

PHYSICS

# FT-IR AND MICRO-RAMAN SPECTROSCOPIC STUDIES OF ARCHAEOLOGICAL POTTERIES RECENTLY EXCAVATED IN TAMILNADU, INDIA

G. Velraj<sup>1\*</sup>, K. Prabakaran<sup>1</sup>, A. Mohamed Musthafa<sup>1</sup> and R. Hemamalini<sup>2</sup>

<sup>1</sup>Department of Physics, Periyar University, Salem-636 011, Tamilnadu, India

<sup>2</sup>Department of Physics, Sri Sarada college for women, Salem-636 016, Tamilnadu, India

## Abstract

The spectroscopic techniques represent one of the most powerful tools to investigate the structure of all the materials and chemical composition of the cultural object like potteries and ceramic. The spectroscopic techniques that are used in the present study are FT-IR absorption and Micro Raman spectroscopy. The technique of Raman spectroscopy was used to examine the composition of ancient potteries. Normal dispersive Micro-Raman spectroscopy is found to be the most effective analytical technique in the study. The potteries maintain aesthetic characteristics so that this type of artifacts can be considered very specific trace of every civilization. Therefore it is of great importance to acquire knowledge about the chemical composition in the clay of archaeological artifacts. In the present study potteries are excavated in Salamankuppam, Tamilnadu, India subjected to record the mid IR in the range 4000–400  $\text{cm}^{-1}$  and the Micro Raman range of 1800 – 100  $\text{cm}^{-1}$ . The clay mineral present in the pottery samples are identified through FT-IR method and was confirmed with Raman Spectroscopy, since the IR and Raman Spectroscopy are complement to each other. The major primary minerals present in the samples are Kaolinite and the secondary mineral present is quartz and the accessory minerals present in the samples are hematite, magnetite and feldspar.

**Keywords:** Ancient potteries, FT-IR absorption, Micro-Raman spectroscopy, Clay minerals

## Introduction

The cultural heritage research field experienced great development during the last decades. The artistic and archaeological approach gives a guideline to the classification of an artwork, analyzing the manufacture's stylistic features to place it in a correct geographical and historical framework. Micro Raman and FT-IR spectroscopy are the most widely utilized for the investigation of archaeological artifacts. This technique has proven very powerful technique used in all areas of scientific research<sup>1</sup>. In art and archaeology, this technique is used to identify the materials such as pigments, binders and mainly the chemical composition present in the archaeological samples like pottery, bricks and tiles<sup>2</sup>. Potteries are the only source which reflects the ancient people life style, mainly the skills utilized during the time of manufacture of potteries. Fragmented pottery samples are collected from Salamankuppam (12°36'N, 80°11'E) archaeological site near the famous Mahabalipuram in Chennai, Tamilnadu. Fig. 1 represents the geological map of excavated site of Salamankuppam in Tamilnadu. In the present study, an attempt has been made to subject the samples for Micro Raman and FT-IR analysis to identify the chemical composition present in the pottery samples. Identification of chemical

composition helps to give clear information about the pottery of particular area mainly the raw materials used.

Fig.1 Geographical Map of Salamankuppam in Tamilnadu

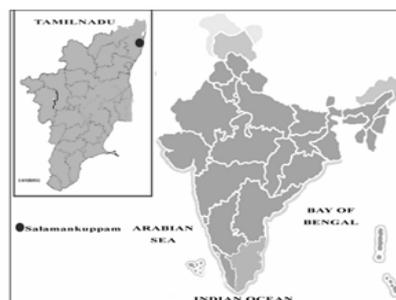


Fig.2. Pottery samples of Salamankuppam



\* Corresponding Author, Email: gvelraj@yahoo.co.uk

## Materials and Methods

Micro Raman spectra were collected in backscattering geometry using a He-Ne excitation source having wavelength 632.81 nm coupled with a Labram-HR800 Micro Raman spectrometer equipped with X50 objective, appropriate notch filter and peltier cooled charge coupled device detector. The incident laser beam was linearly polarised while the scattered light was detected in unpolarised mode. The Infrared spectra were recorded using FTIR Spectrometer RXI-Perkin Elmer. The spectra were recorded in the mid IR region (4000-400  $\text{cm}^{-1}$ ) using KBr pellet technique. The samples were pelletized by mixing with the spectra grade KBr at the ratio of 1:20 by weight<sup>3</sup>. The KBr pellet of 13mm diameter was kept inside the sample holder and scanned at  $1\text{cm}^{-1}$  resolution, which are commonly used standard laboratory investigations as it covers almost all the vibrational and rotational transitions.

