CHEMICAL CHARACTERIZATION OF SINOPEAN ARCHAEOLOGICAL COMMON WARE

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FOR THE DEGREE OF
MASTER OF SCIENCE**

**By
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AUGUST 2004**

I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and in quality , as thesis of degree of Master of Science

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ABSTRACT

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M.S. in Chemistry

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August 2004

Chemical characterization of archaeological common wares is important in order to make quantitative explanations about history and trade relations of nations. Chemistry uses a microscopic point of view by applying spectroscopic methods rather than macroscopic studies that archaeologists usually deal in the structural analysis. The present study is done on the common ware samples which were made of raw clays from Demirci, Sinop, Black Sea Coast of Turkey, because of the geopolitical importance of this region having trade routes.

Elemental and mineralogical analyses of the clay-originated common ware samples found in the archaeological excavations and of the clay taken from Demirci region, which locates at almost 15 km southern of Sinop, were made. While the elemental compositions of the samples were obtained by the spectroscopic method, X-Ray Fluorescence (XRF), the mineral structures were investigated by Powder X-Ray Diffraction (PXRD) and Fourier Transform Infra Red (FT-IR) spectroscopic

method. Furthermore, the characteristic reactions (dehydroxylation, decomposition, transformation) that the clays experienced between the temperatures 50 and 1000 ^{o}C were determined by Thermal Gravimetric Analysis (TGA). Characterizations of the Sinopean samples were made and the similarity and differences between other samples from different regions were investigated. Besides the provenance characterization, the distinctions between the production and firing techniques were observed.

In addition to the experimental studies, chemometric techniques using statistical methods such as the standard clustering method and principal component analysis (PCA) was also applied to identify the groupings in the set of samples.

As a result of this study, it is observed that the raw clays and ceramic samples have minerals of montmorillonite, quartz, feldspars, pyroxene, calcite and hematite at different amounts. From the mineralogical and elemental data, it is concluded that the color variations are resulted from the calcium element occurring in pyroxene mineral. In the light colored samples, amount of this element and mineral is high whereas it is low in red colored ones.

From the interpretation of elemental data by statistical methods, it is observed that a classification among the Demirci samples is possible according to the function of the pottery. In addition, classification among ceramics from two different regions is possible by the interpretation of chemical analysis, even though the ceramics have the same morphological properties of the same period.

Keywords: *X-Ray fluorescence spectroscopy, Powder X-Ray diffraction, Thermal gravimetry, Fourier transform infrared, common ware, Cluster Analysis, Principal Component Analysis, Sinop, clay*

ÖZET

SİNOP ARKEOLOJİK GÜNLÜK SERAMİKLERİNİN KİMYASAL KARAKTERİZASYONU

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August 2004

Arkeolojik günlük kullanım kaplarının kimyasal karakterizasyonu tarih ve ulusların ticari ilişkilerini sayısal olarak açıklamak açısından önemlidir. Kimya spektroskopik metodların uygulanmasıyla mikroskopik bir bakış açısı kullanırken, arkeolojistler genellikle yapısal analizlerin uygulandığı makroskopik çalışmalar yaparlar. Bu çalışma Türkiye'nin Karadeniz kıyısında yer alan Sinop Demirci kökenli killer kullanılarak yapılmış günlük kullanım eşyaları üzerine yapılmıştır. Bunun nedeni ise ticaret yollarını üzerinde bulundurmuş bu yörenin jeopolitik önemidir.

Sinop ilimizin yaklaşık 15 km güneyinde bulunan Demirci yöresinden alınmış killerin ve arkeolojik kazılarda bulunmuş olan kil kökenli günlük kullanım kaplarının elementel ve mineralojik analizleri yapılmıştır. Örneklerin elementel komposizyonları X-Işını Floresans (XRF) spektroskopik yöntemiyle elde edilmişken, mineral yapıları Toz X-Işını Kırınımı (PXRD) ve Fourier Transform Kızıl Ötesi (FT-

IR) spekroskopik metoduyla incelenmiştir. Ayrıca killerin 50 ve 1000 C^o arasında geçirdikleri karakteristik reaksiyonlar (dehidroksilasyon, dekompozisyon, transformasyonlar) Termal Gravimetrik Analiz (TGA) ile belirlenmiştir. Sinop örneklerinin karakterizasyonu yapılmış ve farklı bölgelere ait diğer örneklerle arasındaki benzerlik ve farklılıklar araştırılmıştır. Köken karakterizasyonun yanısıra üretim ve pişirme teknikleri incelenmiştir.

Deneysel yöntemlere ek olarak standart kümeleme yöntemi ve temel bileşenlerine ayırma (PCA) gibi istatistiksel methodları uygulayan kemometrik teknikler de örnekler arasındaki gruplanmaları belirlemek için kullanılmıştır.

Bu çalışmanın sonucu olarak, kil ve seramik örneklerin değişen miktarlarda montmorillonit, kuvarz, feldspar, piroksen, kalsit ve hematit minerallerini içerdikleri gözlemlenmiştir. Mineralojik ve elementel data kullanılarak renk değişikliklerinin piroksen minerali içinde bulunan kalsiyum elementinden kaynaklandığı söylenebilir. Açık renkli örneklerde bu elementin miktarı yüksekken kırmızı renklilerde azdır.

Elementel dataların istatistiksel metodlarla yorumlanması sonucunda Demirci örnekleri arasında seramiğin kullanımına bağlı olan bir sınıflandırmanın mümkün olduğu görülmüştür. Ayrıca kimyasal analizlerin yorumlanmasıyla iki farklı yöreden olan seramikler arasında seramikler aynı dönemin şekilsel özelliklerine sahip olsa bile sınıflandırma yapmak mümkündür.

Anahtar Kelimelers: *X-Işını Floresans Spektroskopisi, Toz X-Işını Kırınımı, Termal gravimetri, Fourier transform kızıl ötesi, günlük kullanım kapları, KümelemeYöntemi, Temel Bileşenlerine Ayırma Yöntemi, Sinop, kil*

ACKNOWLEDGEMENT

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1. INTRODUCTION

1.1- Importance of Sinopean Ceramics

Sinop, where Demirci is located at, has been an important historical center since it is located at the natural port of a trade route. It is on the Black Sea coast of Turkey, at the Northern part of Turkey as shown in Figure 1.1 . Because it was the most secure and the most active port of the Black Sea in the past, it attracted the attention of different centers of the antique world. In the excavations, remains were found as old as Bronze Age. During the Archaic period with the rising population, new colonies were settled at the Anatolian coasts. They formed their own markets and these colonies, one of which was Sinop, became an important trade center.

In addition, many sites were documented in the Demirci valley, ranging from the Chalcolithic to Ottoman (19th c. A.D.) in date. The most extensive period of settlement was the Classic - early Byzantine (about 4th BC - 7th c. A.D.). This extensive settlement pattern must reflect the expansion of agricultural exploitation of the valley in support of the industrial facilities on the coast. Similar results have been observed in other parts of the Roman world, when long prosperity, improved infrastructure and the increased security of long Roman military domination encouraged widespread rural settlement. [1]

Figure 1.1: Map showing the location of Sinop.

A concentration of pottery kilns along the Sinop peninsula probably supported the storage and distribution of agricultural products in the inner valley. The inner valley appears to have been producing goods for export. Perhaps the farmers of the inner Demirci valley , which is shown in Figure 1.2, produced food that was consumed as part of the broader regional economy, they consumed primarily local goods and commodities. The most important trade goods were wine and olive oil for which amphorae were used as containers. These were the ceramic containers made of clays and they had their specific shape for each center since it was like a label showing the quality of wine or the oil. [1]

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Figure 1.2: Demirci valley, excavation field.

The workshop of Demirci was settled 15 kilometers South of Sinop and was an active production center between the 3rd and the 6th c. AD. As a result of excavations, a typology of the amphorae and common wares, which were produced there, could be established. [2]

The Demirci valley was an excellent place to begin systematic investigations because a Roman industrial settlement at its mouth has been under investigation by Dr. D. Kassab-Tezgör in collaboration with the Sinop Museum for several years (Kassab-Tezgör and Tatlican 1996). There were two zones of excavations in the Demirci, zone A and zone B, as shown in the figure 1.3 and 1.4.

