Recent Research in Science and Technology 2009, 1(2): 088–093
ISSN: 2076-5061
www.recent-science.com

PHYSICS

MINEROLOGICAL CHARACTERIZATION STUDIES OF ARCHAEOLOGICAL POTTERY SHERDS USING FT – IR AND TGA - DTA

R. Palanivel*, S. Meyvel
Department of Physics, Annamalai University, Annamalainagar, Tamilnadu, India

Abstract

The Archaeological pottery sherds excavated in Alagankulam, an ancient port city of Tamilnadu, India, have historical significance owing to the heritage and trade link possessed with the Roman Empire. They were examined by employing the analytical techniques Fourier Transform Infra Red (FTIR) and Thermogravimetry – Differential Thermal Analysis (TGA-DTA) with an objective to identify the mineralogical characteristics of the raw materials used for their production. Based on the mineralogical assemblages observed in FTIR, the nature of the clay used, the textural and vitrification structures were inferred. The reactions associated with the mineral compositions present in the potsherds on controlled heating over the linear temperature ramp from room temperature to 1200°C in an inert atmosphere were realized by TGA-DTA results. The characterization studies were able to indicate the conditions of firing process adopted and firing temperature attained by the artisans at the time of manufacture of the artifacts of the present investigation.

Key Words: Artifacts; Firing condition; Firing temperature; FTIR; TGA-DTA.

Introduction

Pottery is the most stable and abundant material in archaeological and historical contexts. The different cultural aspects can also be derived from them. Therefore a complete characterization of pottery is considered as important for identifying the archaeological and historical aspects (1). The study of pottery can yield information concerning past cultural and technological evidences on the type of products that people cooked, stored or prepared for the living in their daily life (2).

The pottery artifacts were selected for the reason as they are resistant to time and their maintenance of aesthetic characteristics with respect to time. These types of artifacts can be considered as a very specific trace of every civilization. The clay mineral commonly found in the samples and their phase transformations during firing process have been studied by using various well known method of analysis. For the present investigation, FT-IR is utilized to identify the mineralogical compositions of the pottery shreds both in the received state and refired states from the characteristic transmission peaks.

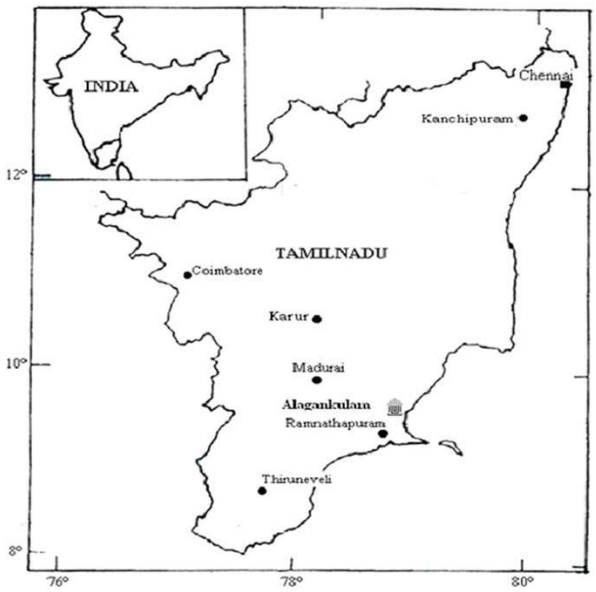
The characterization of archaeological pottery shards can also be supplemented by thermal analysis, especially in the estimation of firing temperature concerned. Thermal modifications of minerals in respect of their crystalline structure during firing of clay artifacts are important for appreciating and understanding their manufacturing processes. Clay mineral compositions are the main pertinent factor for pottery production. Some characteristic reactions occurring (dehydroxylation, decomposition, transformation) during the course of firing (heating effects) and several thermo analytical criteria can be used for reconstruction of former production conditions. It is well known that thermal analysis (TGA-DTA) is a relevant characterization method to understand the reaction process and properties of the raw materials used in manufacture of pottery.

Thermo gravimetric analysis reveals changes in the samples weight as well as in thermodynamic properties.

