CHAPTER 3

MATERIALS AND METHODS

The use of scientific techniques through analytical investigation and ethnographic surveys to study antiquities and ancient raw materials has received much attention in the recent past. There are a considerable number of methods available for the study of ancient technology and for tracing the source of objects or their raw materials. This chapter deals with the materials (iron objects) obtained from various excavated Early Historic sites of Gujarat and the methods employed to procure essential archaeological, chemical, metallurgical and ethnographic data for their study.

The first part of the chapter deals with information on iron objects obtained from various excavated Early Historic levels, their sampling and state of preservation. The second part describes the methods adopted for this study such as typology, chemical analyses, spectroscopic analysis, metallography and ethnography. The metallographic study includes preparation of the specimens by grinding, polishing, and etching and their examination under the microscope. Chemical analysis has been carried out using wet chemical analysis and spectroscopic methods. An ethnographic approach is also undertaken in the course of this study.

From the material evidences of the Early Historic scenario of Gujarat, it has been observed that many of the excavated Early Historic sites did yield iron artefacts. The sites which have yielded iron objects from Early Historic
levels are Akota (Subbarao 1953); Amreli (Rao 1966); Bharuch (IAR 1959-60); Devnimori (Mehta and Chowdhary 1966); Dhatva (Mehta and Chowdhary 1975); Dwarka (Ansari and Mate 1966); Nagal (IAR 1957-58); Nagara (Mehta and Shah 1968); Shamalaji (Mehta and Patel 1967); Prabhas Patan (IAR1971-72); Timbarva (Mehta 1955) and Vallabhi (IAR 1979-80). Evidences of iron smelting are reported from Dhatva, Shamalaji, Prabhas Patan and Vallabhi. Of these, Nagara and Devnimori are the best-documented sites to illustrate the various aspects of technology of the Early Historic period. Most of the iron objects are corroded, fragile and thickly encrusted. The objects from Nagara and Timbarva (of early date) are heavily corroded leaving hardly any core in it. The objects from Shamalaji and Devnimori (of late date) show a comparatively unaffected core part.

Sampling

It is worthwhile to mention the stratigraphic context of the iron objects selected for analytical study. They belong to Period I of Nagara, dated between 5th Century BC and the beginning of the Christian era (Mehta et.al. 1968), Period I of Timbarva associated with Northern Black Polished Ware (NBPW) (Mehta 1955); slag from iron smelting industry at Dhatva dated to 500 BC- 200 AD (Mehta et.al. 1975) and iron objects from Early Historical levels of the Buddhist site of Devnimori dated to 3rd/4th Centuries AD to 7th Century AD (Mehta and Chowdhary 1966). Of the total collection from all these sites mentioned above, twenty-five representative samples are chosen for the study. They are selected on the basis of their state of preservation, probable function and relevance to the overall research design. One sample of slag from Dhatva is also analysed. For ethnography, five specimens of
recycled iron objects; that is, the objects made out of scrap iron by the contemporary blacksmiths have been analysed. These are selected on the basis of function and mode of recycling they undergo in the hands of the smith.

The methods adopted to study the iron specimens are outlined here.

Typology:

A detailed survey of iron antiquities obtained from stratified context of excavated Early Historic sites of Gujarat has been undertaken. The aforesaid survey was carried out with the objective of classifying the iron artefacts from various sites. This may well help to identify the type groups, specific types and sub-types. The artefact possesses a set of human imposed attributes that act as an independent variable within a specific artefact system (Clarke 1968:188). Further, in a broader perspective, this exercise helped to estimate the distribution of different types of iron objects from different sites belonging to different areas. A typological approach was been adopted to distinguish types by assigning them to functional groups. Typology allows for a quantitative comparison of traits from site to site and layer to layer within the individual site.