Figure 1.3: Photograph of the excavation field, zone A and B.
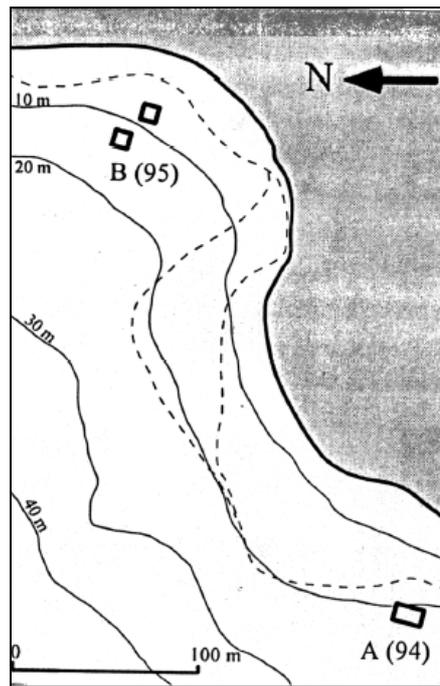
Figure 1.4: Plan of the excavation field, zone A and B.

The geographical survey maps of the excavation field, Demirci, zone A and B had been obtained as shown in Figure 1.5 and 1.6. These maps were obtained prior to the excavations by GPRS (Geographical Position Remote Sensing) methods. By the help of these, positions of the kilns were determined and excavated accordingly.

The shaded areas on Figure 1.5 and Figure 1.6 shows the positions of archaeological excavation areas as indicated by the arrows in figures.
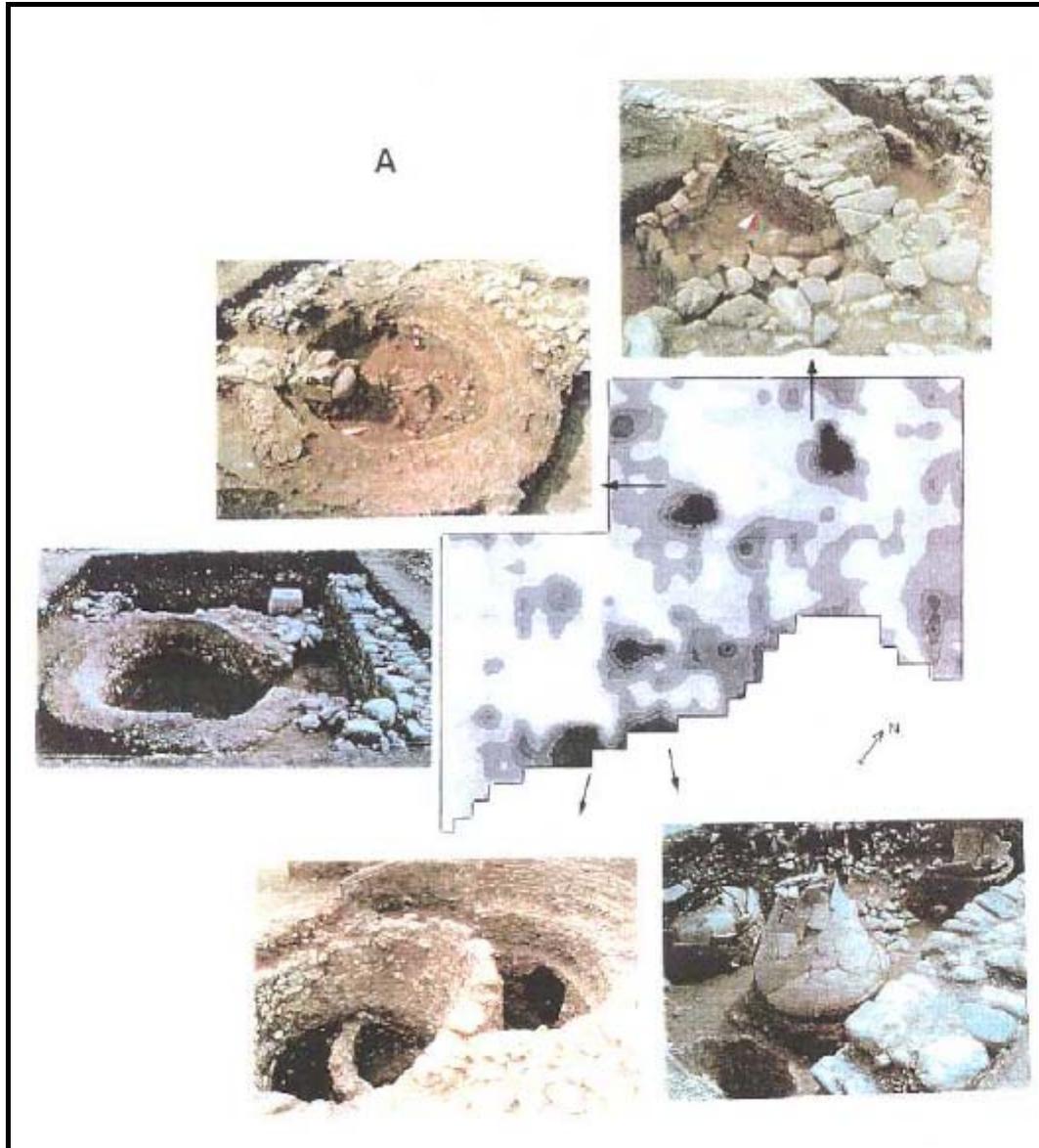
Figure 1.5: The geographical survey map of the excavation field, Demirci, Zone A.
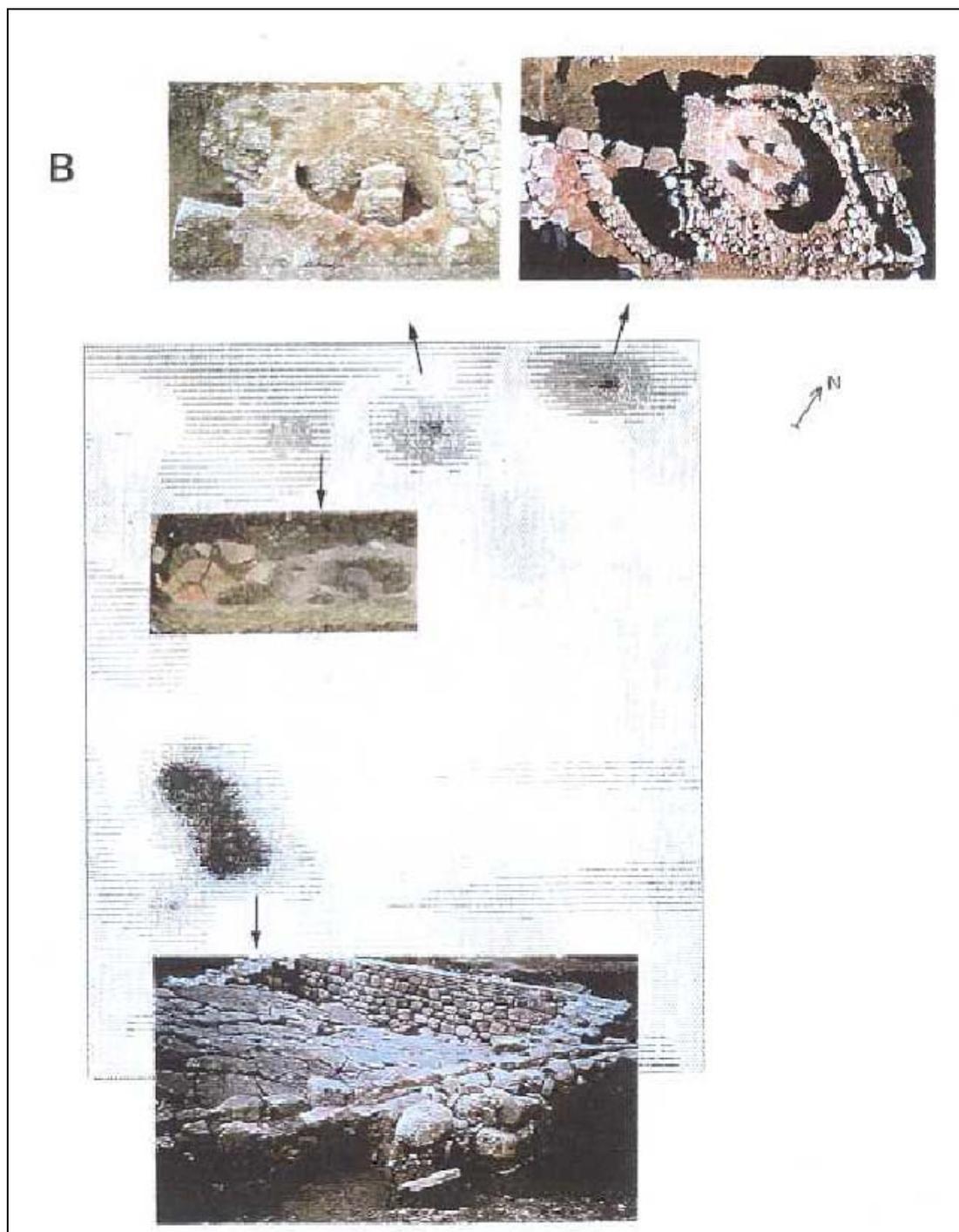
Figure 1.6: The geographical survey map of the excavation field, Demirci, Zone B.

