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Characterization of archaeological ceramic materials collected from recently excavated site in India using spectroscopic techniques

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ABSTRACT - *The five ancient pottery samples collected from the recently excavated archeological site Uraiyur in South India. All the pottery samples were subjected to spectroscopic techniques. The spectroscopic technique is one of the most powerful tools to examine the structure of all the materials and chemical composition of the archaeological artifacts. The FT-IR study was helpful for the evaluating firing temperature achieved at the time of manufacturing of the pottery and the ranges obtained in the selected samples are from 700-800°C. From XRD studies multi crystalline mineral phase were identified and these results were also correlated with FT-IR results. The chemical composition analysis shows that all the samples are non calcareous nature and oxidizing atmosphere condition was adopted during at time of manufacturing the pottery samples. The samples having no vitrification stage which indicates that they might have fired below 800°C. Through factor analysis results found to be different types of clay source materials were used to making pottery. Whereas Group-1 as Al, Si and K, Group-II as Na, Mg and Ti & third groups on Ca and Fe, the factor analysis results revealed that the different types of clay source materials were used for making the potteries.*

KEYWORDS : Ceramics, Firing temperature, SEM with EDS and Factor analysis.

1. INTRODUCTION

Characterization of ancient ceramic artifacts has been carried out to determine its provenance and this involves a number of analytical techniques in order to compile and extract relevant compositional information. Ceramics are the most stable 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 studies [1].The significance of pottery is that, it is the most abundant tracers in all archeological excavations. Thus, studies on such artifacts to unravel past human activities and trade/exchange patterns [2,3]. FTIR spectroscopy is a frequently used method to investigate the structure, bonding and chemical properties of clay minerals. XRD is to define identical gatherings of mud based materials as indicated by their mineralogical composition. In the present work, FTIR, XRD, SEM with EDS techniques have been used to characterize the potteries obtained from Uraiyur site, Tiruchirappalli District, Tamil Nadu, India. In the present work firing temperature, mineralogical investigation, micro structural, vitrification stages and chemical composition of selected pottery samples has been obtained.

2 MATERIALS AND METHODS

2.1 About Samples

The collected five clay pottery samples namely U-1, U-2, U-3, U-4 and U-5. The Uraiyur archaeological site samples under excavated by Department of ancient history and archaeology, Madras University, Chennai. The samples were powdered and used for the experimental works.

2.2 Experimental Methods

The FTIR spectra were recorded in the mid infrared region 4000 cm^{-1} to 400 cm^{-1} using an ALFA-T FTIR spectrometer. The FTIR spectra were recorded at room temperature. To identify different mineral phases in the samples. The XRD patterns have been recorded on Rigaku miniflex II diffractometer using CuKα radiation in the range from 10 to 60°. The operating voltage at 40 kV and 20 mA with CuKα radiation of λ = 1.5405 Å. The Micro morphological examination done by SEM (Quanta 250) and elemental concentration determined by EDS (INCA, Oxford). The samples were prepared for the SEM-EDS analysis by carbon coated prior to the analysis for Morphology and determination O, Na, Mg, Al, Si, K, Ca, and Fe components.

3 RESULTS AND DISCUSSION

3.1 FT-IR Analysis

Fig.1. Shows that the FT-IR spectra of Uraiyur (U-1 to U-5) site pottery samples. The absorption band at around 3453-3437cm^{-1} indicates the O-H stretching of absorption of adsorbed water in all the samples. The weak absorption bands around at 2928-2927cm^{-1} indicates the C-H stretching mode and reveals the presence of organic contribution in all the Uraiyur pottery samples. The weak absorption band at 1633-1625 cm^{-1}, which indicates that the presence of H-O-H bending of water in all the samples [4]. The Uraiyur site pottery shards have Si-O stretching of clay minerals, which indicated due to the absorption bands at around 1037-1044 cm^{-1} [5]. All the pottery samples having Si-O stretching band positioned around at 1040 cm^{-1} revealed that the firing temperature during pottery manufacturing may be fall at around 800°C. The above result also conformed, by Al(OH) vibrations band at 915 cm^{-1} is due to octahedral sheet structure which is starts to disappear which increasing temperature. The firing temperature 500°C that band was absent in order to complete destruction of clay mineral present in samples.