After dividing the artefact assemblage into groups, types and sub-types; a statistical analysis of the artefact types was undertaken. The parameters taken for classification are morphology, size, shape and probable function. The whole iron tool assemblage was divided into different functional types. The main types are arrowhead, knives, nails, dagger, spearhead, sickle and
ploughshare. Some types are classified into sub-types based on its morphology. The variants and miscellaneous ones have also been catalogued.

Metallography:

Metallography is the study of structural characteristics, that is, the constitution of a metal or an alloy in relation to its physical and mechanical properties (Garside 1957:156). Microscopic studies facilitate an adequate understanding of various stages of manufacture of the object from the extraction of metal, constitution of metal, fabrication treatment, non-metallic inclusions, extent of corrosion etc. The microstructure reveals features such as grain size, grain shape, dendrites, inclusions and matrix constituents. Each of these is a characteristic feature of the technique of manufacture. These characteristics indicate the sort of treatment undergone by the object in the hands of the smiths. In any archaeological context these studies assume great significance. The most important part of metallography deals with the microscopic examination of a prepared metal specimen in a reflected light system employing magnifications from 10x to 100x (Khel 1949).

Specimen Preparation for Metallography:

The heavy calcareous and corrosion deposits on the artefacts were removed and the specimens were mechanically cleaned with metallic brushes.
Samples were removed from each artefact by using an electric saw. Thin samples were scraped from the edge to take out a small amount.

**Grinding**: The specimens were mounted for proper polishing. The mounting material used was the cold setting compound DPI-RR Cold Cure, Acrylic Repair Material. The first step in specimen preparation was to obtain a flat, semi-polished surface. For this, the surface of the specimens were made plain by polishing on a motor driven rough grinder. They were then rubbed on a series of emery paper of various grades (3,2,1,0, 1/0, 2/0, 3/0, 4/0.). For this, the specimen was held under moderately applied pressure and gently rubbed back and forth across the entire length of the paper. While being ground, the specimen was held so that the new finer scratches being introduced on the surface were approximately at right angles to the old scratches resulting from the previous flattening operation. Thus, while changing from one paper to the next, the direction of rubbing changed through a $90^\circ$ angle which removed the scratches developed on the surface due to the earlier coarser paper.

**Fine polishing**: Fine polishing was done for the purpose of removing the scratches introduced during grinding. The polishing of the ground specimen was done on a polishing machine consisting of brass wheel covered with velvet cloth, rotating at a specified speed. Diamond paste applied on the velvet cloth was used as abrasive. During polishing, kerosene was used as the lubricant. Through this procedure, the specimen was polished till it attained a mirror finish.

**Etching**: Etching was done in order to reveal the surface structural characteristics of the specimens, such as, surface defects, non-metallic
inclusions, corrosion, metallic features etc. Care was taken of the method used and the temperature at which etching was done. Etching reagent - 5% Nital solution (5 ml. Nitric acid and 95 ml. Methyl alcohol) was applied on the prepared surface of the specimen by swabbing. The specimen was washed thoroughly in running water and then dried in absolute alcohol. For the thorough understanding of the constitution of the metal, its fabrication and heat treatment, to identify characters like grains, slip lines and twinning, the etched specimen was examined under a polarising microscope with both transmitted and reflected light facilities (Leitz Laborlux 12 Pol D); and inverted type metallurgical microscope (CARLZEISS, Neophot-2).

Chemical Analysis:

This method includes qualitative and quantitative analyses. Qualitative analysis deals with the detection and identification of the constituents of an object. All qualitative tests give an indication of the reacting constituent whether by precipitate, intensity of colour or density of a spectral line on a photographic plate. Quantitative analysis is for determination of the amount of components.

