CHAPTER – I
INTRODUCTION AND EXPERIMENTAL TECHNIQUES

ABSTRACT

A brief account of archaeology, the significance of various antique relics (pot shreds, bricks and tiles) excavated and the historical information about the archaeological sites of interest at different locations of Tamilnadu in India is given as an introduction. Besides that the spectroscopic, microscopic and X-ray diffraction methods adopted for the investigation of the artifacts are also summarized.
CHAPTER – I

INTRODUCTION AND EXPERIMENTAL TECHNIQUES

1.1. Introduction

Archaeology is the scientific study of the human past through the analysis of material remains that are left behind by human activities. Based on the investigation of these leftovers, we try to reconstruct the daily lives and customs of past societies and offer possible explanations for changes in the social order and cultures over time. The visible remnants of human occupation, in general, of buildings, burial places, implements, utensils, and ornaments belonging to periods about which there are no written records, the excavation at these archaeological sites may reveal the depth of civilization. Also, the unearthed clayware, broken statues, ceramic shreds, corroded armor, weapons, etc., may give valuable information about the material environment during the ancient times\(^1,2\).

Artifacts are the object that have been intentionally designed and shaped through human efforts. They are imperative non-renewable remnants that used to piece together the history of a people and draw conclusions about customs and ways of an earlier life. Ceramic artifacts are among the more resistant to natural weathering processes man-made objects and a very informative evidence of the past\(^3\). Of various archaeological finds, pot shreds, bricks and tile fragments are the major source of information about the material culture, the technical ability of the artisans and the connections between the continents through the history\(^4\).

Potteries are the oldest and most significant technological innovations in the history of humankind, the first truly synthetic material. It is a durable artifact, which was utilized by various cultures and survives over the period of centuries in spite of
the variation of time and atmospheric condition\textsuperscript{5,6}. Pottery artifacts are the indicators of artistic and technological advances reached by ancient society and hence their analysis helps to produce a better knowledge about trade routes linking populations of different areas and exchange\textsuperscript{7,8}.

Bricks are the most popular ceramic building materials of human societies have ever put to use. From the first villages settled before the invention of pottery to many modern towns and cities, bricks have kept people warm in the winter and cool in the summer for thousands of years. Just bricks have provided human societies with an invaluable foundation. Thousands of archives have been discovered, but an enormous amount of material has been lost. Only a fraction of available archaeological sites have been surveyed, and only a fraction of surveyed sites have been excavated. Hence, it is important to understand that remain as the primary source of authority.

Archaeology series of ceramic tile is one of the impressive ancient architecture of civilizations gone by. They covered roofs, floors and the huge stoves that helped heat cavernous high-ceilinged rooms. Tile as a water and sewage management vehicle made great changes in human society. Therefore to be concerned with the clay tile products there must be a good understanding of how they were made, the properties of the clays that they were made of and knowledge of the traditional techniques that were used for the continuous evolution of the majestic buildings\textsuperscript{9,10}.

Knowledge of the materials that constitute objects of cultural heritage is very important to be able to extract information about the techniques used in their manufacture, the origin of the materials used, the commercial trade that allowed
these products to be obtained, and their use by their owners. This kind of study can furnish valuable information about the best way to conserve and, if necessary to apply the most suitable methodology for a possible restoration\(^\text{11}\).

Physics based methods in particular spectroscopic techniques play a vital role to the world of cultural heritage to investigate the structure of materials constituting the cultural object as a fingerprint. It provides a direct and precise scrutiny of the samples and usually requires only a small amount of material\(^\text{12}\). From the spectral profiles the chemical composition and the physical properties of a material can be determined with great accuracy\(^\text{13}\).

The analysis of antique ceramics is a very complex and challenging task. Their main constituents, in addition to quartz and clays, are feldspars - the most abundant minerals among silicates, characterized by a wide range of compositions and temperature-dependent miscibility\(^\text{14}\). Additional difficulties can be caused by the inhomogeneity of samples and the presence of amorphous phases formed during thermal treatment of raw materials\(^\text{15}\). Multi-analytical approaches are therefore necessary to provide the best possible insight into the chemical and mineralogical composition of antiquities and to offer information about its origin and production methods.