## Results and Discussion

The FT-IR and Micro Raman spectra were recorded for the four archaeological pottery shreds are named as SMK1, SMK2, SMK3 and SMK4. The FT-IR spectra of all the samples are shown in Fig. 3, 4, 5 and 6. The absorption observed in the spectra with their relative intensity and the tentative vibrational assignments are given in the Table 1. Similarly, the Micro Raman spectra of all the samples are shown in Fig.7, 8, 9 and 10. The results obtained from the spectra and their tentative assignments are clearly give in the Table 2.

The sample SMK1 shows strong band at  $3447\text{ cm}^{-1}$  which may be assigned to OH Stretching of kaolinite<sup>5</sup>. Medium band in the region  $1639\text{ cm}^{-1}$  were identified due to H-O-H bending of water<sup>7</sup>. The medium band at  $1417\text{ cm}^{-1}$  in SMK1 is assigned to calcite<sup>4,5</sup>. The presence of Walsonite<sup>8</sup> was observed in SMK1 with very strong intensity peak at  $1085\text{ cm}^{-1}$ . The appearance of absorption band at  $784\text{ cm}^{-1}$  in the sample of the study indicates the presence to Quartz<sup>7</sup>. The presence of absorption band around  $577\text{ cm}^{-1}$  is due to magnetite and hematite respectively<sup>9,10</sup>. In the sample around  $462\text{ cm}^{-1}$  is due to presence of hematite<sup>6</sup>.

The sample SMK2 shows very strong band at  $3488\text{ cm}^{-1}$  which is assigned to OH - Stretching adsorbed water<sup>5</sup>. A very weak band of  $1883\text{ cm}^{-1}$  is found which is due to the presence of Calcite stretching vibrations. The presence of weak band around  $1419\text{ cm}^{-1}$  frequency shows the presence of Calcite<sup>4,5</sup>. The strong band of  $1046\text{ cm}^{-1}$  in SMK2 is due to kaolinite<sup>8</sup>. The presence of  $693\text{ cm}^{-1}$  and  $782\text{ cm}^{-1}$  frequency is due to Si-O Quartz and the bonding is weak and medium respectively<sup>7</sup>. The  $463\text{ cm}^{-1}$  is

attributed to the presence of hematite and it has strong bonding<sup>6</sup>.

The FT-IR spectrum of the SMK3 sample is taken and it shows a strong band of  $3439\text{ cm}^{-1}$  and it is due to O-H stretching<sup>5</sup>. The frequency of  $1883\text{ cm}^{-1}$  is due to calcite stretching and it is very weak. A medium band around  $1638\text{ cm}^{-1}$  is due to H-O-H bending of water. The presence of  $1426\text{ cm}^{-1}$  frequency is attributed to the presence of calcite and it is medium<sup>4,5</sup>. A very strong band around  $1041\text{ cm}^{-1}$  is due to the presence of kaolinite. The presence of  $694\text{ cm}^{-1}$  and  $784\text{ cm}^{-1}$  frequency is due to Si-O Quartz and the bonding is weak and medium respectively<sup>7</sup>. Hematite<sup>6</sup> is confirmed by a strong band around  $466\text{ cm}^{-1}$ .

From the FT-IR spectrum of the sample SMK4 the strong band in the region  $3448\text{ cm}^{-1}$  were identified due to O-H stretching<sup>5</sup>. The frequency of  $1882\text{ cm}^{-1}$  is due to calcite stretching and it is very weak. A strong band around  $1641\text{ cm}^{-1}$  is due to H-O-H bending of water<sup>7</sup>. kaolinite<sup>8</sup> is confirmed by a very strong band around  $1037\text{ cm}^{-1}$ . The presence of  $781\text{ cm}^{-1}$  frequency is due to Si-O Quartz and the bonding is medium respectively<sup>7</sup>. Hematite<sup>6</sup> is confirmed by a strong band around  $459\text{ cm}^{-1}$ .

