ANALYSIS

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SPECTROSCOPIC AND NUCLEAR ANALYTICAL STUDIES OF ARCHAEOLOGICAL POTTERY SAMPLES RECENTLY EXCAVATED FROM URAIYUR, TAMILNADU, INDIA

S. Tamilarasu[1], G. Velraj[2*], R. Acharya[3], A.V.R. Reddy[4], K.K. Swain[4], N. Basavaiah[5]

[1] Department of Physics, Periyar University, Salem, Tamilnadu, India
[2] Department of Physics, Anna University, Chennai, Tamilnadu, India
[3] Radio Chemistry Division, Bhabha Atomic Research Centre, Mumbai, India
[4] Analytical Chemistry Division, Bhaba Atomic Research Centre, Mumbai, India
[5] Indian Institute of Geomagnetism, New Panvel (W), Navi Mumbai, India
(Email: stamilarasu12@gmail.com)

Abstract

These studies focus on firing temperature, elemental study and provenance studies of the ancient pottery collected from the recently excavated site in Uraiyur in Tamilnadu, South India. The samples were subjected to analysis as in the received state. Fourier Infrared Spectroscopy (FTIR), Particle induced X-ray emission (PIXE) and The Particle induced gamma ray emission (PIGE). PIXE has been proved to be a very rapid and accurate method for the elemental analysis of ancient artifacts. Using protons whose energy is lower than   3 MeV, it is possible to obtain, in a few minutes, the actual composition of narrow parts of artifacts, without any sampling, even at microscopic level. (PIGE) method using 4 MeV proton beam was standardized for simultaneous determination of Si, Al and Na for archaeological pottery samples. The FTIR studies using to analysis the firing temperature and the firing conditions adopted at the time of manufacturing of the pottery also determined. The Uraiyur samples were fired in the range of 700-800 °C. The PIXE and PGE results provided persuasive evidence Uraiyur pottery used at least two different clay sources. The cause of the distinct group separation could be because of the possible exchange between communities, as it is known that communities, which produced these wares, did not live in isolation from each other.
Keywords: Provenance study, PIXE, PIGE and Uraiyur Pottery.

1. Introduction

Modern archaeology generates amazing amounts of data, thanks to advances in instrumental analysis. Thus, in recent years, the characterization of ancient pottery to determine its provenance has involved the development, exploration, and testing of a large number of analytical techniques in order to compile and extract relevant compositional information. Ceramics are the most stable and abundant material in archaeological and historical contexts and different cultural aspects can be studied from them. Therefore, a complete characterization of ceramics is very important for archaeological and historical purposes [1].The significance of pottery as the most abundant tracer in all archeological excavations and the key role that the classification of such manufacts plays in historical studies has, in the last decade, addressed attention to the wide opportunities that archeometry opens to classification of pottery [2,3], to understanding of fabrication techniques and also to the identification of provenance. In the latter context archeometry [3-5] can play a significant role in supplementing the information gathered from documents to achieve a better knowledge of trade routes linking populations of different areas which is one of the essential ingredients for the knowledge of their history. Particle induced X-ray emission has been used successfully in the analysis of pottery [6-9], being capable of identifying major, minor and trace elements. In the present work Current normalized PIGE and

minor and major element technique PIXE used to collect the archaeological artifacts elemental concentration and provenance was carried out.