Hence the present work is addressed to the characterization of archaeological artifacts excavated from five distinct archaeological sites of Tamilnadu by a combination of powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) and X-ray fluorescence spectroscopy (XRF) to give a detailed picture of the mineralogical assemblages, type of vitrification and elemental
composition. An attempt has been made to define the firing process that leads to the information about the firing temperature achieved and the firing conditions maintained during the firing in kiln by the artisans at the time of manufacture.

1.2. Archaeological context – sample and site details

Cultural heritage is the legacy of physical artifacts and intangible attributes of a group or society that are inherited from past generations, maintained in the present and bestowed for the benefit of future generations. Tamilnadu has a great tradition of heritage and culture that developed over 2,000 years ago and still continues to flourish. Archaeological evidence points to this area being one of the longest continuous habitations in India.

For the present investigation ceramic artifacts are unearthed from five different archaeological sites namely Alagankulam, Salavankuppam, Gangaikondacholapuram, Porunthal and Nagapattinam in Tamilnadu, India. The thirty five samples of interest are dated back to 3rd - 4th centuries BC and 8th - 12th centuries AD.

The location map of the above mentioned archaeological complexes from which the samples collected are indicted in Fig. 1.1 and additionally, the nature and ID of relics found, location of the excavated sites and their geographic coordinates are given in Table 1.1. The photographs of recovered antique artifacts related to each site are displayed in Plate 1.1 - 1.5.
Fig.1.1 The location map of five archaeological complexes of interest in different regions of Tamilnadu, India
Table 1.1 Nature of relics, location details and geographic coordinates of archeological sites

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Nature of the relics found</th>
<th>No. of relics</th>
<th>ID of relics</th>
<th>Excavated Site</th>
<th>Location (Town/District)</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pot shreds</td>
<td>5</td>
<td>AGMP-1 to AGMP-5</td>
<td>Alagankulam</td>
<td>Ramanathapuram</td>
<td>9° 21’ N</td>
<td>78° 97’ E</td>
</tr>
<tr>
<td>2</td>
<td>Bricks</td>
<td>3</td>
<td>SLKB-1 to SLKB-3</td>
<td>Salavankuppam</td>
<td>Kanchipuram</td>
<td>11° 00’ N</td>
<td>77° 28’ E</td>
</tr>
<tr>
<td>3</td>
<td>Tiles</td>
<td>3</td>
<td>SLKT-1 to SLKT-3</td>
<td>Salavankuppam</td>
<td>Kanchipuram</td>
<td>11° 00’ N</td>
<td>77° 28’ E</td>
</tr>
<tr>
<td>4</td>
<td>Pot shreds</td>
<td>5</td>
<td>GKSP-1 to GKSP-5</td>
<td>Gangaikondacholapuram</td>
<td>Ariyalur</td>
<td>11° 15’ N</td>
<td>79° 27’ E</td>
</tr>
<tr>
<td>5</td>
<td>Bricks</td>
<td>5</td>
<td>GKB-1 to GKB-5</td>
<td>Gangaikondacholapuram</td>
<td>Ariyalur</td>
<td>11° 15’ N</td>
<td>79° 27’ E</td>
</tr>
<tr>
<td>6</td>
<td>Tiles</td>
<td>5</td>
<td>GKST-1 to GKST-5</td>
<td>Gangaikondacholapuram</td>
<td>Ariyalur</td>
<td>11° 15’ N</td>
<td>79° 27’ E</td>
</tr>
<tr>
<td>7</td>
<td>Bricks</td>
<td>4</td>
<td>POLB-1 to POLB-5</td>
<td>Porunthal</td>
<td>Dindigul</td>
<td>10° 44’ N</td>
<td>77° 47’ E</td>
</tr>
<tr>
<td>8</td>
<td>Bricks</td>
<td>5</td>
<td>NPMB-1 to NPMB-5</td>
<td>Nagapattinam</td>
<td>Nagapattinam</td>
<td>10° 79’ N</td>
<td>79° 84’ E</td>
</tr>
</tbody>
</table>
Plate 1.1 Archaeological pot shreds of Alagankulam site