* *Corresponding Author, Email: mail2meyvel@yahoo.co.in*

TGA is commonly employed in research to determine characteristics of investigated materials, degradation temperatures and absorbed moisture content of materials (3). DTA curves enable to detect the Exo – Endo thermic peaks (effects due to gain/ loss of enthalpy) occurring in the samples when undergoing controlled heating and relative to an inert reference material. Therefore, in the present study attention has been focused on the characterization of ancient pottery sherds by thermal (TGA - DTA) analysis. The analysis of the data obtained in the thermograph were utilized for the estimation of the firing temperature of artifacts concerned. The geological site map of Alagankulam is given in Fig. 1.

Fig.1 Geographical map of the excavation site, Alagankulam (Tamilnadu)



Archaeological pottery sherds

The three representative pottery shreds of the shreds found in Alagankulam have been coded by the authors as AKM1, AKM2, and AKM 3 respectively for the present studies.. They were procured with the courtesy of State Archaeology Department, Government of Tamilnadu, Chennai, India from the excavation conducted at Alagankulam recently. The pottery shreds were collected from layers of different depth. It is stated by the archaeological department that the variation in depth of the layers at the excavation can also represent the age of the shred buried chronologically in the past. The nature of the faces of the shreds is distinct one from the other in appearance. The faces of the shreds AKM1 and AKM3 are glazed whereas the AKM2 is line embossed. The physical attributes of pottery shreds are given in Table. 1.

Fig.2 Pottery sherds of Alagankulam (AKM 1, AKM 2 and AKM 3)

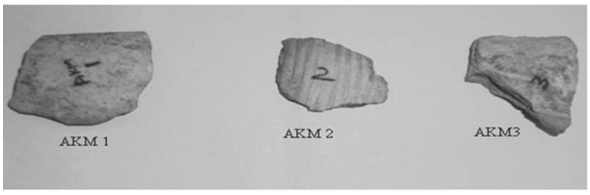


Table 1.1 Physical attributes of pottery shreds

Pottery shred	Trench Depth (m)	Thickness (10^{-3} m)	Physical Characteristics
AKM1	1.90	3.614	Red ware, Glazed surface
AKM2	5.10	4.632	Black ware, line embossed
AKM3	6.40	14.622	Brownish ware, Glazed surface

Experimental Details

Fourier Transform Infrared Spectro metry (FT-IR)

The pottery samples were analyzed from the FT-IR absorption spectra in transmittance mode to characterize their mineralogical composition from the specific transmittance peak observed. The samples were powdered, pelletized with spectra grade KBr in the ratio of 1:20. The spectra were recorded in the region 4000 – 400cm^{-1} at room temperature using Perkin Elmer FTIR Spectrometer with precision of $\pm$4 cm^{-1} in 4000-2000cm^{-1} region and $\pm$2 cm^{-1} from 2000 - 400cm^{-1} region.

Thermogravimetric Analysis

Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out in SDT Q 600 V.8.3 thermal analyzer in Central Electrochemical Research Laboratory (CECRI), Karaikudi, Tamilnadu, India. The experiment was carried out by heating the samples from room temperature to 1200°C in step of 20°C min^{-1} in a static nitrogen atmosphere.

Results and discussion

The mineralogical compositions of the archaeological potteries are mainly depending on the nature of the relevant raw material, firing atmosphere, the process of firing and the depositional changes (4). The minerals present in the shreds can be identified by the FT-IR analysis and thereby the range of firing temperature can also be estimated. The FT-IR spectrum of the shreds AKM1, AKM2 and AKM3 respectively are shown in figure 3. The tentative vibrational assignments of IR peak in the as- received state of the samples are given in the table 1.2.