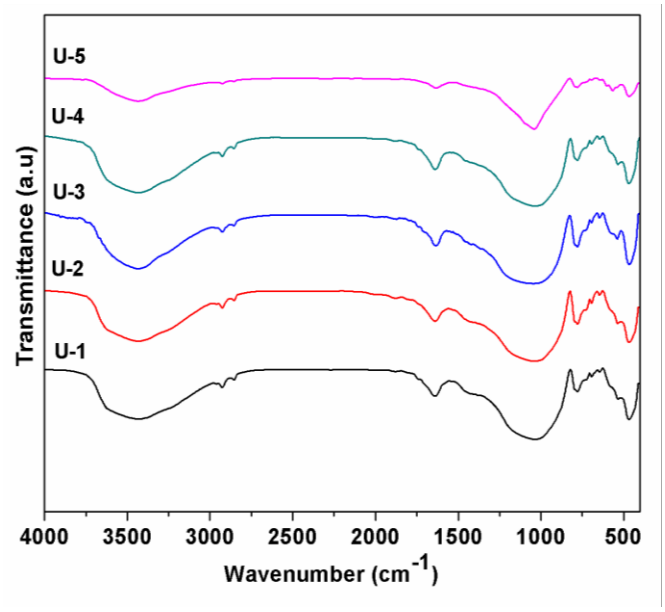

Fig - 1: FT-IR Spectra of U 1-U5 Pottery shards

In the present investigation no absorption band appear at 915 cm^{-1} so all the Uraiyur site pottery samples fired over 500°C at the time of manufacture [6,7]. The absorption region 1100 - 400 cm^{-1} is due to Si-O, Si-O-Si and Al-O, Al-Si-O was detected in Uraiyur site and these vibrational groups could be attributed Quartz and feldspar respectively. Quartz was observed through the presence absorption band around at 792 and 691 cm^{-1} [8].

In Uraiyur site all samples have hematite as evidenced by the band around at 540 cm^{-1}. These samples might have been fired in the open air. The red colour in the samples may be due to the higher hematite content [9]. From this study Uraiyur site samples fired below 800°C and red clay origin.

3.2 XRD Analysis

The collected pottery samples specifically (U-1, U-2, U-3, U-4 and U-5) were subjected to X-ray diffraction study at 2θ range in 10°-60°. Identification of crystalline mineral phases were compared using the Joint Committee of Powder Diffraction Standards (JCPDS) data bank [10] and overlapping XRD pattern of U site pottery shards shown in Fig.2. From XRD studies crystalline mineral phase were identified in all samples and (U-1) samples result tabulated in Table 1. The primary minerals present in all samples with d-spacing values. Quartz secondary minerals present in all samples. The identification of other minerals such as Feldspar, Calcite, Muscovite, Diopside, Dolomite, Orthoclase, Dicikite, Hematite and Mullite. The Iron oxide mineral like hematite minerals present in the all samples. The presence of Illite/muscovite indicates that the firing temperature was lower than 900°C [11], whereas the presence of hematite indicates a firing temperature of about 850°C [12].