Plate 1.2 Archaeological tile and brick fragments of Salavankuppam site

Plate 1.3 Archaeological pot shreds, brick and tile fragments of Gangaikondacholapuram site

Plate 1.4 Archaeological brick fragments of Porunthal site

Plate 1.5 Archaeological brick fragments of Nagapattinam site
The collection of examined samples consists of 35 items i.e. 10 ceramic shards of grey and red potteries found in archaeological excavations carried out at the site Alagankulam and Gangaikondacholapuram respectively, 17 samples of antique briquette specimens unearthed from Salavankuppam, Gangaikondacholapuram, Porunthal and Nagapattinam sites dated back to eighth and eleventh centuries AD and 8 fragments of archaic tiles exhumed from Salavankuppam and Gangaikondacholapuram excavations in Tamilnadu state.

The exact location and significance of each archaeological site of interest are given in the following paragraphs

1.2.1. **Alagankulam (AGM)**

Alagankulam is an ancient port city situated at 24 km east of Ramanathapuram and 3 km from the coast of Bay of Bengal on the northern bank of river Vaigai, Ramanathapuram District, Tamilnadu, India. The excavation at this site was conducted by the State Department of Archaeology, Egmore, Chennai. The examined Alagankulam grey pottery shards were dated back to around 3rd - 4th centuries BC \(^{16}\).

A king named Alagendran ruled it and consequently the place was called Alagendramangalam, which is later called Alagankulam. Alagankulam is far-famed ancient Pandia’s port, played significant role in trading with Romans around 500 BCE to 1200 CE. The most significant findings among other things collected are the large number of pot shreds, roman coins, semiprecious stone beads, conch bangle pieces, terracotta hop scotches, iron objects and terracotta beads \(^{17}\).
1.2.2. **Salavankuppam (SLK)**

The renewed excavation at Salavankuppam close to Tiger cave near Mamallapuram was carried out by the Archaeological Survey of India (Chennai Circle). Mahabalipuram (Mamallapuram) is a wonder of Pallava art and architecture and it was once a flourishing seaport with a brisk trade with countries in south-east Asia and the Mediterranean in the Pallava dynasty. Mahabalipuram is a natural heritage of a fine seacoast together with abundant man-made historical and archaeological monuments.

According to archaeologists, the inscriptions confirm that a structural temple built of bricks, dedicated to Subrahmanya, existed at the spot on the beach. It belonged to the pre-Pallava period or late Tamil Sangam age of circa second century AD and could be 1,700 years old\(^5\). Several artifacts have been unearthed from the ruins of a Muruga temple that includes broken hard portion with a bangle of a sharcco lamps, beads, roofing tiles made of terracotta figurine, hop-scotches and different varieties of potteries and the archaeologist predicts that the potteries belongs to 100 BC- 10 AD\(^6\).

1.2.3. **Gangaikondacholapuram (GKS)**

Gangaikondacholapuram is located in Jayangondam Taluk of Ariyalur District. The state archaeology department (Chennai) has taken excavations at Utkottai Maligaimedu near Gangaikondacholapuram, where Rajendra Chola I (11\(^{th}\) century CE) had built his palace and Gangaikondacholapuram had remained the capital of the Chola dynasty for about 250 years. The city seems to have had two fortifications, one inner and the other outer.

Excavation conducted at two locations at Maligaimedu revealed the remains of royal palace, built with burnt bricks. The ceilings were covered with flat was
fortified with laterite fort wall which throwing light on the link between the Chola
dynasty and South-East Asia, during the period from the 10th century to 13th
century. The thickness and height of the fortified wall measured 2.15 m and 1.35 m
respectively.

The exposed palace remains accounted for an area of 7 m by 3.5 m. During
the course of excavation, coarse red ware sherds, decorated knobs, decorated pot
sherds, iron nails of various sizes, lid portion, Chola tiles, Chinese celedon ware and
porcelain ware sherds, terracotta figurine of calf, carvings on bone, metal objects
and bricks had also been recovered20, 21.