According to the maps shown above, the plan of these two zones A and B, Figure 1.7 and 1.8, were drawn after the excavations to show the results. The field is divided into squares (as in the plans) to be able to make clear definitions of the locations for the samples taken from the excavation area.
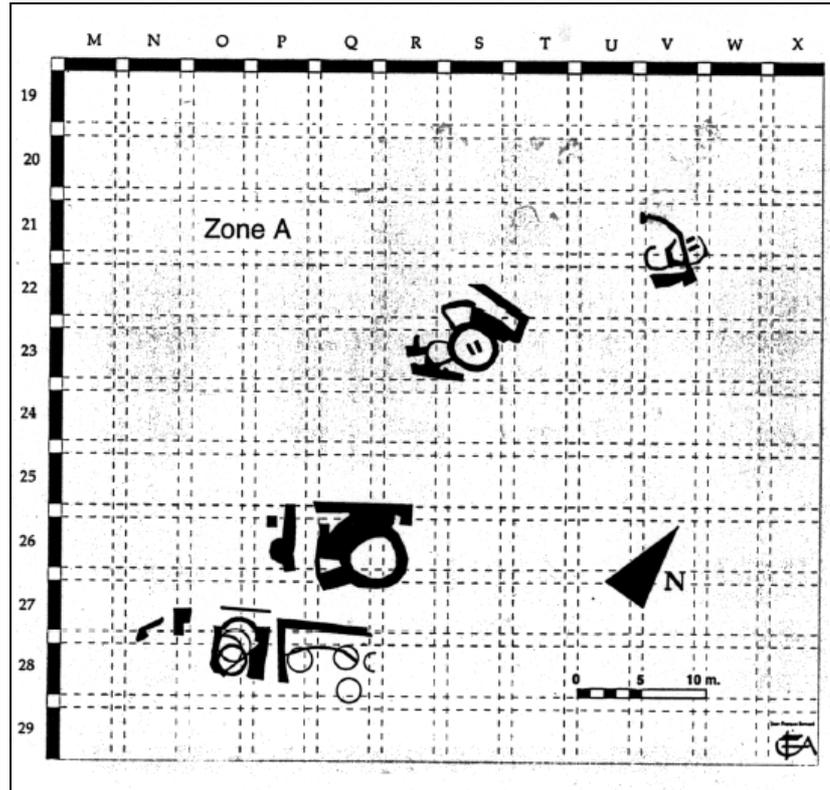
Figure 1.7: The plan of Zone A.
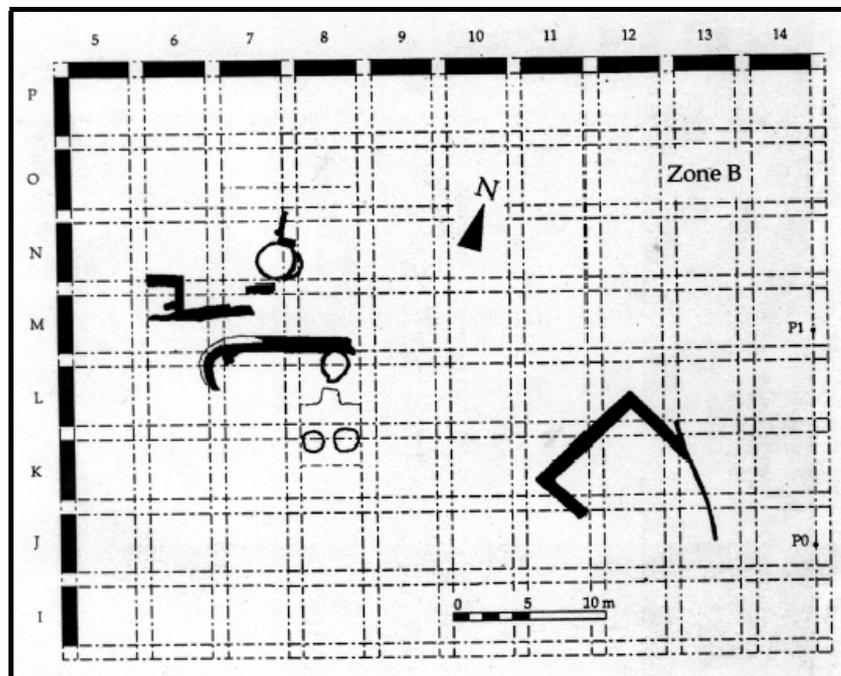
Figure 1.8: The plan of Zone B.

1.2- The Objective

The objective of this study is to investigate the ancient ceramics, especially the common ware samples, originated from Demirci. Chemical analyses were done in this study to make comparisons between common wares, cooking pots and local raw clays.

All the common wares were functional, but since the cooking pots were used for cooking purposes, they should be stronger because of function. This makes the cooking pots have different characteristics from the other common wares. One of the aims of this study is to find out the reasons for these variations in the ceramics. In a previous study, the characterization and provenance determinations of amphora, tubulures, and tiles were done by I. R. Türkmen in 2003 in our laboratories in Bilkent University, Chemistry Department. In that study, amphoras were the origin of the study. [3] In our study, we mainly focused on common wares.

In addition to the identification and characterization of common wares, one other purpose of this study is to see whether scientific methods used in archaeometry correlates with the conclusions obtained by simple archaeological observations in morphology, shape and color.

The characterization of the ceramics made in Sinop has importance because the earliest container production centers of the Black Sea region were Sinop and Pontian Heraclea and they established close economic links with Greek colonies of the Black Sea coast from the early 4th century BC. Sinopean and Heraclean wine and oil were very popular and ceramic containers of the centers were widely spread all over the region. Amphorae produced in different centers that are influenced by the technique and the shape of Sinopean and Heraclean containers, may be considered an evidence of the popularity of these goods. Such replicas had a commercial character usually and were made to facilitate the wine trade for different producers. Besides the trade relations, some scientists suppose that similar features of the vessels were the result of close interaction of potters or that some craftsmen migrated had taken a direct part

in setting up the amphorae manufacture in several places of the northern and eastern coasts. There is a hypothesis about migration of several Sinopean potters to Colchis in the middle 4th century BC, but there are not direct evidences of it.[4] To be able to discuss about this latter hypothesis, common wares should be investigated first. The reason is that common wares are thought not to take part in trades as extensively as amphorae. Common wares and especially the cooking pots generally belong to the archeological excavation fields where they were found. As a result, chemical characterization of the common wares and their comparison with the clay of the area are found to be helpful for the discussions.

In archaeology, grouping and historical classification of the ceramics are generally done according to the appearance of the clay, the shape and morphological properties. However, this kind of classification in some cases may give misleading results and accordingly wrong conclusions. For example, sometimes it may occur that the same shape (type) of ceramic may appear to be produced in two different places (two different origins with different clay compositions according to the different rock formations) when a potter moves from one place to another, because they usually conserve the method of production. Once sensible, functional forms are established they tend to remain the same over a long period of time. Major changes in form appear to have been caused by shifts in the source of supply from one period to another.

The samples investigated in this study have characteristic forms showing the period of production. Despite the fact that they were found as small fragments, from the features, such as curvature, articulated neck, and potential variations of rim, estimations about the full body of the ceramic samples can be done. The Roman and Early Byzantine Pottery have some characteristic forms also. To illustrate, the common ware and amphorae fragments found in excavations at the Mediterranean coasts, such as Anemurium, were investigated and depending on the specific features or characteristic textures, the samples were differentiated according to the period that they belong. Comparing with the periods of productions, researchers may obtain chronological results. [5]

Archaeological ceramics produced in Demirci region have diversity in color; while some are pink and white, some are red in color. The differentiation and similarities of color is related with the origin of raw clay, the production technique, and firing temperature. By the chemical characterization techniques applied, the reasons for different colorations can also be found.

1.3- Methods used for Characterization in Literature

In order to characterize the potteries, archaeometrists use different methods. The widely used methods are petrological and chemical methods. Petrology and typology is a common method for archaeologists. The analysis of ceramic fabrics has been revolutionised by the adoption of petrological techniques. These enable visually similar wares to be differentiated, for example by the recording of the quantities of certain 'heavy minerals' present in the clay, or by the counting of grains of specified minerals present in a thin section. The allocation of fabrics to sources may be achieved by comparison with kiln-associated fabrics, or with geological samples.