Fig.3 FTIR spectrum of the sample SMK1

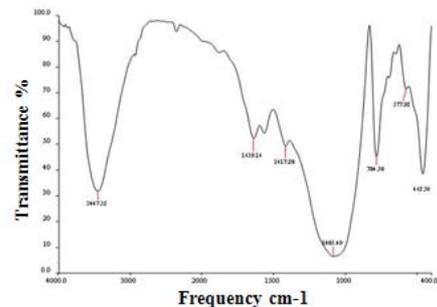


Fig.4 FTIR spectrum of the sample SMK2

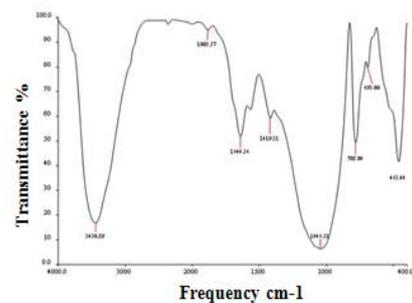


Fig.5 FTIR spectrum of the sample SMK3

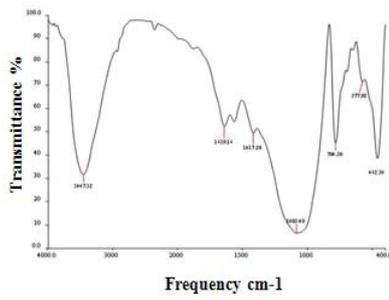


Fig.6 FTIR spectrum of the sample SMK4

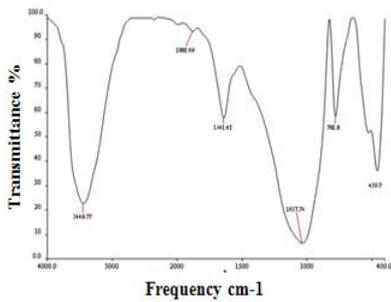


Fig. 7 Micro-Raman spectrum of sample SMK1

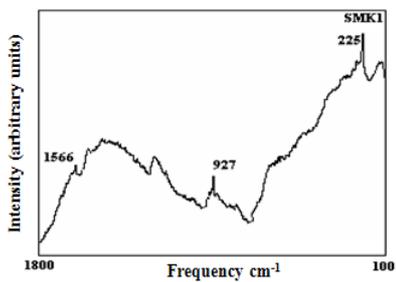


Fig 8 Micro-Raman spectrum of sample SMK 2

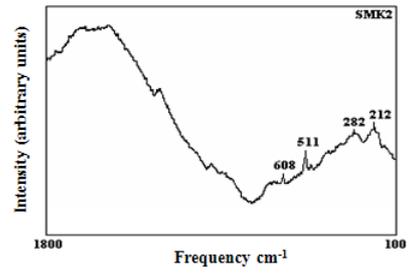


Fig 9 Micro-Raman spectrum of sample SMK 3

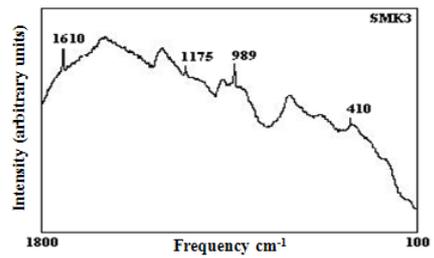


Fig 10 Micro-Raman spectrum of sample SMK 4

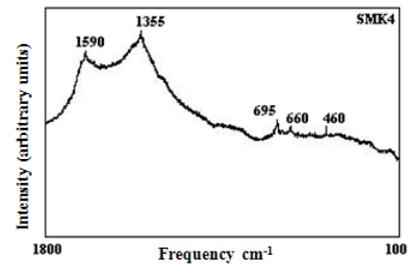


Table-1 FT-IR absorption frequencies [cm<sup>-1</sup>] and relative intensities of ancient pottery samples with tentative Vibrational assignment

SMK1	SMK2	SMK3	SMK4	Tentative vibration assignment
3447 S	3488 VS	3439 S	3448 S	O-H Stretching. absorbed water
-	1883 VW	1883 VW	1882 VW	Calcite stretching vibration
1639 M	1640 M	1638 M	1641 S	H-O-H bending
1417 M	1419 W	1426 M	-	Calcite
1085 VS	-	-	-	Wollasonite
-	1046 VS	1041 VS	1037 VS	Kaolinite
784 M	782 M	784 M	781 M	Si-O quartz
577 W	-	-	-	Magnetite
-	693 W	694 W	-	Si-O quartz
462 M	463 S	466 S	459 S	Hematite

V.S-Very Strong; S-Strong; M-Medium; W-Weak; VW-Very Weak

Table 2 Micro Raman shifts of Salamankuppam pottery shreds and the vibrational assignments

