Received: 08-12-2013
Accepted: 02-01-2014

ISSN: 2321-4902
Volume 1 Issue 4

Online Available at www.chemijournal.com

International Journal of Chemical Studies

FT-IR spectroscopic studies of Ancient Pottery from Kaveripakkam, Vellore Dist, Tamilnadu, India

A. Naseerutheen[1], R. Ravisankar[2*], A. Rajalakshmi[3], G. Raja Annamalai[4] A. Chandrasekaran[5]

1. Department of Physics, C. Abdul Hakeem College, Melvisharam-632509, Tamilnadu, India
2. Post Graduate and Research Department of Physics, Government Arts College, Tiruvanamalai-606 603
3. Department of Physics, SSN College of Engineering, Kalavakkam-603110, Chennai, Tamilnadu, India.
4. Department of Physics, Shri Krishnaa College of Engineering Technology, Mannadipet, Puducherry-605501,
5. Department of Physics, Global Institute of Engineering & Technology, Vellore-632509, Tamilnadu, India.

*[Email: ravisankarphysics@gmail.com]

Technical examination of art works plays an essential role in providing historical, artistic and technical information. It is important in furthering the understanding of our cultural heritage, notably in connection with the restoration, conservation, dating and authentication of artefacts. FT-IR spectroscopy is a powerful tool for assessing both mineralogical composition and to estimate the firing temperature of the archaeological pottery shreds. This paper discusses the mineral and firing temperature analysis of potsherds from kaveripakkam, Vellore dist, Tamilnadu, India. From the analysis, the sample was fired above 750 ºC during manufacturing.

Keyword: Ancient Pottery, Firing Temperature Analysis, FT-IR.

1. Introduction

Potteries are among the oldest and most significant technological innovations in the history of human achievement, and were the first truly synthetic material. They are often found in large quantities in archaeological excavations in almost all societies. It consists of different minerals which are formed by weathering of rocks and sediments. The study performed on pottery objects is relevant within several research fields and many questions have to be solved. Kaolinite and montormorlinite are the most widely used clay mixtures in the manufacturing of pottery. In the unfired matrix, it is possible to find, as major components, clay minerals mixed with quartz, feldspar and firing produce differences in the products as a result of the initial composition and different operative conditions [1]. One of the most frequent questions in archaeometric research of potteries concerns the determination of the firing temperature [2]. The minerals identified in archaeological artifacts can be classified as primary minerals and secondary minerals. The primary minerals are those that were present in the raw material, like quartz, which does not undergo reactions in a wide range of temperatures. Finally, the secondary are those formed after the production of wares, during their use and mainly their burial, as a result of either transformation of metastable firing minerals. Therefore the identification of the minerals is a powerful tool for the semi-quantitative determination of the maximum temperature of ancient potteries. The minerals change their structure, decompose and finally, new minerals are formed during firing process. For instance, hematite is produced during pottery firing only if the process is carried out in oxidizing conditions [3]. In the present study, ancient potteries obtained from settlement of Kaveripakkam, Vellore dist, Tamilnadu, India were subjected to mineral analysis by FT-IR spectroscopic technique.

2. Materials and Methods

2.1 Excavation site

Kaveripakkam (12.901667^{0}N and 79.463889^{0}E) is about 100 km west of Chennai, 40 km east of Vellore and 28 km west of Kanchipuram. Kaveripakkam has more than 50 small villages around it. It is the entry town of Vellore Dist. It is a tourist spot known for a lake built by King Nandivarman III of Pallava dynasty. This place was called 'Kavithapakkam' during the reign of the Pallavas. Recent excavations have unearthed 16th century artefacts such as pottery materials and burnt clay products. These artefacts are now displayed at Government Museum in Vellore.

2.2 Sample Collection

The pottery samples were recovered from the ancient settlement of Kaveripakkam village from Vellore dist, Tamilnadu India. The samples were collected at 8 m depth from the surface of the soil. The pottery shreds of Kaveripakkam village belonging between 100 BC and 300 AD in South India. The typical collection of pottery samples is shown in Fig 1. The samples are labelled as KP1, 2, 3 & 4. After removal of surface layers, the pottery shreds were ground into fine powder using agate mortar. This fine powder is used for mineral analysis.