Fig.3 FT-IR spectrum of pottery shreds AKM 1, AKM 2 and AKM 3

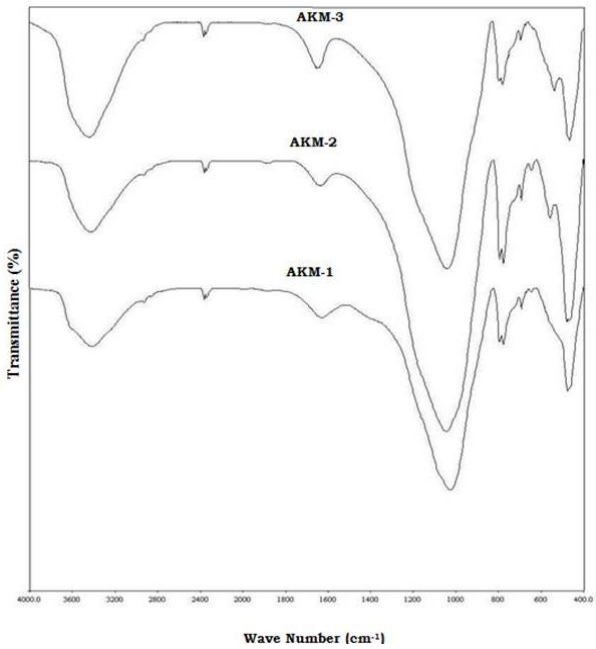


Table 1.2 FT – IR peak assignments of coded pottery sherds

Sherd Code			Tentative vibrational assignments
AKM 1	AKM 2	AKM 3	
3625	-	3625	O-H Stretching
vw		vw	
3414	3421	3419	O-H Stretching
w	w	w	
1635	1628	1636	H-O-H bending water
vw	vw	vw	
1032	-	1035	Kaolinite Si-O stretching
vs		vs	
-	1083	-	C-O stretching Wollasonite
	vs		
796	796	795	Si-O quartz
w	w	w	
778	778	778	Si-O-Si stretching
w	w	w	
694	694	695	Si-O bending
vw	vw	vw	
647	647	646	Si-O-Si bending Gehelanite
vw	vw	vw	
-	539	536	Fe – O of Hematite
	w	w	
468	466	469	Si-O Microcline
m	m	m	

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

According to Bikiars et al (5) the broad absorption band around 3423cm^{-1} is an indicative of crystalline hydroxyl group and is always accompanied by a band around 1628cm^{-1} which is assigned to H-O-H bending of adsorbed water molecules. From the FT-IR Spectra, the absorption band around 3414, 3421 and 3419cm^{-1} of AKM 1, AKM 2 and AKM 3 respectively are associated with the band at 1635, 1628 and 1636 reveals that the hydroxyl group and H-O-H bending of water molecules are present in the sample (6).

Dowty, Russtien and white have stated that the absorption band at 1085cm^{-1} is due to wollasonite (7, 8). The mineral wollasonite is present only in AKM 2 as evidenced by the very strong intensity band at 1083 cm^{-1} which is in agreement with the reference cited. The other samples AKM 1 and AKM 3 have no corresponding peak at 1085 cm^{-1}. So it can be inferred that the samples are not having wollasonite in their composition.

Farmer had suggested in the study of IR spectra of clay minerals that the absorption band at 1034cm^{-1} is due to the red clay origin of the kaolinite (9). Therefore the strong intensity band observed at 1032 and 1035 cm^{-1} for the sample AKM 1 and AKM 3 respectively have been assigned to red clay orgin of kaolinite and the corresponding peak which does not present in AKM 2 indicates the absence of kaolinite.

According to Russel` (6) a medium intensity band appearing around 778cm^{-1} and 795cm^{-1} are due to Si-O-Si silicates. All the three pottery samples in the present study, have exhibited the medium intensity doublet bands at 778 and 796cm^{-1}. So they can be assigned to Si-O-Si of silicates. The reports from the earlier study revealed that the presence of absorption band around 692cm^{-1} is due to Si-O mode of quartz (10). Hence the samples AKM1, AKM2 and AKM3 showing a band around 694 cm^{-1} are attributed to Si-O mode of quartz.