Samples				Tentative Vibrational Assignments
SMK1	SMK2	SMK3	SMK4	
Freq. ( $\text{cm}^{-1}$ )	Freq. ( $\text{cm}^{-1}$ )	Freq. ( $\text{cm}^{-1}$ )	Freq. ( $\text{cm}^{-1}$ )	
R.I	R.I	R.I	R.I	
-	-	1610VS	-	C-C Str.(Amorphous Carbon)
1566 M	-	-	1590 VS	C-C Str. (Amorphous Carbon)
-	-	-	1355 VS	C-C Str.(Amorphous Carbon)
-	-	1175 S	-	S-O Str. (Anhydrite)
-	-	989 M	-	Si-O Str. (Feldspar)
927 W	-	-	-	AlOH Bend (Montmorillonite)
-	-	-	695 VW	S-O Bend (Gypsum)
-	-	-	660 VW	Al-O-Si Bend (Kaolin)
-	608 VW	-	-	Fe-O Str.(Hematite)
-	511S	-	-	Al-O-Si Bend (Feldspar)
-	-	-	469 VW	Si-O-Si Bend(Quartz - Illete)
-	-	410VW	-	Fe-O Bend (Hematite)
-	282VS	-	-	O-H-O, Fe-O Bend (Kaolin - Hematite)
225VS	212VS	-	-	Fe-O Bend (Hematite)

W-Weak; VW-Very Weak ; M-Medium; S-Strong; V.S-Very Strong

The Raman spectra of the samples recorded in the region 1800-100 $\text{cm}^{-1}$ . The very strong Raman band appearing around 225  $\text{cm}^{-1}$  and 212  $\text{cm}^{-1}$  in SMK1 and SMK2 and very weak band around 410  $\text{cm}^{-1}$  and 608  $\text{cm}^{-1}$  in SMK2 and SMK3 are due to the red iron (III) oxide<sup>11</sup>. The reddish colour of the pottery shreds is due to the presence of high hematite content which only forms during the firing process. Frost et al<sup>12</sup> suggested very strong band around 282  $\text{cm}^{-1}$  which represent the O-H-O, Fe-O bend indicates the presence of Kaolin/Hematite. The presence of Feldspar (albite) in SMK2 shows the strong Raman band around 511 $\text{cm}^{-1}$ <sup>13</sup>. The medium band around 1566  $\text{cm}^{-1}$  in SMK1 and very strong peak around 1610  $\text{cm}^{-1}$  in SMK3 are due to the presence of amorphous carbon present in the sample<sup>14</sup>. According to Chio and Sharma<sup>15</sup>, the sample SMK3 shows the strong band around 1175 $\text{cm}^{-1}$  indicates the presence of anhydrite ( $\text{CaSO}_4$ ). This indicates the component could either have been part of the clay minerals or developed during the processing. As shown in the spectral representation of sample SMK3, a medium band at 985 $\text{cm}^{-1}$  is due to the presence of Feldspar<sup>16</sup>. According to Frost and Rintoul<sup>17</sup>, a very weak band around 927 $\text{cm}^{-1}$  in SMK1 is normally associated with Montmorillonite clay mineral. The very strong peak around 1590 $\text{cm}^{-1}$  in SMK4 is due to the presence of amorphous carbon in the sample<sup>14</sup>. The band around 1355  $\text{cm}^{-1}$  in sample SMK4 is due to the presence of amorphous carbon<sup>22, 23, 24</sup>. The presence of Kaolin (albite) in SMK4 shows the very weak band around 660 $\text{cm}^{-1}$ <sup>12</sup>. The very weak band around 690 $\text{cm}^{-1}$  is due to presence of Gypsum<sup>25,26,11</sup>. According to D. Bikiaris et al<sup>18,19,20,21</sup>, a very weak band around 469 $\text{cm}^{-1}$  is associate with quartz and Illite.

## Conclusion

The FT-IR and Micro Raman spectroscopic techniques were applied on the archaeological samples collected from the recent excavations at Salamankuppam to know the cultural sequence of a particular archaeological site. The FT-IR spectra was recorded in the mid IR region 4000-400 $\text{cm}^{-1}$  and the Micro-Raman in the range of 1800-100 $\text{cm}^{-1}$ . The clay minerals present in the pottery samples are identify through FT-IR method was conformed with Raman spectroscopy, since IR and Raman spectroscopy are compliment to each other. The major primary minerals present in the samples are kaolinite. The secondary mineral present is quartz and the accessory minerals present in the samples are hematite and magnetite. The different kinds of clay minerals (primary, secondary and accessory minerals) present in the pottery samples were identified by estimating the relative intensity and thereby from tentative vibrational assignments by

referring the reported data available in the literature. It is concluded that the presence of rich hematite in all the pottery samples may be due to the fact that the samples might have been fired in the oxidizing atmosphere. The artisans in this site were well aware of the oxidizing method of firing or in the open air firing. This also reflects the red color of the potteries taken for the present study.