Fig 1: shows the ancient potteries of Kaveripakkam

2.3 FT-IR Technique

The major and minor minerals were qualitatively determined by FT-IR technique. The KBr pellet technique was followed for the mineral analysis [4]. A ground sample of 2 mg was mixed with 40 mg KBr in the ratio 1:20 using a mortar and pestle and pressed to 5 tons for one minute in preparing the disc. Before mixing, necessary amount of KBr powder was dried at 120 °C for 6hours in an oven. Otherwise the broad spectral peak due to free OH will seriously affect the interpretation on the bound hydroxyls associated with any of the minerals. The Bruker Alpha FT-IR spectrometer was made use of in the present work for recording the IR spectra of the samples at room temperature.

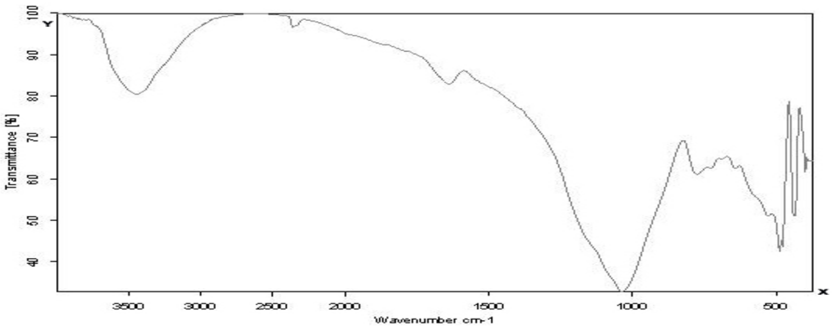

Fig 2: shows the typical FT-IR spectrum of potteries

For each of the samples, the spectra were taken in the mid region of 4000-400cm^{-1}. The instrument scans the spectra 16 times in 1 minute and the resolution is ±5 cm^{-1}. A typical FT-IR spectrum is shown in Fig 2.

3. Results and Discussion

Table.1 lists the constituent minerals identified in the pottery by the IR absorption bands. By comparing the observed frequencies with the available literature, the different types of inclusions identified in the potsherds with quartz, orthoclase, albite, hematite, magnetite, kaolinite, montmorillonite and organic carbon, The two weak peaks observed at 2852 cm^{-1} and 2922 cm^{-1} reveal the presence of some organic contribution due to CH stretching mode [5]. These peaks are observed in all the samples. Russell [6] reported that the presence of bands at 795, 775 and 695 cm^{-1} indicate the pottery fragments are due to quartz. According to Elsass and Oliver [7], the presence of the sharp band at 695 cm^{-1} indicates thin particles. The peak at 695 cm^{-1} in the sample KP1 & KP4 indicates thin particle size.

The presence of absorption bands at 545 cm^{-1} is due to the presence of orthoclase [8]. The presence of the peaks at 435 and 405 cm^{-1} indicate albite. The absorption band at 1635cm^{-1} is due to the H-O-H bending of water molecule [9]. This peak in received samples due to the absorption of moisture present in the samples. The peak centered and broad at 1035 cm^{-1} is kaolinite. All the samples showed this peak (1035 cm^{-1}) with the strong intensity indicating the type of the clay is red clay origin of kaolinite and it is used for making of potteries.

Table 1: FT-IR Vibrational Assignment with Minerals identification of Potsherds from Kaveripakkam

KP1	KP2	KP3	KP4	Tentative Vibrational Assignments	Mineral Name
3438	3440	3437	3438	O-H stretching of adsorbed water	Montmorillonite
2925	2922	2925	2924	C-H stretching	Organic Carbon
2855	2854	2853	2855	C-H stretching	Organic Carbon
1639	1637	1635	1638	O-H adsorbed water	Montmorillonite
1035	1037	1036	1035	Si-O stretching of clay minerals	Kaolinte
795	-	-	795	-	Quartz
778	775	776	775	-	Quartz
695	-	-	696	-	Quartz
-	585	585	-	FeO- Fe_3O_4	Magnetite
545		545	545		Orthoclase
535	475	-	535	FeO- Fe_2O_3	Hematite
476	-	-	475	FeO- Fe_2O_3	Hematite
435	-	-	435	-	Albite
405	-	405	405	-	Albite

The bands at 535, 475 and 585 cm^{-1} were due to hematite and magnetite. Hematite is observed in KP1. KP2 & KP4 and magnetite was observed only in KP2 & KP3. The appearance of peak at 535 cm^{-1} in the samples indicates that the potteries were fired in an oxidizing condition [10].