The nature and proportions of the minor constituents may be a useful pointer to the source of ores, methods of extraction and of working, in the case of an unalloyed metal. When one is examining objects made of recycled alloys, often scrap metal derived from many sources, the minor constituents are less likely to be of value in interpretation. On analysis, even the metal derived from a single ore will not give a proportion -by-proportion reflection of the elements present as minor constituents in the
ore, due to the loss which occurs during roasting, smelting, refining and casting. Many elements are liable to volatilise or oxidise and thus lost to the alloy during any process involving excessive heat. One must therefore, expect the results of chemical analyses to reflect the vagaries of primitive working methods. The use of scrap metal in antiquity necessarily complicates the interpretation of the source. The difference in chemical composition of metals may result from a number of factors such as:

a) working with different ore deposits
b) different methods of working and
c) degree of efficiency in the preparation and smelting of ores.

Chemical analysis was carried out in order to understand the percentage composition of various components, the carbon content, trace elements present and the quality of iron. The methods of chemical analysis adopted were 1) Carbon analysis, 2) Wet Chemical analysis, and 3) Atomic Absorption spectroscopy.

**Carbon Analysis:**

This method was used to determine the carbon content of the specimen. From the known data it was presumed that the iron buried under the earth, even if it becomes completely oxidised, does not absorb carbon. Further, carbon does not get impregnated into the body of iron under normal conditions of pressure and temperature of the environment. Usually, carbon occurs in a combined form as carbides in most of the steels. The total carbon content represents the combined carbon content of the carbides. For
analysis, the sample was kept on a bedding material and inserted into a tube which was heated to about 1000°C under the stream of pure oxygen. The gases caught in the eudometer were measured. The eudometer was filled with dilute sulphuric acid and has a scale in which 1 cm³ at 15°C represents 0.5% carbon in one gram of sample. The percentage of carbon was detected by using Strohlein Apparatus.

**Wet Chemical Analysis by Gravimetric Method.**

Wet chemical analysis is one of the oldest and most accurate means used for the determination of components. This process is time consuming and requires substantial amount of sample. The major types of analysis are Volumetric and Gravimetric. Gravimetric analysis was used in this study to find out the composition of iron and other impurities present in it. This method involves isolating and weighing an element or a compound in its purest form. Determinations by gravimetric analysis are largely concerned with the transformation of the element or radical that readily converts into a form suitable for weighing (Vogel 1959:100). The weight of the element or radical is then calculated from the formulae of the compound and the atomic weights of the constituent elements. Precipitation method was used for the separation of the element.

**Preparation of Gravimetric solution and Analysis:**

After selecting the samples, a small portion of it was cut and weighed. This piece of metal was then dissolved in concentrated Hydrochloric acid,
adding a few drops of concentrated Nitric acid. To enhance the reaction, it was heated for a few minutes. When the metal was dissolved completely, excess dilute Hydrochloric acid was added to the solution and was completely evaporated. When the solution dried, it was again dissolved in dilute Hydrochloric acid. To this, Ammonium hydroxide was added which resulted in the precipitation of the metal. The liquid was filtered through a Whatman 42 filter paper. The precipitate was washed with 1% ammonium nitrate solution and was filtered through the filter paper. When the filter paper dried completely, the precipitate was transferred into a crucible and incinerated. When the ignition was over, the crucible was removed and kept in a dessicator containing CaCO₃ and allowed to cool. The ignition is repeated twice and then the crucible was weighed. The increase in weight was taken as the weight of pure iron.

Atomic Absorption Spectroscopy:

Atomic absorption method has been widely used for the analysis of archaeological objects. Atomic absorption has a number of features such as versatility, sensitivity, accuracy and speed which makes it particularly suited for analysis of archaeological objects (Hughes et.al. 1976:19). In this method, the sample, in the form of a homogeneous liquid is aspirated to a flame where a thermal and chemical reaction causes the compounds present in the solution to dissociate into their constituent atoms. In other words, this method of analysis depends upon the absorption by atoms (present in the sample of an object) of light emitted from a hollow-cathode lamp of the element being analysed (Price 1974). These free atoms are capable of absorbing light of characteristic wavelengths. A light source emitting a
narrow spectral line of the characteristic energy/wavelength is passed through the flame and is used to excite the free atoms formed in the flame whereby, a certain amount of light is absorbed by the ions of that element. As per Beer-Lambert’s Law: Absorbance = log 10 \( \frac{I_0}{I_t} \) = \( C \) where, \( [I_0 = \text{Intensity of incident radiation emitted by the light source; } I_t = \text{intensity of transmitted radiation; } C = \text{Concentration of the sample}] \), the energy absorption is proportional to the concentration of free atoms in the flame i.e., the rate of absorption is directly proportional to the concentration of the particular element. Thus, the total amount of light absorbed is measured and by comparison with standards, the concentration of the element can be calculated.