A major disadvantage of petrological analysis is its cost in terms of time and money, which effectively restricts its application. Furthermore, the differentiation of visibly-similar wares is not always successful. It would be difficult to justify the use of petrological techniques to differentiate visibly dissimilar wares, and the use of visual techniques is a necessary prelude to the use of these techniques.

Although it is time and money consuming, in literature it is easy to find examples of successive petrographic characterizations. For example, there is a recent study that blue-and-white pottery from Iran dating to between about AD 1550 and AD 1700 were subjected to petrographic analysis in order to characterize groups which may be attributed to production at specific centres. Five discrete groups were characterized, and these are tentatively attributed to the historically known principal centres of ceramic production. [6]

However, despite the widespread use of petrological analysis some scientists had discussions about how reliable is the point counting which is simply counting the minerals on thin sections applied in petrology. The most used statistical references for point counting show that there are some problems with its use. This is where the concept of "300 points ought be good enough" was expressed in the petrographic literature. [7, 8]

Modern analytical techniques for elemental analysis such as X-Ray Fluorescence (XRF) becomes very important for classifying the origin of materials because they can simultaneously determine several trace elements (variables) in the same sample at very low concentrations. Determination of the elemental compositions can be combined with statistical methods such as principal component analysis used for provenance studies of archaeological ceramics.[9-11] The element concentrations of each sample, can be used as raw data to find the correlation between each pair of elements. This kind of analysis gives an idea about the elemental exchanges within the mineral structures. However, for a statistical analysis to be meaningful there should be many samples from each group of pottery differing in either provenance or structure. Otherwise, some possible errors due to some outliers may cause wrong results in classification. In our studies, we have used more than 50 samples not to have misleading results.

In the literature, XRF studies similar to the one in this study were applied before, such as the Energy Dispersive X-Ray Fluorescence (EDXRF) study of Tupi-Guarani archaeological ceramics. [12] The main objective of that study was to characterize the ceramic paste, as well as the superficial layer of the ceramic fragments, in order to get qualitative information about the pigment composition of the plastic decoration. To make characterization EDXRF methodology was employed to obtain the ceramic paste composition, as well as the superficial layer of the ceramic fragments. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is also an available and widely used method supplementing EDXRF for elemental analysis of archaeological and geological samples. [13-15]

From the critical review of the literature on provenance study of archaeological pottery presented by Kuleff and Djingova, for elemental analysis, the most sophisticated techniques are neutron activation analysis (NAA), ICP-AES, proton-induced X-ray emission, atomic absorption spectrometry, XRF and secondary ion mass spectrometry. [16] On the basis of the literature survey, 23 elements (Al, Ca, Ce, Co, Cs, Cr, Cu, Fe, Hf, La, Mg, Mn, Na, Ni, Rb, Sc, Si, Sm, Sr, Ti, Th, V and Zr) are established to be the most important for the classification of the historical pottery.

Furthermore, application of the thermal gravimetric analyses (TGA) and identification of some specific reactions of some clay types in certain temperature range, allows the comparison of the amounts of minerals like calcite, which has a great influence in color. The thermal behavior of limestone and monocrystalline calcite tempers in a clay matrix and their use in ancient pottery was examined before by Fourier transform infrared spectroscopy (FTIR) and thermospectrometry by Shoval et al. [17]

Scanning electron microscopy (SEM) is another widely used method for the characterization of ceramics. The usefulness of SEM in clay studies is much enhanced by the provision of an add-on energy dispersive X-ray analysis system. Not only can a rapid qualitative analysis of a morphological feature of interest be obtained but with appropriate specimen conditions quantitative chemical analysis is possible and elemental distribution maps may be obtained. In this method, because the electron beam carries a charge, the sample has to be coated with a very thin coat of gold enabling any charge to drain off. The advantages of SEM over conventional microscopy include very high resolution and greater depth of field.

1.4- Techniques used in The Present Study

In this thesis work, chemical characterization is achieved by the determination of the elemental and mineral composition of the archaeological samples found in the excavations.

1.4.1- X- Ray Fluorescence (XRF)

X-ray fluorescence is one of the applications in analytical chemistry for concentration determination of elements. The main advantages of XRF are its inherent specificity and sensitivity. [18]

Each of the atomic elements present in a sample produces a unique set of characteristic X-rays that is a fingerprint for that specific element. Energy Dispersive X-Ray Fluorescence (EDXRF) analyzers determine the chemistry of a sample by measuring the spectrum of the characteristic X-rays emitted by the different elements in the sample when it is illuminated by high energy photons (X-rays or gamma rays).

A fluorescent X-ray is created when a photon of sufficient energy strikes an atom in the sample, dislodging an electron from one of the atom's inner orbital shells (lower quantum energy states). The atom regains stability, filling the vacancy left in the inner orbital shell with an electron from one of the atom's higher quantum energy orbital shells. As it is shown in Figure 1.9 , the electron drops to the lower energy state by releasing a fluorescent X-ray, and the energy of this fluorescent X-ray (typically measured in electron volts, eV) is equal to the specific difference in energy between two quantum states of the dropping electron.
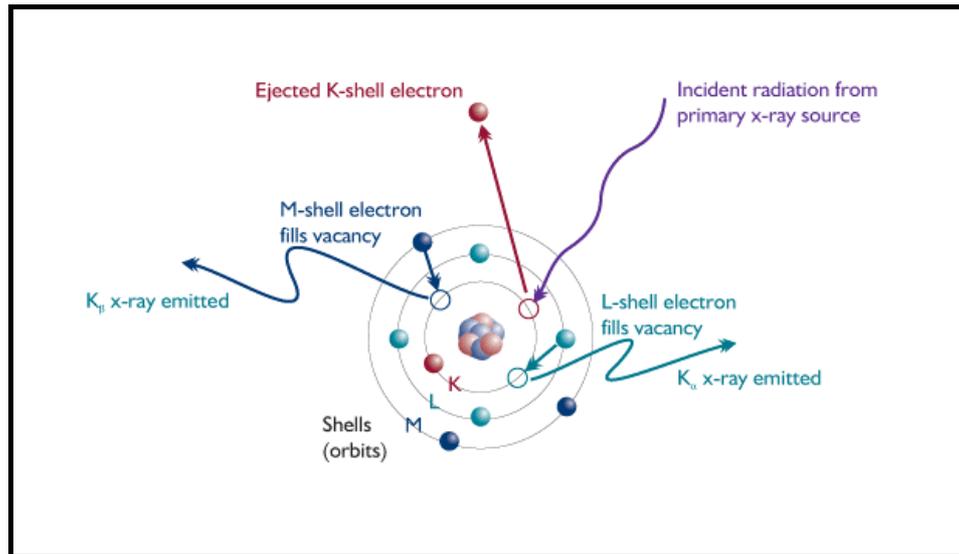
Figure 1.9: X- Ray Fluorescence Phenomenon

Because the quantum states of each electron orbital shell in each different type of atom (each of the atomic elements) is different, the energies of the fluorescent X-rays produced by different elements are also different. When a sample is measured via XRF, each element present in the sample emits its own unique fluorescent X-ray energy spectrum. By inducing and measuring a wide spectrum of the range of different characteristic fluorescent X-rays emitted by the different elements in the sample, XRF analyzers can rapidly determine the elements present in the sample and their relative concentrations,in other words, the elemental chemistry of the sample.

By measuring the characteristic fluorescence X-rays emitted by a sample, up to 30 or more elements may be quantified simultaneously. However, it is important to note that light element XRF analysis is best performed in a vacuum chamber in a laboratory environment. The X-rays with energies below 2 keV - including the characteristic X-rays of all elements lighter than sulphur - are largely absorbed in air within a short distance. In tightly controlled lab conditions, XRF may be used to measure elements as light as beryllium and boron in highly uniform samples.

Energy dispersive spectrometers are used to analyze the fluorescent spectra and provide rapid concentration estimates for one or more pre-calibrated elements. Since all elements of the X-ray spectrum are collected and processed simultaneously

instead of sequentially, Energy Dispersive (ED) systems can usually complete analysis much faster than their equivalents. [19] This is why, elemental composition of the Sinopean ancient ceramics and raw clays were determined by the feasible Energy Dispersive X-Ray fluorescence (ED-XRF) measurements.

1.4.2- Powder X- Ray Diffraction (PXRD)

X-Ray Diffraction technique was applied to figure out the mineralogical composition of the archaeological common wares and the clay minerals used during the production of these ceramics. X-Ray diffraction is the principal tool for the identification of crystalline soil minerals.

The diffraction pattern of a pure substance is like a fingerprint of the substance. In other words, for a pure substance there is only one specific pattern that it always gives. When there is a mixture of substances, as in the composition of clay or ceramic, each substance (minerals) produces its pattern independent of others present.