Sevim Akyuz et al avowed that the band at 647cm^{-1} indicates the presence of Gehelanite in the clay samples (11). From the observation, it is evident that the band around 645cm^{-1} present in all the pottery samples might be due to Gehelanite. According to Velraj et al, it is reported that the absorption band around 535 cm^{-1} is due to hematite present in the sherd (12). Therefore the band observed at 539 and 536cm^{-1} in the present samples AKM 2 and AKM 3 shows presence of hematite and this band does not appear in AKM 1 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 as stated by (4& 13).

The firing temperature of the pottery shred

The compositions in the ceramic materials are the "fingerprint" of the stable or meta stable solid phase formed during firing, the production processes of ceramics and pottery can be derived from their assemblage (14,15). The recognizable phases of minerals and of their association are dependent more on the chemistry, raw materials, maximum heating temperatures, heating ratio, firing and kiln atmosphere. These factors would help in understanding the course of reactions.

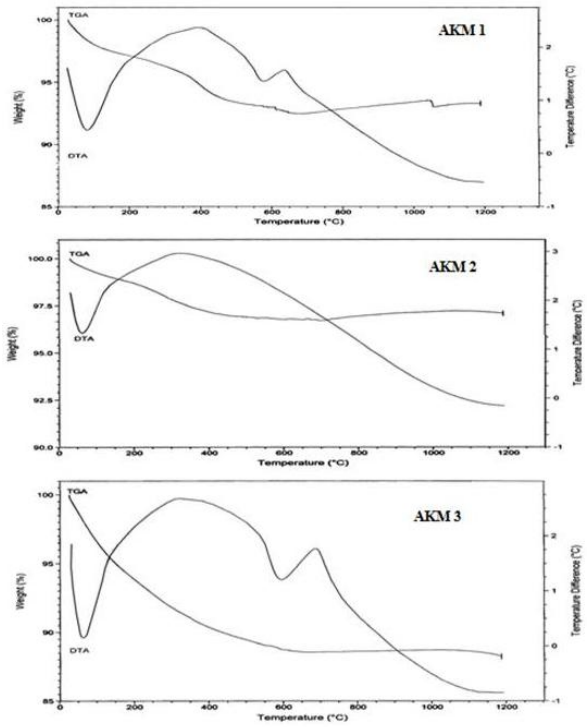
Mendelovici et al (16) reported that the IR band around 3630cm^{-1} is due to crystalline hydroxyl group which will continue to persist up to 800°C. The FT-IR spectra of the shred AKM 1 and AKM 3 shows the absorption band around 3622 and 3628cm^{-1} respectively.

Thus the samples AKM 1 and AKM 3 would be fired around 800°C. Conversely, AKM 2 does not show the absorption band at 3630 cm^{-1} in the received state which indicates that the sample might have been fired at a temperatures higher than 800 °C.

According to Velraj et al the firing temperature of archaeological potteries during manufacturing is referred as 800 °C from the band occurs at 1030 cm^{-1} which is due to Si-O stretching of kaolinite minerals (12). For the present samples, the strong intensity band observed around 1032 cm^{-1} in AKM 1and AKM 3 shows the Si-O stretching of kaolinite and also indicates that the samples were subjected to the firing temperature of 800 °C during manufacturing. The absence of the band at 1030 cm^{-1} in AKM 2 indicates that it has been fired above 800°C. The strong intensity band at 1082 cm^{-1} for the sample AKM2 reveals the presence C-O stretching of wollastonite. Hence it might have been fired at 1000 °C as suggested by Chiristina Rathossi et al (17). From the analaysis it is concluded that the sherds AKM 1and AKM 3 have been fired not above 800°C and AKM 2 fired around 1000 °C.

Thermogravimetric Analysis

Fig. 4 TGA –DTA curves of Alagankulam pottery samples



The TGA-DTA curves of pottery samples AKM 1, AKM 2 and AKM 3 are shown in Fig.4. According to Moropoulou et al and Franquelo et al the endothermic peak around 100 to 200°C is due to the adsorbed water (18, 19). An endothermic peak appeared in the range of temperature 100 to 200°C in DTA curves of the samples AKM 1, AKM 2 and AKM 3 are ascribed to adsorbed water. The appearance of exothermic peak from 250 - 500°C is due to combustion of organic material in the pottery shreds as reported by Clerk et al (20). The exothermic peak in the temperature region 250 – 500 °C are due to combustion of organic material in all the samples.