2. Materials and Experimental Method

The samples for the present work from Uraiyur, all five pottery samples named as URP-1, URP-2, URP-3, URP-4 and URP-5. The clay minerals, if we fired in the open air firing might be different from closed atmosphere firing. An attempt has been made to identify the minerals, which are present in the pottery samples at the same time those which fired. The collected samples were subjected to the spectroscopic technique (identification of minerals) and a nuclear analytical technique (identification of elements) had been done. The samples were subjected to analysis as in the received state. The characterization studies for the analysis of the composition of the Pottery using FT-IR, PIXE and PIGE reveals the skill and style of the artisan lived in the ancient civilization. Ion Beam Analysis (IBA) techniques PIGE and PIXE are very useful for obtaining qualitative information on almost all important element of interest. The IBA techniques like PIGE and PIXE allows the identification of the element present in the samples and determine their mass concentrations. PIGE and PIXE used determined low Z element namely Na, Al, Si, Li and high Z element namely K, Ca, Ti, Mn, Fe, Ni, Cu, Zn. PIGE and PIXE is a non-destructive chemical fingerprinting method used for a range of archaeological materials. It is a surface technique requiring minimal sample preparation where a magnetically focused, high energy, proton beam strikes the sample with beam penetration in the order of 10s of micrometers. The X-rays and gamma-rays emitted are counted by energy dispersive multi-channel and alpha particle analyzers. Sample preparation for PIGE and PIXE analysis sample weighing 350 mg was mixed with high purity graphite in 3:1 ratio and The PIGE and PIXE dataset is referenced to two standards from the IAEA SL-3 and Soil-5. These standards were selected because they are comparable matrices. The resultant mixture was compressed using a 2-4 ton hydraulic press into pellet of 12 mm diameter and 1 mm thickness. These vacuum ($\sim 10^{-6}$ torr) scattering chamber to perform the analysis. Pellet were placed on an aluminum ladder in the PIGE chamber at 45° to the beam direction and radioactivity measurement were carried out using HPGe gamma rays detectors. The experiment was carried out using 4 MV tandem accelerator at Institute of Physics (IOP) Ion Beam Laboratory, Bhubaneswar in odisha with 4 Mev energies (current ~ 10-15 nA) were used for PIGE above three or four element by PIGE was determined. Pellet were placed on an aluminum ladder in the PIXE chamber at 45° to the beam direction and radioactivity measurement were carried out using cooled LN_2 Si(Li) for x-rays detectors. The experiment was carried out using 3 MV tandem accelerator at Institute of Physics (IOP) Ion beam laboratory, Bhubaneswar in odisha with 3Mev energies (current ~ 10-15 nA) were used for PIXE. The characteristic X-rays of the elements present in all the samples were measured by using Si (Li) detector with a resolution of 160 eV at 5.9 keV. A PC based multi-channel analyzer (MCA), calibrated with 55Fe X-ray source was used to record the spectra. The spectra were analyzed by using GUPIXWIN software.

3. Results and Discussion

3.1 Fourier Transform Infrared Spectroscopy Studies (FTIR)

FT-IR spectroscopy has been a frequently used method for to investigate the structure, bonding and chemical properties of clay minerals [11]. To get the final products of the pottery are heated to higher temperatures and as a result thermal changes are taking place mainly on structure and bonding of the clay minerals, which can be studied using FT-IR spectroscopy [12]. The Fig. 1 shows the FT-IR spectra of the samples URP1-URP5. The tentative Vibrational assignments with relative intensities of the samples are given in the Table 1.The band at around

3453-3437cm^{-1} indicates the O-H stretching of absorption water in all the samples [13]. The weak absorption bands at 2928-2927cm^{-1} indicates the C-H stretching mode and reveals the presence of organic contribution in the URP samples. The weak absorption band at 1633-1628 cm^{-1}, which indicates that the presence of H-O-H bending of water in the URP-1, URP-2, URP-3, URP-5 samples [14]. The samples URP-2 and URP-4 have Si-O stretching clay minerals, which indicated due to the absorption bands at around 1040 and 1042cm^{-1} [15,16].

Table 1. FT-IR Vibrational frequencies of the Pottery samples from Uraiyur

IR absorption bands in Wave number (cm^{-1})					Tentative Vibrational Assignments
URP-1	URP-2	URP-3	URP-4	URP-5	
3697(M)	3694(W)	-	-	-	O-H stretching of hydroxyl group
3624(M)	3626(W)	-	-	-	O-H stretching of hydroxyl group
3453(M)	3450(W)	3445(W)	3446(VW)	3437(W)	O-H stretching absorbed water molecule
2928(VW)	2927(VW)	2927(VW)	2927(VW)	2927(W)	C-H stretching Vibrations
1631(W)	1634(VW)	1625(W)	1628(W)	1633(W)	H–O–H bending of water
1079(S)	-	1078(VS)	1074(VS)	1079(VS)	Al-O-Si Stretching of Amorphous
-	1040(VS)		1042 (VS)	-	Si–O stretching. Clay mineral
789(S)	786(W)	781(M)	782(W)	785(S)	Si–O of Quartz
685(M)	684(VW)	-	-	689(M)	Si–O of Quartz
-	-	-	582(VW)	-	Fe–O of Fe_3O_4. (magnetite)
537(S)	536(M)	536(VW)	536(VW)	-	Fe-O of Fe_2O_3 (hematite)
467(VS)	466(M)	461(M)	459(W)	463(S)	Si–O–Si bending