The theory of operation of XRD is that when X-ray radiation passes through matter, the radiation interacts with the electrons in the atoms, resulting in scattering of the radiation. If the atoms are organized in planes (i.e. the matter is crystalline) and the distances between the atoms are of the same magnitude as the wavelength of the X-rays, constructive and destructive interference will occur. This results in diffraction where X-rays are emitted at characteristic angles based on the spaces between the atoms organized in crystalline structures called planes. Most crystals can have many sets of planes passed through their atoms. Each set of planes has a specific interplanar distance and will give rise to a characteristic angle of diffracted X-rays. The relationship between wavelength, atomic spacing (d) and angle was solved geometrically by Bragg as it is shown in the Figure 1.10.
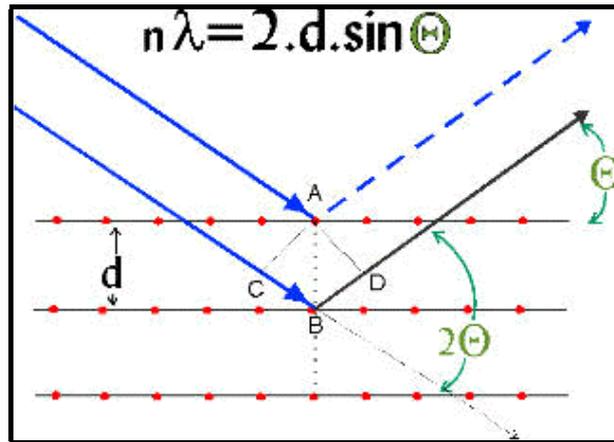
Figure 1.10: Bragg Equation

If the wavelength is known (depends on the type of X-ray tube used) and the angle can be measured (with a camera or diffractometer) then the interplanar distance can be calculated from the Bragg equation. A set of d-spaces obtained from a single compound will represent the set of planes that can be passed through the atoms and can be used for comparison with sets of d-spaces obtained from standard compounds.

In this study, mineral compositions were determined by the peak fit (search-match) method to the well-defined mineral positions and intensities by Power X-Ray Diffraction (PXRD) method. In this method powders of crystalline materials diffract X-rays. PXRD provides less information than single crystal diffraction, but since it is much faster and simpler method, it is widely used. The identity of the clay fraction and powdered ceramics can be confirmed by powder diffraction. Moreover, the peak area can be related to the amount of each component present in the analyzed sample. In addition, XRD spectra of the clay samples can provide information about the possible structural changes taking place in clay lattice during firing.

1.4.3- Fourier Transform Infra Red (FTIR) Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy was also used as a complementary method to determine mineral structures and the similarities and diversities between the clays and the common wares. Since the infrared absorption

spectroscopy is rapid, economical and nondestructive method universally applicable to structural analysis, the technique is so versatile that it can be used both as a source of the physical parameters of crystal lattice determinations, and as a means of eliciting purely empirical qualitative relationships between specimens. It is an intrinsically simple technique that deserves to be more widely used in clay mineralogy and soil science.

The absorption of infrared radiation by clay minerals depends critically on atomic mass, and the length, strength and force constants of inter atomic bonds in the structure of these minerals. It is also controlled by the constraints of the overall symmetry of the unit cell, and the local site symmetry of each atom within the unit cell. In addition, the absorption of infrared radiation is also strongly influenced by the degree of crystalline order (Lazarev, 1974) and the size and the shape of the mineral particles (Farmer and Russell, 1966; Rendon and Serna, 1981; Serna et al., 1982). Absorption bands of adsorbed molecular water appearing at 3400 and 1630 cm^{-1} and C-H absorption bands at 2850-2960 cm^{-1}, which arise from organic contaminants, can be minimized by pretreatment. [20]

1.4.4- Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) is used to examine the process of mass changes as a function of time, temperature and other environment conditions that may be created within the apparatus as shown in Figure 1.11. Temperature changes by the heat applied in the high temperature furnace. Then the sample undergoes some reactions according to the conditions created in the closed apparatus by purging an oxidizing or inert gas. As a result, the balance senses the differentiations occurring in mass and they are processed by software on a computer.
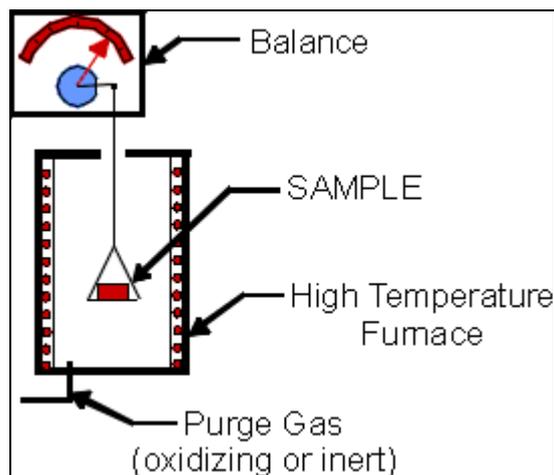
Figure 1.11: Schematic diagram of TGA

Thermogravimetry (TG) differs slightly from other thermal analysis techniques in that recorded data includes the change in sample mass as a function of temperature. The change in mass versus temperature curve provides information concerning the thermal stability and composition of the initial sample, as well as the thermal stability and composition of any intermediate compounds that may be formed when a specimen is heated or cooled under uniform conditions. To produce this information, the sample must evolve a volatile product, which can originate by various physical or chemical processes.

In a single-stage reaction, like that shown in Figure 1.12 , two temperatures are selected off of the mass-change versus temperature curve: T_i, the inital temperature at which the cumulative mass-change reaches a magnitude that the thermobalance can detect, and T_f, the final temperature at which the cumulative mass-change first reaches its maximum value, corresponding to complete reaction.
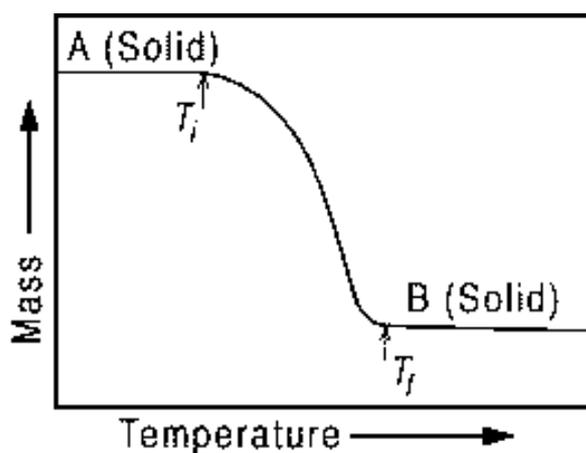
Figure 1.12: Mass-change versus temperature curve

The TGA data is also represented in its first derivative or differential thermal gravimetry (DTG) format. In this format it is easier to identify the reactions occuring during heating.

1.4.5- Statistical Methods

Statistical treatment of the analytical data is a widely used approach in archaeology and in all other sciences. Since it is difficult to deal with thousands of variables obtained from the experimental results, statistical analyses are used as complementary methods for the interpretation of the data obtained by chemical analysis. For this purposes special software packages were improved. The main applications of factor analytic techniques are to reduce the number of variables and to detect structure in the relationships between variables, that is to classify variables.

In this study, two of the statistical methods; principal component analysis and cluster analysis, were applied. These two methods are the most commonly used ones for the archaeological purposes.[21-24] The experimental data are used in both analyses as programmes codes in input files to run the different sub-programmes in Statistical Analysis Software (SAS) Package.

1.4.5.1- Principal Component Analysis (PCA)

When multivariate data are collected it is common to find some correlated variables. One implication of these correlations is that there will be some redundancy in the information provided by the variables. In the extreme case of two perfectly correlated variables (x and y) one is redundant. Knowing the value of x leaves y with no freedom and vice versa. Principal Components Analysis (PCA) exploits the redundancy in multivariate data, enabling us to pick out patterns (relationships) in the variables and reduce the dimensionality of a data set without a significant loss of information.

PCA is one of a family of related ordination or projection techniques that includes Factor Analysis and Principal Co-ordinates Analysis. It covers standard deviation, covariance, eigenvectors and eigenvalues.

Principal component analysis is a mathematical procedure that transforms a number of (possibly) correlated variables into a (smaller) number of uncorrelated variables called principal components. The objective of principal component analysis is to reduce the dimensionality (number of variables) of the dataset but retain most of the original variability in the data. The first principal component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible.