Table 1.3 Thermal data in TGA – DTA of pottery samples

Sample code	Weight loss				
	Dehydration (room temperature - 200° C)	Decomposition Of hydroxyls (400 - 650° C)	Decomposition of calcite (700 - 800° C)	Intense weight loss	Total weight
AKM 1	2.9 %	1.9 %	0%	(50- 440) 5.4%	6.7 %
AKM 2	2.3 %	1.2 %	0 %	(50- 400) 2.2%	2.9 %
AKM 3	6.5 %	1.7 %	0 %	(50 - 530) 3.6 %	11.75 %

Mackenzie has stated that the endothermic peak appearing from 550 – 650 °C is due to the decomposition of kaolinite (21). In the present investigation, the decomposition of kaolinite evidenced by the endothermic peak in the range 575 -665°C in AKM 1 and 500 – 675°C in AKM 3. According to Moropoulou et al the decomposition of kaolinite peak is the indication that the pottery is not fired above 800°C (18). So it is concluded that the pottery sherds AKM 1 and AKM 3 might have been fired around 800°C. The absence of the endothermic peak in the sample AKM 2 indicates that it was fired above 800°C as evidenced in the IR spectral characterization.

Clerk et al have reported in the study of fired clay products that the absence of exothermic peak in the range 900 - 1000°C in pottery samples is the indication that the products were not fired above 900 - 1000°C (20). The sample AKM 2 has exothermic peak in between 900 - 1000°C reveals that they were fired around or below this region of temperature as estimated in FT – IR study.

Data on the thermal decomposition of three archaeological pottery samples are summarized in Table 1.2. In the thermo gravimetric analysis, the heating of pottery shreds show significant mass loss due to (I) the dehydration from room temperature (30°C) to 200°C, (II) decomposition of hydroxyls 400-650°C and (III) decomposition of carbonates, mainly calcite 700 - 800°C. The mass loss on the temperature intervals change irregularly, indicating that the changes occurred in mineral composition of the pottery sherds.

In TGA curves the mass loss between room temperature (30°C) to 200°C due to dehydration of water. The mass losses between room temperature to 200°C attributed to dehydration of water the weight loss due to dehydration are 2.9 %, 2.3% and 6.5% for the samples

AKM1, AKM2 and AKM3 respectively. The weight loss occurred in the region of temperature 400 – 650°C are attributed to decomposition of hydroxyls or dehydroxylation. The three samples showed less than 2% of weight loss due to dehydroxylation.

According to Drebushckak et al reported that the weight loss between 700 - 800°C is due to decomposition of calcite (22). The pottery samples of the present study AKM 1, AKM 2 and AKM 3 showed no mass loss in between 700 - 800°C indicating the absence of calcite in its mineral composition. Clerk et al have stated that a broad exothermic peak in the range 250 - 500°C is due to the combustion of organic material in the pottery sample and also the weight loss occurred in this region is attributed to the combustion of organic material (20). The weight loss corresponding to organic material are (3.5%), (3.0%) and (0.9%) in AKM 1, AKM 2 and AKM 3 respectively.

Conclusions

The pottery sherds excavated from Alagankulam, were characterized by FT –IR and TGA – DTA techniques. The components of pottery ceramic material are the solid phase formed during firing of antique pottery. From the assignments of minerals present in the IR vibration of the sherds and TGA – DTA data, under nitrogen atmosphere in the temperature range 30 – 1200 °C, the range of firing temperature from the exo therm and endo therm peaks were identified. So it is inferred that the sherds AKM 1and AKM 3 were fired at 800°C, whereas AKM 2 was fired around 1000 °C by the artisans at the time of manufacture. Thus the results obtained from TGA – DTA techniques are in agreement with FT – IR results.