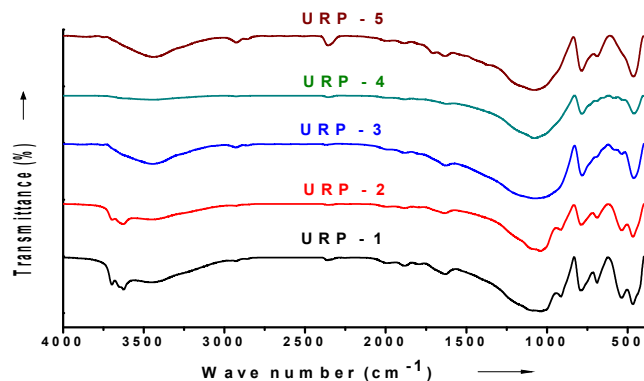VS-Very Strong, S- Strong, M-Medium, VW- Very Weak

Fig.1 FT-IR spectra of Pottery samples URP1-URP5

This evolution of the FTIR spectra with temperature, as well as the changes in the position and width of the Si-O stretching band and its splitting pattern are in very good agreement with the existing literature (Shoval, 1994).To be precise two different absorptions of wave number around 1040 cm^{-1} and around 1079 cm^{-1} caused by silicate band indicate that the firing temperature ranges achieved would be 800°C and 900°C respectively [17]. For the pottery URP1, URP3 and URP5, the Si-O stretching band positioned around 1078-1079 cm^{-1} reveals that the firing temperature reached during pottery manufacturing may be fall at above 800°C. Accordingly, the silicate bands situated in the wave number at 1038 cm^{-1} and 1040 cm^{-1} for URP2 and URP4 respectively shows that the temperature at which the pottery might have been fired in the range at 700^{0}C [18].
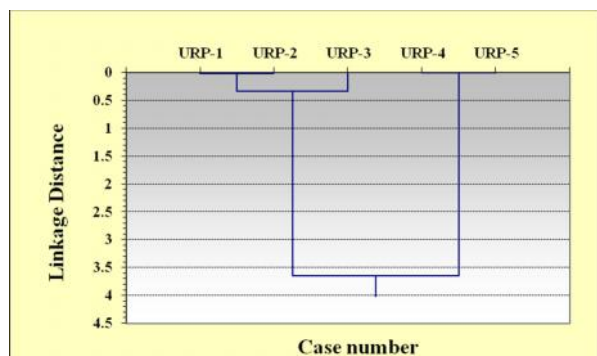
3.2 PIXE and PIGE spectra of Uraiyur pottery samples

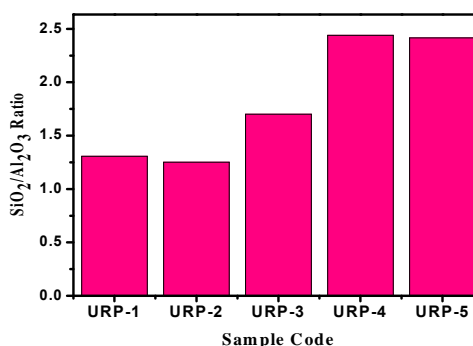Fig. 2. Cluster analysis Ward's method of URP Samples by PIXE

Fig. 3. Histogram of concentration ratio of SiO$_2$/Al$_2$O$_3$ of URP Pottery Samples by PIGE

In figure 4 and 5typical PIXE and PIGE spectral are shown Uraiyur pottery samples more than ten element K, Ca, Ti, V, Cr, Mn, Fe Ni, Cu, Zn, Rb, Sr and Zr were determined by PIXE and Low Z element like F, Na, Al and Si were determined by PIGE. Elemental concentrations namely K, Ca, Ti, V, Cr, Mn, Fe Ni, Cu, Zn, Rb, Sr and Zr were determined in ancient potteries as well as IAEA RMs SL-3and Soil-5. Results of two IAEA RMs and two ancient pottery samples are given in Tables 1 and 2 respectively. Results of ten elements in three different potteries are given in Table 1. Elemental concentrations including transition elements like Fe, Mn, V, Cr, Cu and Ni are used for grouping the objects under study. As seen in the Table

2, potteries G-4 and S-4. The results were used in statistical cluster analysis, which revealed that the samples under study fell into broadly tow groups [10].

