O-H str. of water
1636 vw	1628 vw	1622 vw	H-O-H bend of water
2926 vw	2925 vw	2929 vw	C-H str. of Organic matter
2854 vw	2854 vw	-	C-H str. of Organic matter
1075 s	-	1077 vs	Al-O-Si str. of Amorph. Al-Si
-	1027 vs	-	Si-O-Si str. of Kaolin
797 w	796 w	796 w	Si-O bend of Quartz
778 w	778 w	777 w	Si-O-Si str. of Quartz
694 vw	694 vw	694 w	Si-O bend of Quartz
648 vw	648 vw	648 vw	Al-O-Si str. of Feldspar
558 vw	558 vw	559 vw	Muscovite
-	530 w	-	Fe-O bend of hematite
466 m	467 m	463 m	Si-O of Microcline

vw- very weak, w - weak, m- medium, s- strong, vs- very strong

The broad symmetry band observed around 1077 cm^{-1} with very strong intensity in AGMP-1 and AGMP-7 indicates that the samples were made of white clay and the band at 1027 cm^{-1} in AGMP-5 reveals the red clay type (Ghosh, 1978). The presence of the bands at 795 cm -1 and 775 cm-1 along with 695 cm-1 in all the representative grey pottery fragments is due to quartz (Russell, 1987). The sample AGMP-1, AGMP-5 and AGMC-7 which show the absorption band positioned around 648 cm^{-1} may be assigned to Al-O-Si stretching of Feldspar (Legodi M A and de Waal D, 2007). Moreover, the absorption bands at 558 cm^{-1} in three pot sherds are related to muscovite (De Benedetto et al., 2002).
According to Velraj et al, it is reported that the absorption band around 535 cm^{-1} is due to hematite present in the sherd (Velraj et al., 2009). Therefore the band observed at 530 cm^{-1} in the present samples AGMP-5 shows presence of hematite and this band does not appear in AGMP-1 and AGMC-7 indicates the absence of hematite in the sample. The IR spectra of the all the samples shows a medium band around 466 cm^{-1} which indicates the presence of microcline (Kieffer S W, 1979 and Ciancio 1994).

X-ray powder diffraction pattern (XRD) analysis
In order to assess the validity of mineral phases in archaic pottery, the typical earthenware of three sherds was characterized by XRD. The diffractograms of the sample AGMP-1, AGMP-5 and AGMP-7 are shown in Fig. 2. The presence of major minerals is identified by comparing 2θ values with the JCPDS (Joint Committee on Powder Diffraction Standards) file 2003.

Fig. 2 X-ray diffraction pattern of Alagankulam pot sherds



From the diffraction pattern, it is viewed that the minerals quartz and feldspar were almost present in all sherds. The peaks of quartz are high and narrow (especially d = 0.335 nm, 0.427 nm and 0.182 nm), showed a good crystal state. But feldspar had wide peaks (especially d = 0.319 nm, 0.449 nm), showed a worse crystal state. The presence of kaolinite was observed only in shred AGMP-5 with low intensity peak. Furthermore, the mineral hematite and muscovite were also existed in all of the sherds under investigation. The presence of kaolinite, feldspar, muscovite and hematite in all the pottery fragments were also evidenced by FTIR.

Conclusion

Fourier Transform Infrared spectroscopy (FT-IR) and X-ray powder diffraction pattern (XRD) analyses performed on ceramic pottery samples coming from excavations in the Alagankulam area have permitted the fundamental components of each studied pottery class to be established and allowing the sherds to be distinguished based on the clay origin. The sherd AGMP-1 and AGMP-7 belongs to red clay origin whereas the sherd AGMP-5 is of white clay type. The results obtained from different complimentary analytical techniques were showed good agreement with one another.