3.1 Firing Temperature Analysis by FT-IR Spectroscopy

Potteries are made up of clay minerals which are found in sheet structure. When the pottery is fired, the structure gets collapsed depending on the level of temperature of firing conditions, which can be monitored by FT-IR study. When the clay is fired between 300 °C and 500 °C dehydroxylation of octahedral layers of most clay minerals takes place [11]. At 600 °C silicate structure collapses and a broad symmetry band is observed at 1030 cm^{-1} for red clay and 1080 cm^{-1} for white clay [12]. In all the samples a broad symmetry band is observed around 1030 cm^{-1} in all the samples indicate red clay was used for making of the pottery samples. Ramasamy and Kamalakannan [13], studied the effect of temperature on various clay and concluded that the disappearance of Al-O-(O_4) band at 910 cm^{-1}

with the appearance of band at 635 cm^{-1} around 600 °C is the indication of the formation of Al_2O_3. Such type of band 635 cm^{-1} is not noticed in all samples indicates absence of the formation of Al_2O_3.

Maritin et al. (2005) [5] stated that magnetite is formed at a temperature 800-850 °C. The iron oxide mineral magnetite originates from chemical reaction between quartz and carbonates when the temperature is 900 °C. The presence of magnetite and absence of calcite in the samples KP1 and KP3 indicate that the sample was fired above 800 °C. According to Yariv and Mendelovici [14], a shoulder band at 875 cm^{-1} indicates that dehydroxylation of kaolinite mineral which is completed at 800 °C and octahedral sheet structure in the clay mineral disappeared. None of the samples show the presence of the peak at 875 cm^{-1} indicating that samples were fired above 800 °C. The peaks around 540 cm^{-1} observed in the samples indicate the presence of hematite which also confirms the firing temperature above 800 °C. The color of the potteries is due to hematite which is red brown solid and decides the atmospheric conditions (oxidizing/reducing) where the artifacts were fired. The potteries collected from the Kaveripakkam were red ware (KP1& KP4) show the presence of hematite and hence fired in the oxidizing atmosphere.

3.2 Estimation of firing temperature of refied samples by FT-IR spectroscopy

The samples were fired in the laboratory to temperatures 250, 500 and 750 ºC for one hour using muffle furnace. The spectra are then recorded with these refired samples. The infrared spectra of the refired samples are presented in Fig 3.