Table 1: Elemental concentrations (ppm unless specified '*' for %) of two URP ancient pottery samples analyzed by PIXE

Element	IAEA RMs Soil-5 by PIXE		PIXE	
	CV	MV	URP-1	URP-5
K *	1.86±0.15	3.73±0.04	1.21±0.02	1.21±0.01
Ca *	-	0.27±0.01	0.82±0.01	0.27±0.01
Sc	15.5	14.96	7.68	3.05
Ti *	1.8±0.4	2.07±0.02	1.39±0.01	1.10±0.01
V	-	84.1	112.5	131.6
Cr	28.9±2.8	21.0	103.1	71.3
Mn	0.11±0.02	0.12±0.01	0.09±0.01	0.023±0.01
Fe *	4.45±0.9	4.98±0.02	4.22±0.01	3.15±0.01
Co	14.8±0.7	13.9±0.4	11.2±0.4	12.9±0.8
Zn	368±8	435.5	164.3	145.6

The cluster analysis of the excavated pottery from URP was successfully done from the elemental concentration determined from PIXE is shown in the Fig.2. It showed the ability of concentration to distinguish between objects even when they are macroscopically similar and therefore, to classify the resulting groups based on their elemental composition. The material composition study carried out showed that two distinct source raw material was employed to produce the pottery. The Fig. 3. Shows the histogram diagram of Si_2O/Al_2O_3 ration method and this result has been correlation with the cluster analysis (ward's method). The both results were in good agreement of the finding source materials used to make ancient pottery samples.

Table 2: Elemental concentrations (ppm unless specified '*' for %) of two URP ancient pottery samples analyzed by PIGE

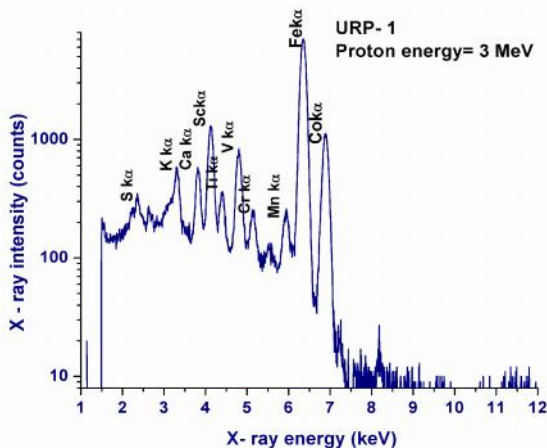| Element	IAEA RMs SL-3		PIGE	
	CV	MV	URP-1	URP-5
Na_2O -440 %	1.80±0.05	1.70±0.8	ND	1.95±0.42
Al_2O_3 -844 %	9.26±0.27	10.49±0.11	12.67±0.49	17.17±0.7
SiO_2-1778 %	48.3±1.1	47.9±0.4	39.27±1.34	37.52±1.80

Fig. 4: X-ray spectrum of URP-1 pottery
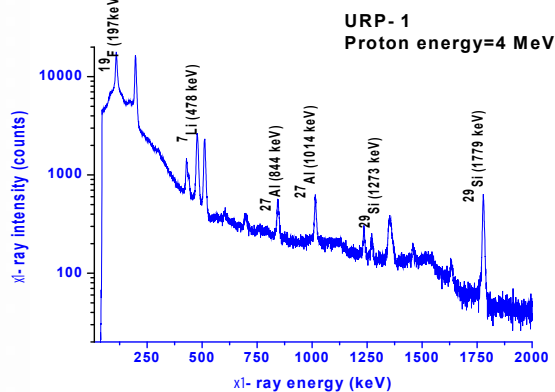

Fig. 5: γ-ray spectrum of URP-1 pottery

Conclusion

PIXE and PIGE analysis have been utilized to analyze 5 pottery samples from Uraiyur up to 10 elements were determined. These elemental concentration values were utilized in a multivariate statistical analysis method. In this study, most of the samples could be divided into two categories, which are characterized by different concentration levels of particular elements. The results provided persuasive evidence URP pottery used at least two different clay sources. The cause of the distinct group separation could be because of the possible exchange between communities, as it is known that communities, which produced these wares, did not live in isolation from each other.

Acknowledgements

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