**Preparation of Sample Solution for AAS:**

After selecting the samples, a small portion of it was removed by using portable drill of the type used by jewellers. 20 mg. of each sample was weighed and put in a 25ml. ‘borosil’ beaker and dissolved in 1ml. Aquaregia (1vol.con.HNO₃:3 vol.con.HCl). The powder which remained undissolved was again treated with 1ml. aquaregia and heated gently. It is then allowed to cool and added with 10 ml. distilled water. After that, the solution is filtered through Whatman 40 filter paper. The solution is transferred quantitatively to a 250 ml. graduated flask and diluted to the same volume with distilled water. Same solution was used for determinations of elements without further dilution.

The elements analysed were Fe, Cu, Mn, Mg, (using air-acetylene flame) and Si, Ca, Al and Ni (using nitrous oxide-acetylene flame) by using GBC
902 Double Beam Atomic Absorption Spectrophotometer. Standard solutions of a given range of the representative elements were prepared and were used to calibrate the instrument. A series of concentrated standard solutions containing 1000 ppm. of each element to be measured were prepared. Perkin-Elmer methods were used for preparing standard solution (Perkin-Elmer 1973). From the standard solution that is (1000 ppm. solution) required standard solution of various known concentrations were prepared. These standard solutions were aspirated and the absorbance of the above elements for varying concentrations was determined. Thus the instrument was first calibrated using a set of standard solution. Once the calibration was over, the instrument was switched over to concentration mode and the concentrations of the archaeological samples were directly measured. After determining the concentration of different elements at parts per million level, the weight percentage in the object were calculated.

Ethnographic Approach

Archaeological artefacts being mute, those who made and used them cannot be interrogated. It is from contemporary society that one can attempt to understand cultural systems and their relationship with the artefacts. Then it can be abstracted and applied to the archaeological context. The ethnographic analogy stands as a source of inference in interpreting use, form, function, significance and meaning of ancient artefacts. An ethnographic approach to archaeological problems is very useful and allows “direct observation of an on-going society” (Yellen 1977:11) which in turn permits one to understand past activities and technology to a certain extent by co-relative study of products that may be preserved in the archaeological
The ethnographic data allows one to understand metals and metal-related artefacts more meaningfully as cultural signifiers. (Lahiri 1995: 116).

The factor of variation in elemental compositions of metal in antiquity must be understood in relation to ethnographically well documented tradition of recycling objects and scraps of old metal. Lahiri suggests that one should argue that the history of the use of metals in Indian archaeological records is much more than the catalogue of artefact types and their technological make up: it also denotes a cultural situation which seems to be very specifically Indian (Lahiri 1995: 117).

A survey of working of the contemporary blacksmiths settled on the outskirts of a cosmopolitan city like Baroda, town area of Chota Udaipur, village areas of Savli, Sevasi, Kamrol, Padra and tribal area of Panvad, Kavant, Kadipani, Ambadungar and Hampeshwar was carried out. The blacksmiths were interviewed regarding their method of making iron objects and recycling processes were studied and documented. The recycled specimens collected from these areas were analysed chemically and metallographically. The above mentioned methods were used for analysing the iron objects.

To understand the cultural context within which the present study is framed, the archaeological details of the relevant Early Historic sites, their relative chronology and their material testimony are given in the following chapter.