Acknowledgements

The authors acknowledge with thanks The Director, State Department of Archaeology, Chennai, Tamilnadu, for his courtesy of giving the Archaeological samples for the present work. Further, the authors submit their sense of gratitude to Dr.AN.Kannappan, Professor and Head, Department of Physics, Annamalai University for his constant encouragement to bring a success to this work.

References

1. Rice P.M (1987). Pottery analysis. University of Chicago press, Chicago
2. Charters, S.,Evershed,R.P., Goad, L.J., Heron, C., Blinkhorn, P (1993). Identification of an adhesive used to repair jar. *Archaeometry,* 35, 91-101.
3. Maritan, L., Nodari, L., Mazzoli, C., Milano, A., Russo, U (2006). *Appl.Clay Sci*.311.
4. 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.
5. Bikiaris, D., Daniila, S., Sotiropoulou, S., Katsimbiri, O., Poulidou, E., Moutsatsou, P., Chryssoulakis, Y (1999). *Spectrochim. Acta part A* 56, 3.
6. Russell J D (1987). A handbook of determinative methods in clay mineralogy. (ED) M J willson (Blackie, London), 133.
7. Dowty. E,(1987). Vibrational interaction of tetrahedral in silicate glasses and crystals: II. Calculsion on melilites, piroxenes, silica polymorphs and feldspars, *Physics and Chemistry of Minerals* 14,122-138.
8. Rutestein. M.S, White. W.B, (1971). Vibrational spectra of high – calcium pyroxenes and piorozxenoides, America Mineral, 56,877-887.
9. V.C.Farmer, (1974) Infrared spectra of minerals, Mineralogical society, London.
10. Palanivel, R., Velraj, G (2007). FTIR and FT-Raman Spectroscopic studies of fired clay artifacts recently excavated in Tamilnadu, India, *Indian J Pure & Appl. Phys,* 25, 501- 508.
11. Sevim Akyuz., Tanil Akyuz., Sait Basaran., Cetin Bolcal., Ahmet Gulec (2008). Analysis of ancient potteries using FT-IR, micro – Raman and EDXRF spectrometry. Vibrational spectroscopy 48,276 – 280.
12. Velraj. G., Janaki, K., Mohamed Musthafa, A., 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.
13. S.W. Kieffer, (1979).Thermodynamics and lattice vibrations of minerals: 2. Vibrational characteristics of silicates, Rev. Geophys. Space Phys.17, 20-34.
14. Shoval, S. J (1994). *Thermal Anal*, 42,185.
15. Mirti, P., Appolonia L., & Casoli A (1999). *Journal of Archaeological Science*, 26, 1427.
16. Mendelovici, E., Yariv SII., Villalba (1979). *Clay Miner.*14, 323- 331
17. Chiristina Rathosssi, Panthosso Tsolis – katagas, Christos Katagas,(2002). Tachnology and composition of Roman Pottery in northwestern Pelopnnes, Greece, *Applied Clay Science* 24, 313 – 326.

18. Moropoulou. A, Bakolas. A and Bisbikou. K, (1995). Thermal analysis as a method of characterizing ancient ceramic technologies, *Thermochemica Acta* 2570, 743 -753.
19. Franquelo, M.L., Robador. M.D., Ramirez –Valle. V., Duran. A., Jimenez de Haro. M.C., and J.L. Perez – Rodriguez (2008). Roman ceramic of hydraulic mortars used to build the mithraeum house of merida (Spain). *Journal of Thermal Analysis and Calorimetry*. 92, 331 – 335.3
20. Clerk. G, Leach. B. F and O' Conner. S (Ed). Islands of inquiry: Colonization, Seafaring and the Archaeology of Maritime Landscape papers in honor of Atholl Anderson, Terra Australia, Australian National University press 435 – 452, 2008.
21. Mackenzie. R.C. (1970) In Differential Thermal Analysis 1 and 2, Ist edn., Academic press, London.
22. Drebushchak. V.A.,. Mylnikova, L.N, Drebushchak, T.N and Boldyrev. V.V. The investigation of ancient pottery Application of thermal analysis. *Journal of Thermal Analysis and Calorimetry.* 82 (2005) 617 – 626.