This procedure performs Principal Component Analysis on the selected dataset. A principal component analysis is concerned with explaining the variance covariance structure of a high dimensional random vector through a few linear combinations of the original component variables. Consider a p-dimensional random vector $\underline{X} = (X_1, X_2, ..., X_p)$. k principal components of $\underline{X}$ are k (univariate) random variables $Y_1, Y_2, ..., Y_k$ which are defined by the following formulae.

$$Y_1 = l_1' \underline{X} = l_{11}X_1 + l_{12}X_2 + ... + l_{1p}X_p$$
$$Y_2 = l_2' \underline{X} = l_{21}X_1 + l_{22}X_2 + ... + l_{2p}X_p$$
$$\vdots$$
$$Y_k = l_k' \underline{X} = l_{k1}X_1 + l_{k2}X_2 + ... + l_{kp}X_p$$

The principal components are linear combinations of the original variables which maximize the variance of the linear combination and which have zero covariance (and hence zero correlation) with the previous principal components.

It can be proven that there are exactly p such linear combinations. However, typically, the first few of them explain most of the variance in the original data. So instead of working with all the original variables X_1, X_2, ..., X_p, you would typically first perform PCA and then use only first two or three principal components, say Y_1 and Y_2, in subsequent analysis.

As a result, instead of dealing with numbers of data, as in our case the data consists of hundereds of concentration data of different elements for differnt samples, application of statistical methods such as PCA is the most feasible method to observe the classes and subclasses that may occur as an output data plot of first principal component versus second principal component. Because of its feasibility PCA has a widespread application in different science fields, such as food and chemical engineering, atmospheric science and even by psychologists. [25-28]

1.4.5.2- Cluster Analysis

Cluster analysis classifies a set of observations into two or more mutually exclusive groups based on combinations of internal variables. The purpose of cluster analysis is to discover a system of organizing observations. Cluster analysis seeks to identify a set of groups which both minimize within-group variation and maximize between-group variation.

Cluster analysis starts with a data matrix, where objects are rows and observations are columns. A table is constructed where the numbers in the table are measures of similarity or differences between the two observations.

By the output of cluster analysis obtained by a software, a dendogram is drawn. A dendrogram is a tree diagram often used to represent the results of a cluster analysis in which lines indicate the degree of similarity or dissimilarity between cases.

Since it is easier to recognize the similarities and variations in a picturized form, interpretation of the spectroscopic data by the statistical analysis methods is a very feasible way for chemists. [29] Besides the feasibility of application to chemistry, cluster analyses have also been used for social sciences because of its simplicity. [30]

1.5- Clay used as Raw Materials

Raw clays were used for the manufacture of the common wares in history. Even today they are used as raw materials for the ceramics that is the mostly used material for kitchen and fine wares. For each kind of clay there is a specific temperature for baking, that is vitrification. This is the hardening, tightening and finally the partial glassification of the clay. Vitrification results from fusions or melting of the various components of the clay. The strength of fired clay is increased by the formation of new crystalline growth within the clay body. These lace the structure together, giving it cohesion and strength. Thus, it is very important to reach the vitrification temperature. Potters work with clays with vitrification temperature range as wide as possible. They generally know the properties of the local raw clay they used very well. This is why potters do not want to use a new raw material. However, sometimes to have different properties for usage, such as resistance to heat for cooking pots, some temper may be added to the raw clay used in production. It is another problem to differentiate between natural inclusions and a temper.

1.6-   Samples

Samples used in this thesis project are the ceramics from the excavation of Demirci taken from Sinop Museum with permission to be investigated and the raw clays taken from the excavation fields. The ceramic samples and the raw clays are all from the same origin, Demirci.

Descriptions of the samples are given in the Table 1.1. In the table, sample names are given such as 'Dm 222'. The 'Dm' stands for the sample location, Demirci. While cataloguing, some numbers were used for identification. The samples used in this study are numbered from Dm 34 to Dm 43 and from Dm 201 to Dm 236. In addition to these ceramic samples, the raw clays were numbered from Dm 98 to Dm 102, and one more clay sample was numbered as Dm 128. Since there are other ceramic samples, especially amphoras, used in a previous study, other numbers were used for those samples used in the previous study. In the table, 'type' indicates whether ceramics are amphora, commonware, cooking pot or raw clay. These types are indicated as 'a', 'cw', 'ck', 'rc', respectively. Furthermore, identification of the sample is given in paranthesis in the type coloumn when available. In the type column, color is abbreviated as 'r' for red, 'w' for white, 'pk' for pink and 'b' for black (overfired) samples.

In the 'finding spot' column different zones in the excavation field of Demirci are indicated. The abbreviations used for the finding spots stands as codes used for locations in different zones in the excavation area. For example, Dm A.A1.FR A means the zone A, A1 square, the kiln FR (fırın) while Dm B.00.L8.M8.BR means the zone B, excavated in 2000, between the squares L8 and M8, the vehicle way (abbreviated as BR, from the French word). For further considerations, refer to the plans of zone A and B given on page 7.

'Color' and 'Fragment' columns are also tabulated for identification. For some samples, specific 'observations' are given such as how much inclusion occurs in the sample. Photographs and the brief descriptions of the samples are given in the

appendix for identification. In the Figure 1.12, Dm 222 is shown to illustrate and summerize what the abbreviations stand for.

Abbreviations:

❖ The first letters of the sample name denote sample's finding spot:

Dm: Demirci (Sinop)

❖ The numbers that come next are the sample-numbers used for cataloguing.

❖ The letters that come after the sample-number denote the type and color of the sample:

a: amphora

rc: raw clay

cw: common ware

ck: cooking pot

❖ The letters that come after the type denote the color of the sample:

r: red

w: white

pk: pink

b: black

Eg:

Dm 222.cw.r

Finding spot : Demirci, from surface

Sample number :222

Tpye: common ware

Color: red (red clay)

Figure 1.13: Photograph of Dm 222.cw.r

Table 1.1: Ceramic and raw clay samples

Sample	Type	Finding spot	Colour	Fragment	Observation
Dm 34	ck.r	Dm A	red and gray-black interior	bottom	layer formation
Dm 35	ck.r	Dm A	red, violet layers	handle	tree layers
Dm 36	cw.r (vase for liquid)	Dm A	red	handle	no layer
Dm 37	ck.b	Dm A	black (overfired)		
Dm 38	ck.r	Dm A	red, brownish-red exterior		layer formation
Dm 39	ck.r	Dm A	red exterior, brownish interior		inside is brown
Dm 40	ck.r	Dm A	orange-red		soft surface
Dm 41	ck.r	Dm A	orange-red, violet-red		layer formation
Dm 42	ck.r	Dm A	orange-red		no layer
Dm 43	ck.r	Dm A	gray		very thin
Dm 98	rc	Dm A	grayish yellow		
Dm 99	rc	Dm A	grayish yellow		
Dm 100	rc	Dm B	grayish yellow		
Dm 101	rc	Dm North-Side	grayish yellow		
Dm 102	rc	Dm A	grayish yellow		
Dm 128	rc	Dm B. N6.5	white		mixed with refused material

Table 1.1(*continued*): Ceramic and raw clay samples

Sample	Type	Finding spot	Colour	Fragment	Observation
Dm 201	a.r (type1)	Dm A.A1.FR A	orange		
Dm 202	cw.r (open vase)	Dm A.A1.FR A	orange	rim	
Dm 203	cw.w (vase for liquid)	Dm A.A1.FR A	white/pinkish	rim	
Dm 204	a.r (carrot type)	Dm A.A1.FR A	orange		
Dm 205	ck.r	Dm A.A1.FR A	red/brownish (violet interior)	bottom	
Dm 206	cw.pk (stand)	Dm A.A1.FR A	beige/pink/orange	rim	small Fe inclusion
Dm 207	ck.r	Dm A.A1.FR A	red/brownish (violet interior)	bottom	
Dm 208	cw.pk (container)	Dm A.A1.FR A	pink/orange(less)	shoulder	pure clay
Dm 209	a.w ?	Dm A.A1.FR A.81	beige/orange	neck	
Dm 210	a.pk ?	Dm A.A1.FR A	pink/beige (whitish to reddish)	neck	
Dm 211	a.pk ?	Dm A.A1.FR A	pink/violet	neck	
Dm 212	ck.r	Dm A.A1.FR A	orange/black(inside)	wall	
Dm 213	cw.w (jar)	Dm A.A1.FR B	white/gray	rim	
Dm 214	cw.w (vase for liquid)	Dm A.U21.V21.V22.V23	white/pinkish	down part of body	
Dm 215	cw.r (vase for liquid ?)	Dm A.U21.V21.V22.V23	orange/reddish	part of body	
Dm 216	cw.r (vase for liquid)	Dm B.00.L8.M8.BR	orange/beige/pink (not certain)	rim with part of handle	
Dm 217	cw.r (jar)	Dm B.00.L8.M8.BR	brick orange	rim	
Dm 218	ck.r	Dm B.00.L8.M8.BR	orange red	part of body	
Dm 219	cw.pk (plate)	Dm A.S23.FR1.al2	beige/pink	bottom	pure clay
Dm 220	cw.r (closed vase)	From surface	orange	bottom	less inclusion
Dm 221	cw.r (vase for liquid)	From surface	orange	part of body	