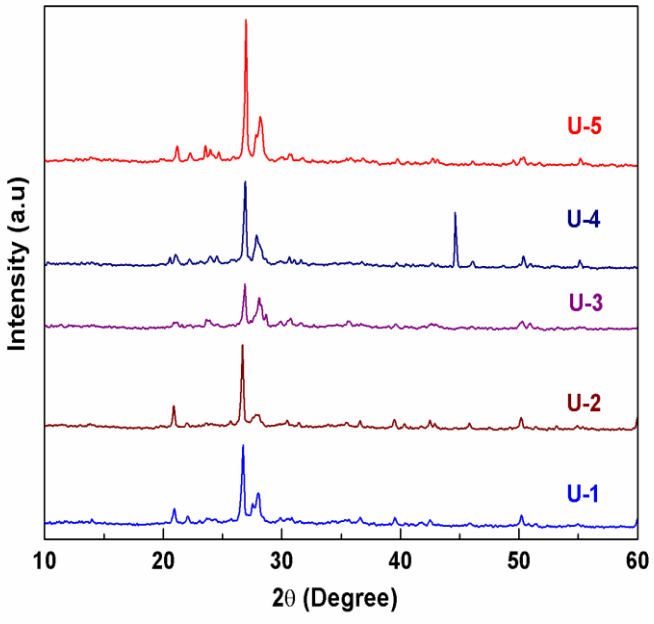

Fig - 2: XRD pattern of U1-U5 Pottery shards

Table -1: XRD data and crystalline phase identified in U-1 Pottery shard

Minerals	2θ	d-spacing	I/I_o
Quartz	20.70	4.327	33
	26.80	3.390	100
	59.60	1.542	22
Feldspar	22.07	2.987	25
	27.65	3.223	39
	28.12	3.169	49
Muscovite	29.88	2.987	23
Diopside	30.50	2.910	23
Dolomite	30.83	2.886	25
Orthoclase	50.15	1.796	25
Calcite	36.10	2.489	24
	39.45	2.286	23
Dicikite	42.43	2.122	21
Hematite	35.70	2.511	21
Kaolinite	55.03	1.670	8

The high temperature minerals were indentified like Feldspar, Orthoclase and muscovite from this study Uraiyur site pottery samples were fired below 800°C with multi minerals were investigated these results are good agreement in FT-IR analysis.

3.3. SEM with EDS Analysis

Scanning electron Microscope (SEM) for precise examination of the morphology and Energy Dispersive X-ray Spectroscopy (EDS) for the qualitative and semi-quantitative determination of the chemical elements which is present, provide information for the most complete characterization of artifacts. The microphotographs of SEM and EDS spectrum of Uraiyur site sample (U-1) are given in Fig.3. Elemental concentration results are tabulated in Table 2. The elemental concentration of Low Z, Major and trace elements are indentified. From EDS information, it ought to be noticed all samples having non calcareous nature (Concentration of calcium oxide less than 6%) [13].

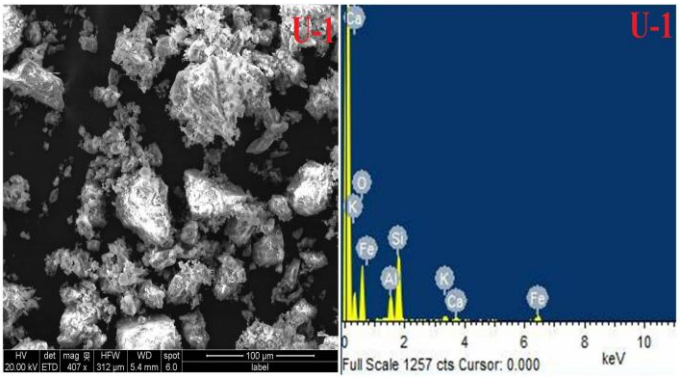

Fig -3: SEM photograph and EDS spectrum of U-1 pottery shard

The SEM image of the samples U-1, U-2, U-3, U-4 and U-5 shows that it was in no vitrification stage which means that initial vitirfication previous stage. No vitrification stage artifacts it may be fired < 800°C [14]. From EDS studies Uraiyur pottery samples contain major composition of Silica, Alumina and Iron. The other fluxes present in these samples are Na, Mg, K, Ca and Ti. The chemical composition analysis shows that all these samples were non-calcareous (concentration of CaO less than 6%) and also low refractory, clay fired in oxidizing atmosphere condition were adopted.

Table - 2: Elemental concentrations of Uraiyur Pottery shards

Ele. in W(%)	U-1	U-2	U-3	U-4	U-5
O	58.47	52.71	55.46	56.22	54.79
Na	-	-	0.56	0.87	0.99
Mg	-	-	0.89	1.19	1.09
Al	8.12	6.55	8.49	7.87	7.73
Si	22.38	25.82	20.18	22.91	22.28
K	2.33	3.72	2.08	2.1	2.32
Ca	1.58	1.29	1.42	1.56	1.56
Ti	-	-	-	-	0.81
Fe	7.12	9.91	10.92	7.28	8.43

The samples U-1 and U-2 contain elemental namely Alumina, Silica, Potassium, Calcium and Iron present in the samples. The remaining U-3, U-4 and U-5 samples having Sodium, Magnesium, Alumina, Silica, Potassium, Calcium and Iron. U-5 sample alone present in Ti. From the calcium oxide (in the range of 1.80-2.21%) the clay type of all the samples belongs to low refractory, non-calcareous nature. The firing

techniques and its corresponding vitrification stages are shown in Table 3.