Acknowledgement

The authors would like to thank The State Archeology Department, Tamilnadu, India for providing the pottery samples. We are also grateful to Dr.A.N. Kannappan, The Professor and Head, Department of Physics, Centralized Sophisticated Instrumentation Lab (CSIL), Annamalai University, Annamalai Nagar and Dr. C. Sanjeeviraja, The Professor and Head, Department of Physics, Alagappa University, Karaikudi for granting permission to record FT-IR and XRD spectra respectively.

References

Bantiguies J L, Mouline & Dexpert H, (1997). Wettability contrasts in kaolinite and illite clays: characterization by infrared and X-ray absorption spectroscopies, Clays Clay Miner., 45, 184.

Bertelle M, Calogero S, Leotta G and Stievano L, (2001). Firing techniques of the impasti from the protohistoric site of Concordia Sagittaria (Venice). Journal of Archaeological Science, 28, 197-211.

Ciancio.A., Dell'Anna A, Laviano.R (1994).Indagini chimicomineralogiche suceramica a pasta grigia proveniente dalla Puglia centrale, Ceramica Romana e Archmetria: Lo Stato Degli Studi, Edizionl all'isegna del Giglio, Firenz, 261-276.

Colombini M P, Giachi G, Modugno F and Ribechini E, (2005). Characterisation of organic residues in pottery vessels of the Roman age from Antinoe (Egypt), Micro chemical Journal, 79, 83-90.

De Benedetto G E, Laviano R, Sabbatini L and Zambonin P G, (2002). Infrared spectroscopy in the mineralogical characterization of ancient pottery, Journal of Cultural Heritage, 3, 177–186.

Ghosh S N, (1978). Journal of Material Science, 13, 1677.

Lara Maritan, Claudio Mazzoli, Luca Nodari and Umbeerto Russo, (2005). Second Iron Age grey pottery from Este (northeastern Italy): study of provenance and technology Applied Clay Science, 29, 31-44.

Kieffer S W, (1979).Thermodynamics and lattice vibrations of minerals: 2. Vibrational characteristics of silicates, Rev. Geophys. Space Phys.17, 20-34.

Legodi M A and de Waal D, (2007). Raman spectroscopic study of ancient South African domestic clay pottery Spectrochimica Acta Part A, 66, 135-142.

Manoharan C, Venkatachalapathy R, Dhanapandian S and Deenadayalan K, (2007). FTIR and Mossbauer spectroscopy applied to study of archaeological artifacts from Maligaimedu, Tamil Nadu, India, 45, 860-865.

Mineral Powder Diffraction File, Joint Committee on Powder Diffraction Standards (JCPDS, 2003).

Nakamoto K, (1986). Infrared and Raman Spectra of Inorganic and Coordination Compounds. John Wiley and Sons, New York.

Rice P M, (1987). Pottery Analysis – A Sourcebook, The University of Chicago Press, Chicago.

Russell J D, (1987). A hand book of determinative methods in clay mineralogy, (Ed) Wilson M J, (Blackie, London), p.133.

Schrader B, (1995). Infrared and Raman Spectroscopy: Methods and Applications. VCH, Weinheim.

Sharon Zuckermana, David Ben-Shlomo, Penelope A. Mountjoy and Hans Mommsen, (2010). A provenance study of Mycenaean pottery from Northern Israel, Journal of Archaeological Science, 37(2), 409-416.

Velraj G, Janaki K, Mohamed Musthafa A and Palanivel R, (2009). Spectroscopy and porosimetry studies to estimate the firing temperature of some archaeological pottery sherds from India. Applied Clay Science. 43, 3-4, 303-307.

Venkatachalapathy R, Bakas T, Basavaiah N and Deenadayalan K, (2008). Mössbauer and mineral magnetic studies on archaeological potteries from Adhichanallur, Tamilnadu, India, Hyperfine Interaction, 186, 89-98.

Wagner U, Gebhard R, Grosse G, Hutzelmann T, Murad E, Riederer J, Shimada I and Wagner F E, (1998). Clay: An important raw material for prehistoric man, Hyperfine Interactions, 117, 323-335.