1.2.4. Porunthal (POL)

Porunthal is a tiny village, situated on the foothill of Western Ghat about 12
km southwest Palani lies close to major trade route connecting Madurai (Tamilnadu)
and Vanji in Thirssur District of Kerala. The availability of early historical vestiges
in and around Porunthal like coin hoards, trade guild inscriptions, graffiti marks and
brick structures, was instrumental for selecting the site for excavations.

The excavation was made on ‘paasi medu’ (bead mound), spread over an
area of five hectares, has revealed the presence of a brick wall with width of 90 cm,
probably corner of a building, unearthed in the third trench laid in the southern
fringe of the mound had four courses of brick built by using English bond method.

Two sizes of brick were exposed measuring 7x21x42 cm and 8x24x48 cm,
all in the ratio of 1:3:6 showing the technological skill of the early historic people.
The binding material used in the structure was clay. Such brick structures were
generally found in the urban centres, port towns and capital cities of early historic
times like Kaveripattinam, Uraiyur, Pattanam and Arikamedu.
The present Porunthal evidence reflects its commercial nature. Three floor levels were identified in 1.5 m cultural deposit dating between 1\textsuperscript{st} century AD and 3\textsuperscript{rd} century AD. Other finds include a glass bead-manufacturing unit, ivory dice, earrings, Sangam Age Chera square copper coin, hop scotches and a terracotta figurine. A figurine of a bull is another rare find. The terracotta figurine of a male, with a prominent face, broad shoulders and short legs, is dated 1st century AD\textsuperscript{22}.

1.2.5. \textit{Nagapattinam (NPM)}

Nagapattinam is a unique district with its own historical and cultural significance over 2000 years. Its long stretch of coast line runs along the Bay of Bengal for 188 kms and has one of the most thriving harbours in India. Nagapattinam was also known as Cholkula Vallippattinam. The excavation at Siva brick temple in Nagapattinam was done by Department of epigraphy and archaeology, Tamil university, Thanjavur. The heritage of the town is found in the Burmese historical text dated around the 3rd century B.C\textsuperscript{23}.

In ancient times, “Naganadu,” “Nagatheezam” are the references made only to this town. Buddhist monks in Sri Lanka had close links with this town. During 4th and 5th Century this town gained momentum for developmental activities, even as trade flourished between this port town and China.

Nagapattinam is one of the constituents of Cholamandalam. After the Cholas and the Pallavas, the town was also part of Vijayanagar Empire and later occupied by the Portuguese and Dutch, before becoming a part of the British occupation in 1779. During their occupation, the Dutch released coins with the name Nagapattinam engraved in Tamil. There are a number of religious and heritage structures in and around Nagapattinam.
1.3. Analytical techniques

The scientific approach for the characterization of artifacts is the passion for knowing about the past times and past lives of the human family. By studying the archaeological material through analytical techniques, the complete information about the mineralogical composition, clay origin, manufacturing techniques adopted by the ancients, microstructure, elemental composition present and transformation of clay minerals occurred in the fired relic can be highlighted precisely. Four analytical methods that look at different aspects of archaeological ceramic artifacts were chosen in the present study.

1. Fourier Transform Infrared spectroscopy (FTIR)
   - looking for fundamental vibrations present in sample
   - Analysis of clay mineral constituents and determination of firing technology
     (Firing temperature and atmosphere)

2. X-Ray Diffraction (XRD)
   - looking for minerals present in sample
   - Composition analysis of crystalline phases

   - looking for morphology and major elements
   - Determination of degree of vitrification and range of firing temperature

4. Fluorescent X-spectroscopy (XRF)
   - looking for elements present in the sample
   - Analysis of constructive (major, minor and trace) elements
1.3.1. Fourier Transform Infrared spectroscopy (FTIR)

Using spectroscopic techniques one can search back the composition and processing which were applied during production time. Among FTIR spectroscopy is considered to be an important tool to analyze the clay minerals, mineral transformation due to thermal effects and firing techniques of archeological artifacts\textsuperscript{24}. The progressive dehydroxylation and distortion of the silicate structure with temperature were also monitored by FTIR spectroscopy\textsuperscript{25}.