Table - 3: Vitrification stage and firing temperature of the Uraiyur site pottery samples

Sample Code	% of CaO	Vitrifi. Stage	Firing Temp.	Firing Atmosphere
U-1	2.21	NV	<800 °C	Oxidation
U-2	1.80	NV	<800 °C	Oxidation
U-3	1.99	NV	< 800 °C	Oxidation
U-4	2.18	NV	<800 °C	Oxidation
U-5	2.18	NV	<800 °C	Oxidation

Vitrifi-Vitrification, Temp-Temperature

3.3.1 Factor Analysis

Factorials investigations of data in this work measurable multivariate examination have been carried out for the distinguishing groups of gatherings of ceramics that can be clustered on the origin of a compositional study. This approach permits approving and helpful for archeological hypothesis, contribution an additional characterization tool in regard of basic visual examination and classification. The elemental concentrations (Na, Mg, Al, Si, K, Ca, Ti, Fe and O) were studied by using factor analysis.

Factor 1clarifies 38.48 % of the aggregate difference of the data set due to high positive loadings the components Al, Si and K while Factor 2 clarifies 27.24 % of the aggregate variation of the data set due to of positive loadings components Na, Mg and Ti Finally factor 3 clarifies 25.45 % of the aggregate change of the information because of high positive loadings components of Fe and Ca. It is clear that the three factors extracted in this study explain 91.17 % of the total variance of the data set.

The cumulative values for 91.17% of the elements are greater than 50%. Therefore, the PCA fit to the data set is good [9]. (Fig.4,5) Shows that the Bivariate plot of first to three principal component scores. In addition to PCA loading, this analysis yields factor scores, which quantify the relative intensities of factor strength on each sample. Factor scores are very helpful in interpreting and understanding factor analysis results and can be helpful in finding errors that may exist in the data set.

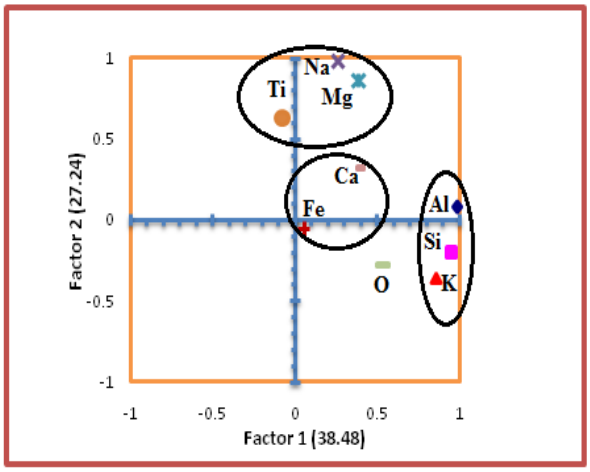

Fig - 4: Bivariate plot of Factor 1 and Factor 2 of Uraiyur pottery shards

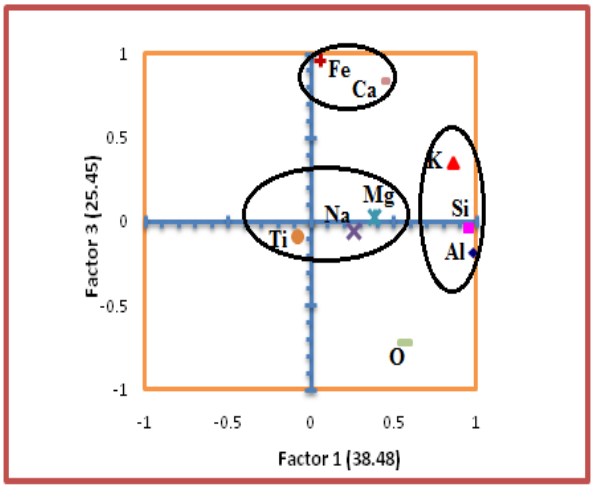

Fig - 5: Bivariate plot of Factor 1 and Factor 3 of Uraiyur pottery shards

In addition, factor scores may be utilized to identify grouping of the samples into particular categories samples with the same factor score. From the PCA analysis, the Uraiyur site samples are classified into three groups. Group-1 as Al, Si and K, Group-II as Na, Mg and Ti & third groups on Fe and Ca.

CONCLUSION

FTIR and XRD studies reveals structural and mineral identification of clay pottery samples along with tentative firing temperature to be 700-800°C. From SEM with EDS micro morphology and vitrification stage were indentified. Uraiyur site pottery samples no vitirification with non

calcareous clay nature and also factor analysis has done using EDS elemental concentration result. From the results the clear evidence that the different types of clay sources may used for making these potteries.

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