Table 1.1(*continued*): Ceramic and raw clay samples

Sample	Type	Finding spot	Colour	Fragment	Observation
Dm 222	cw.r (container)	From surface	orange	part of body with handle	
Dm 223	cw.r	From surface	orange	ring bottom	
Dm 225	ck.r	From surface	brick/on the surface it's violet	part of body	
Dm 226	cw.r (vase for liquid)	From surface	orange (light colored)	part of body	
Dm 227	ck.?	From surface	surface greenish (burning side-outer), gray(middle),pink/beige(inner)	wall	
Dm 228	ck.r	From surface	red orange(interior),brownish red brick (exterior surface)	bottom	
Dm 229	ck.r	From surface	violet red(exterior),(interior)	part of body with handle	
Dm 230	cw (open vase)	From surface	greenish (vitrification,glaziered)	rim, part of body	problem of firing condition
Dm 231	cw.r (vase for liquid)	From surface	orange, a little bit red (for the interior)	part of body	
Dm 232	ck.r	From surface	orange	part of body	characteristic texture, white inclusions
Dm 233	cw.pk	From surface	beige/ pink	down part of wall	
Dm 235	ck? (or cw?)	From surface			big red ferrous inclusion
Dm 236	cw.pk (vase for liquid)	From surface	beige/pink and black on surface	neck	

2. EXPERIMENTAL

Elemental and mineral composition of the archaeological common ware and clay samples were investigated by power X-Ray diffraction and energy dispersive X-Ray fluorescence (ED-XRF) spectroscopy. TGA and FTIR methods were also used in order to investigate the mineral structures of the samples. Prior to the analyses, samples except raw clays were first washed with distilled water in order to eliminate the impurities present on the surface of the ceramics coming from the burial environment. After having been dried completely, they were grounded in a mortar with a pestle. Five gram powder samples were prepared for all the bulk analyses.

2.1- Elemental Analysis by X-Ray Fluorescence (XRF):

The XRF analyses of the samples were done with a high performance Oxford ED-200 EDXRF system located at the Nuclear Research and Training Center of the Turkish Atomic Energy Authority, Ankara. Thirty elements (Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Nd, Sm, Cu, Zn, Ga, As, Se, Rb, Sr, Zr, Pb, Th, Sb, Cs, Ba, La, Ce) were determined throughout the analyses, but only the ones with error less than 20% were included.

The schematic diagram of the experimental setup for the XRF measurements is given in the following figure. In Figure 2.1, as it is shown XRF pellets were positioned in front of a Si (Li) detector and irradiated with X-rays originating from a Rh target. The tube power was 50 W and the maximum current was 1000 μA. Eight different sediment and soil standards were used for the calibration during the measurements and the spectra were acquired and analyzed using Oxford Xpert Ease software.
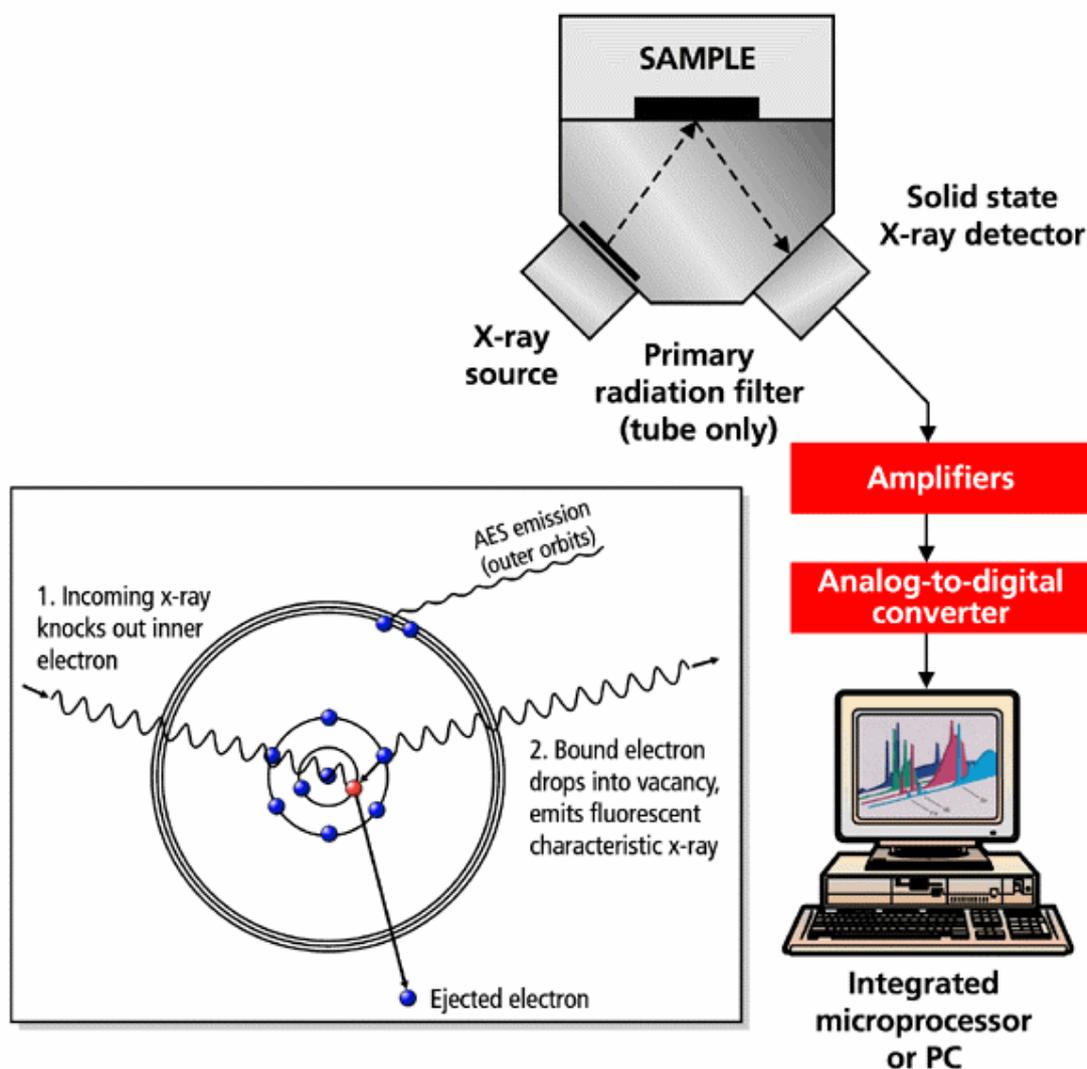
Figure 2.1: Schematic diagram of XRF

In the XRF studies, first of all counts at different energy levels are obtained. Software processes the counts for specific energy levels of specific elements and give out the results as element concentrations. However, since the energy range changes according to the atom number of an element, the energy range appropriate for a heavy element may not be appropriate for a light element. As a result, for different groups of elements different conditions are used during the analysis. These conditions are achieved by the application of different currents. Then, according to the method involved in the software package the counts are processed by using the proper condition for certain elements.