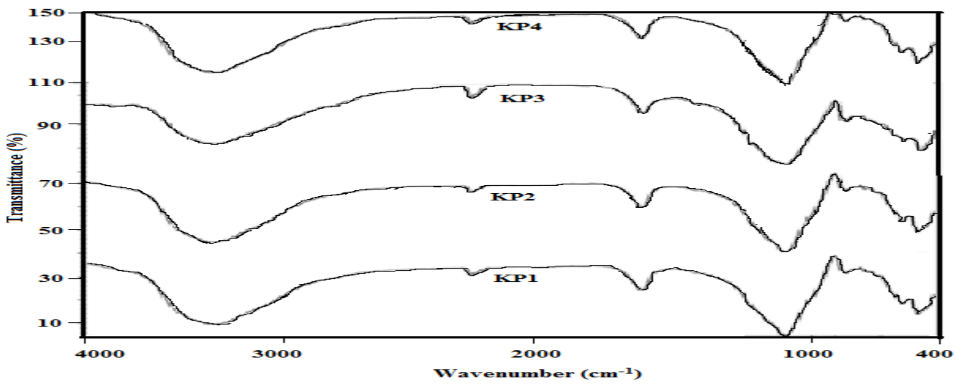

Fig 3: Re-fired FT-IR spectrums of ancient potteries of Keveripakkam,Tamilnadu

The infrared spectra of KP1-KP4 sample show an absorption band at 3445 cm^{-1} and 1645 cm^{-1} in the received state. When refiring these samples to different temperature the above band get diminished. A broad symmetry band at 1035 cm^{-1} is present in the sample. This clearly indicates that the sample has been subjected to firing temperature of above 450 ºC. The symmetry broad band at 1030 cm^{-1} and weak bands at 535 cm^{-1} & 585 cm^{-1} present in the received state. These bands at 250 °C water evaporates and become obvious, and the intensity of the bands remains the same up to 750 °C indicates that they were fired above 750 °C. This explores that the sample was fired above 750 ºC during manufacturing. The presence of iron oxides such as hematite and magnetite observations in the samples (KP1, KP2 & KP4) indicate they were fired open atmospheric conditions with firing temperature of around 750 °C which is also reflected from the red color of the pottery.

4. Conclusion

The mineralogical composition obtained by means of FT-IR analysis carried out on ancient potteries provides useful information about firing temperature. Quartz, kaolinte and Iron oxide minerals were detected in all the samples. The presence of hematite and magnetite reveal that potsherds have been fired at temperature greater than 800 °C and also indicate the firing conditions. From the analysis, the sample was fired above 750 ºC during manufacturing.

The advantages of the proposal of FT-IR approach with respect to the traditional one are tremendous and preparation (no acidic dissolution is necessary), experimental procedure, cleanliness and simplicity) and analysis time. It was possible to infer the fundamental information like technological condition implemented for production of pottery and found to give useful information about firing temperature of the potteries. This is the base line study and more extensive work is needed in the subject for future.

5. References

1. Maggetti M. Composition of Roman pottery from Lousonna (Switzerland). British Museum Occasional Paper 1981; 19:33-49.
2. Ravisankar R, Chandrasekara A, Kiruba S, Senthilkumar G, Maheswaran C. Analysis of ancient potteries of Tamilnadu by spectroscopic techniques. Indian Journal of Science and Technology 2010; 3:858-862.
3. Heimann RB, Maggetti M. Experiments on simulated burial of calcareous terra sigillata (Mineralogical change), Preliminary results. British Museum Occasional Paper 1981; 19:163-177.
4. Ravisankar R, Kiruba S, Shamira C, Naseerutheen A, Balaji PD, Seran M. Spectroscopic techniques applied to the characterization of recently excavated ancient potteries from Thiruverkadu, Tamilnadu, India. Microchemical Journal 2011; 99:370-375.
5. Maritan L, Mazzoli C, Nodari L, Russo U. Second Iron Age grey pottery from Este (northeastern Italy). Study of provenance and technology. Applied Clay Science 2005; 29:31-44.
6. Russell JD, in: Wilson MJ (Ed). A Hand book of determinative methods in clay mineralogy, Blackie and Son Ltd. New York, 1987, 11-67.
7. Elsass FD, Oliver D. Infra red and electron spin resonance studies of clays representative of the sedimentary evolution of the basin of Autun. Clay Minerals 1978; 13:299-308.
8. Farmer VC. Infrared spectra of minerals. Mineralogical Society Monograph London 1974; 42:308-320.
9. Palanivel R, Rajesh KU. Thermal and spectroscopic analysis of ancient potteries. Romanian Journal of Physics 2009; 56:195-208.
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. Applied clay Science 2009; 43(3-4):303-307.
11. Wagner U, Gebhard R, Hausler W, Hutzelmenn T, Reiderer J, Shimada J, Sosa J, Wagner FE. Reducing firing of an early pottery making kiln at Batan Grande, peru. A Mossbauer study. Hyperfine Interactions 1999; 122:63-170.
12. Ghosh SN. Infrared spectra of some selected minerals, rocks and product. Journal of Material Science 1987; 13:1877-1886.
13. Ramasamy K, Kamalakkannan V. Infrared study of some South Indian Clays. Indian Journal of Pure and Applied Physics 1987; 25:284-286.
14. Yariv SH, Mendelovici E. The Effect of Degree of Crystallinity on the Infrared Spectrum of Hematite. Applied Spectroscopy 1979; 33:410-411.