1.3.1.1. Mineralogical composition

Clays and related raw materials have been used by mankind since earliest times for the manufacture of clay-based ceramics like potteries, bricks and tiles. These products are highly complicated multi component heterogeneous systems i.e. different phases including the crystalline and glassy can be distributed in a specific manner. The mineralogical composition analysis is a powerful source of information that indicates the raw material, the firing temperatures and the firing conditions in the kiln (oxidizing or reducing). Variations in the mineralogical characteristics of ceramics reflect source of the raw clay and the different technologies applied for the production of these ceramics\textsuperscript{26}.

Of various spectroscopic techniques, FT-IR is proposed as a quick, inexpensive and reliable method of screening archaeological samples to provide detailed mineral composition and allow more reliable comparison between them\textsuperscript{27}. Infrared absorption by a mineral arises from the vibrations of its constituent atoms, and the frequencies of these vibrations are dependent on the mass of the atoms, the restoring forces of the bonds, and the geometry of the structure.
The resultant spectrum of absorption frequencies is a characteristic property of the mineral which can not only serve as a fingerprint for its identification, but also give, in favourable cases, unique information on features of the structure, including the nature of isomorphous substituents, the differentiation of molecular water from constitutional hydroxyl, the degree of regularity of the structure and an indication of the family of minerals to which an unknown mineral is related\textsuperscript{28}.

Infrared spectroscopy, which acts as a research tool in mineralogy, is most powerful if used in conjunction with X-ray diffraction and other techniques. Unlike XRD which can detect only crystalline phases and offers information concerning the average structure. FTIR spectroscopy provides short-range information and is therefore also sensitive to any amorphous components in the sample.

\textbf{1.3.1.2. Firing temperature}

Firing is one of the most crucial stages in the production of artifacts, as it is the production step that transforms clay into an imperishable product. The firing technique applied has a direct influence on the mineralogy of the raw materials. The craft makers and its end users may not have been familiar with the clays or vessels mineralogy in a direct way, but this mineralogy is reflected in several aspects of the pottery that might be of importance to them, such as the colour of the product and its resistance to mechanical or thermal shock. Therefore, the firing temperature is esteemed on the basis of mineralogical association\textsuperscript{29}. The temperature at which ancient brick, tile ceramics and pottery were fired varies over a wide range (600-1300°C) depending on the type of clay used and the kiln available.

Minerals of an archaeological artifact were classified as the primary minerals – minerals that were present in the raw material and have not undergo reactions in a
wide range of temperature, and the firing minerals – that have been formed during firing. The absence/presence of any firing mineral in the IR absorption spectra of the investigated sample is a clear indication of low/high firing temperature\cite{30}. Hence, the existence or lack of certain mineral phases permits to determine both firing temperature and atmosphere that have been used during artifact making.

From the appearance and disappearance of the hydroxyl bands in clay artifacts and its thermal behavior the lower limit of the firing temperature is estimated. The position of prominent infrared absorption silicate band (Si-O stretching mode) which is influenced by firing T can also be utilized for the determination of firing temperature. The firing methods and conditions of firing were inferred from the characteristic absorption positions and the bands observed due to the presence of magnetite and hematite in the samples\cite{31,32}. The estimation of the firing temperature of the artifacts throws light to identify the purposes for which they had used them in the daily routines of their living at that time\cite{33}.