## References

1. M. A. Legodi and D. de. Waal, *Spectrochim. Acta Part A* 66, 135 (2007).
2. R. J. H. Clark, *Chem. Soc. Rev.* 24, 187 (1995).
3. L. Murray Eiland and Quentin Williams, *Journal of Archaeological Science* 27, 993-1006, (2000).
4. Benedetto, G.E., Laviano, R., Sabbatini, L. and Zamboni, P.G., *Journal of Cultural Heritage*, 3, 177-186, (2002).
5. Russell, J.D., "*A hand book of determinative methods in clay mineralogy*", Wilson, M.J., Blackie and Son Ltd, (1987).
6. Legodi, M.A. and de Waal, D., *Spectrochim Acta Part A*, 66, 135-142, (2007).
7. Palanivel. R and Velraj, G, *FTIR and FT-Raman spectroscopic studies of fired clay artifacts recently excavated in Tamilnadu, India*, *Indian Journal of Pure and Applied Physics* 45 501-508, (2007).
8. Dowty, E, *Vibrational interaction of tetrahedral in silicate glasses and crystals: II. Calculsion on melillites, piroxenes, silica polymorphs and feldspars*, *Physics and Chemistry of Minerals* 14 122-138, (1987).
9. Velraj, G, Janaki, K, Mohamed Musthafa. A and Palnival. R, *Spectroscopic and porosimetry studies to estimate the firing temperature of some archeological pottery shreds from India*, *Applied Clay Science* 43 (3-4) 303-307, (2009).
10. Velraj, G, Janaki, K, Mohamed Musthafa. A and Palnival. R, *Estimation Of firing temperature of some archeological pottery shreds excavated recently In Tamilnadu, India*, *Spectrochimica Acta, Part A: Molecular and Bimolecular Spectroscopy*, 72(4) 730-733, (2009).
11. H. G. M. Edwards, E. M. Newton, J. Russ, *J. Mol. Str.* 550-551, 245 (2000).
12. R. L. Frost, P. M. Fredericks, J. R. Bartlett, *Spectrochim. Acta Part A* 49, 667 (1993).
13. R. Gout, E. H. Oelkers, J. Schott, A. Zwick, *Geochim. Cosmochim. Acta* 61, 3013 (1997).
14. K. Lee, H. Sugimura, Y. Inoue, O. Takai, *Diamond Relat. Mater.* 13, 1422 (2004).
15. C. H. Chio, S. K. Sharma, D. W. Muenow, *Am. Miner.* 89, 390 (2004).

16. J. M. Alia, H. G. M. Edwards, F.J. Garcia-Navaro, J. Parras- Armenteros, C. J. Sanchez- Jimenez, *Talanta* 50,291 (1999).
17. R. L. Frost, L. Rintoul, *Appl. Clay. Sci.* 11, 171 (1996).
18. P. Colomban, F. Treppoz, *J. Raman Spectrosc.* 32, 93 (2001).
19. D. Bikiaris, S. Daniila, S. Sotiropoulou, O. Katsimbiri, E. Poulidou, P. Moutsatsou, Y. Chryssoulakis, *Spectrochim. Acta Part A* 56, 3 (1999).
20. N.Q. Liem, G. Sagon, V.X. Quang, H. Van Tan, P. Colomban, *J. Raman Spectroscopy.* 31, 933, (2000).
21. W. Liu, *Water Res.* 35, 4111, p. 307, (2001).
22. R.L. Frost, P.M. Fredericks, J.R. Bartlett, *Spectrochim. Acta Part A* 49, 667 (1993).
23. H.G.M. Edwards, E.M. Newton, J. Russ, *J. Mol. Str.* 550–551 (2000).
24. J.M. Alia, H.G.M. Edwards, F.J. Garcia-Navaro, J. Parras-Armenteros, C.J. Sanchez-Jimenez, *Talanta* 50, 291 (1999).
25. I.A. Degen, G.A. Newman, *Spectrochim. Acta Part A* 49, 859 (1993).
26. V.C. Farmer, in: H. Van Olphen, J.J. Fripiat (Eds.), *Data Handbook For Clay Minerals and Other Non-metallic Minerals*, Pergamon, Oxford, p. 307, (1979).