1.3.2. X-ray diffraction (XRD)

XRD technique provided us with information about the presence of the different mineral phases and about minerals that were newly formed during firing or burial\cite{34}. The X-ray diffraction patterns of the ancient artifacts exhibited a multiphasic character and its degree of similarity can be a useful aid in grouping samples according to mineral phase content and relative abundance. The supplementary information obtain from the mineral composition of the artifacts may be lead to a better understanding of the manufacturing processes employed by a particular civilization\cite{35}.
X-ray diffraction is a technique that allows identifying the crystalline substances present in the samples, through an investigation of the diffractogram of the different mineral kinds, such as distance between the reticulated planes and the distribution of the atoms on such a plane. The diffraction of X-ray is of great analytical significance, as every crystalline substance would scatter to the X-rays in its own unique diffraction pattern, giving finger print of its atomic arrangement.

In this method X-rays are directed at the upper layers of atoms, which are arranged in regular or periodic spacing according to their individual lattice structures. It uses the spacing between atoms in crystal lattice to cause diffraction of X-ray. The atoms of each mineral diffraet X-rays in a characteristic pattern, which is recorded on a chart and identified by comparison with standard data i.e. the most intense lines in the diffractogram were assigned to known compounds by means of a procedure for searching and matching with lines of known crystalline compounds in the database (JCPDS). However it was possible to identify only the major components in this way, due to the detection limits of the technique.

The XRD investigation was intended to supplement the results revealed and reported in the chapter III through FTIR analysis for the representative archaeological artifacts. To fully understand the materials mineralogy, however, one should also bear in mind its elemental composition, since mineralogical and chemical compositions are interrelated. Whenever needed, we will refer to results of our chemical analysis, obtained by scanning electron microscopy (SEM-EDS) and XRF.
1.3.3. *Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS)*

In order to identify the range of firing temperature, next to the composition data, very important is the microscopic data. A detailed knowledge of the micro-chemical and microstructural nature of an archaeological ceramic artifact is critical in finding solutions to problems of restoration, conservation, dating and authentication in the art world. It is also used to investigate the technical manufacturing aspects (information on raw materials and their processing) and the deterioration phenomena (the effect of ageing during burial)\(^{39}\).

The SEM examination of the artifacts in the as-received state provided information on the internal morphology developed during the original firing in antiquity and in particular, on the extent of vitrification (the glassy phase) and the pore structure. Semi-quantitative elemental analysis using the energy dispersive X-ray fluorescence spectrometer attachment to the SEM showed both non-calcareous and calcareous clays used in the manufacture of the pottery, brick and tile artifacts under consideration\(^{40}\).

SEM is a valuable method for characterizing and distinguishing between the different traditions in ceramic technology in antiquity (because information is obtained on both the extent of vitrification and the firing temperature). The extent of vitrification provides a useful property for characterizing the quality of a pottery, since it influences several microstructural and physical properties which are relevant to its suitability for the various uses to which it might have been put. SEM registers extended vitrification, which is interpreted by the firing temperature\(^{41}\).

EDS determines major elements present. Samples bombarded by electrons (in a scanning electron microscope) emit X-rays that are characteristic of the
composition of the sample. These X-rays can be collected by a solid-state detector from which a display of intensity vs. X-ray energy can be obtained hence the term energy dispersive X-ray analysis. The energies of the X-rays depend upon the elements present in the sample while the intensities depend upon how much of those elements are present.

Scanning electron microscopy (SEM) for an accurate observation of the morphology and energy dispersive X-ray microanalysis (EDS) for the qualitative and semi-quantitative determination of the chemical elements present, provide information for the most complete characterization of artifacts. This kind of information enhances the archaeological information obtained by stylistic observation.

1.3.4. X-ray fluorescence (XRF) spectroscopy

X-ray fluorescence (XRF) analysis is widely used for determining the content of various chemical elements in materials and is an excellent tool for investigations of historic relics, works of art and archaeological finds. It is very useful for multi-elemental analysis with good precision and accuracy qualitatively and quantitatively. It provides valuable information on the composition, provenance and production technology. The differences in abundance of trace elements may reflect the geological diversity.

The X-rays causes the atoms of the specimens to become excited and to generate fluorescent radiation that can be collected by a detector. The characteristic X-rays generated by the sample are identified by their energy. The amount of the element is related to the size of the peak. Hence the chemical investigations of the relics of interest clearly reveal the variety of raw materials used that is related to the natural diversity of the environment.
References