To illustrate, the peak at the characteristic energy level for calcium (Ca) is high for the Dm 128rc sample as shown in Figure 2.2. This indicates high concentration of this element in the sample.
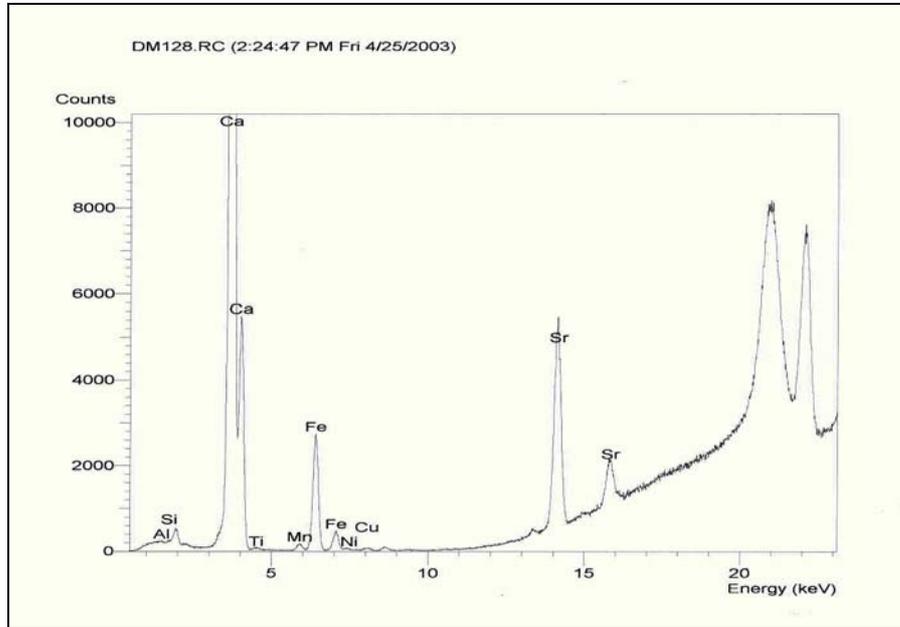
Figure 2.2: XRF outputs as counts at different energy levels for Dm128rc sample

In the following figure, Figure 2.3, different graphs showing the counts at different energy levels are given. For one sample, Dm 37 ck.b, to illustrate three of the conditions are shown. For example, to determine the concentration of element silicium (Si) neither the graph in Figure 2.3 part (a) nor (b) was used. The appropriate condition for the Si element is the condition at which the graph in figure 2.3 (c) is obtaned. These conditions are named according to the methodology which varies for different sample types.
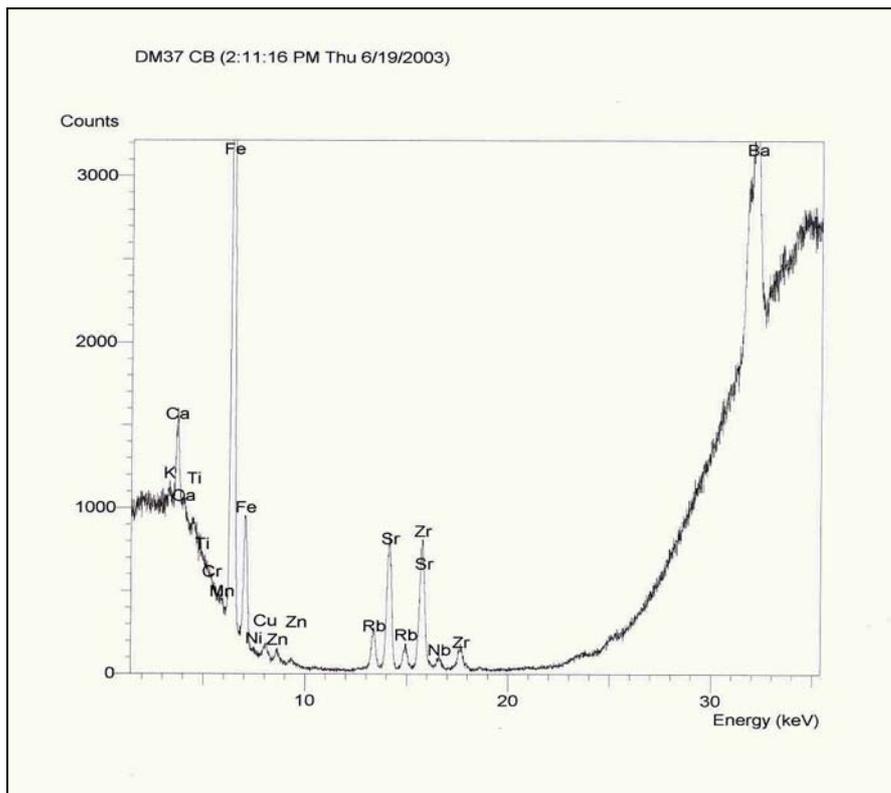
(a)
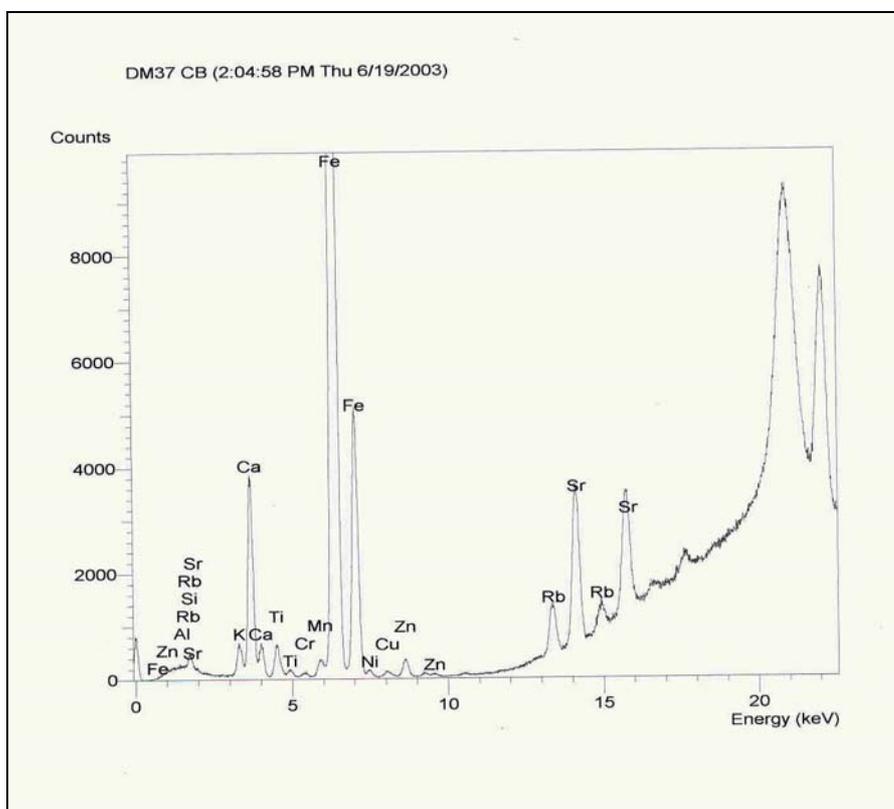
(b)
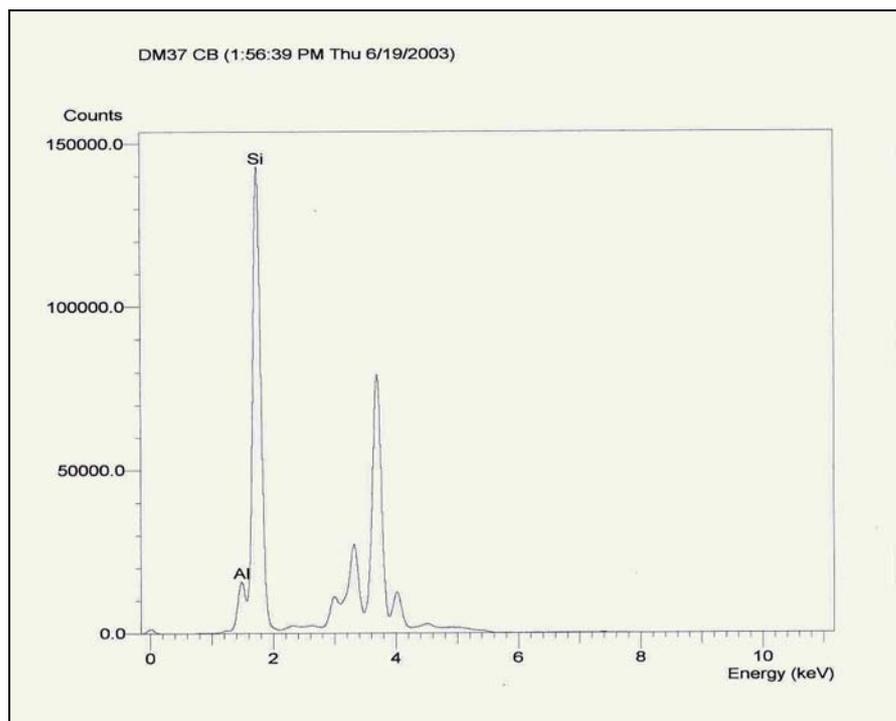
(c)

Figure 2.3: XRF outputs as counts at different energy levels for sample Dm 37ck.b at three different conditions (a), (b), (c).

2.2- Identification of Minerals by Powder X-Ray Diffraction (PXRD):

PXRD analysis was carried out using a Rigaku Miniflex model instrument as schematically illustrated in Figure 2.2. X-rays are produced by bombarding metal foil made of Cu with electrons accelerated by high voltage applied in order to emit polychromatic radiation. This radiation is filtered by another metal foil made of Ni in the case of Cu source to produce monochromatic radiation which is Cu $K_{\alpha1, 2}$ doublet with a wave length of 1.54 Ǻ.
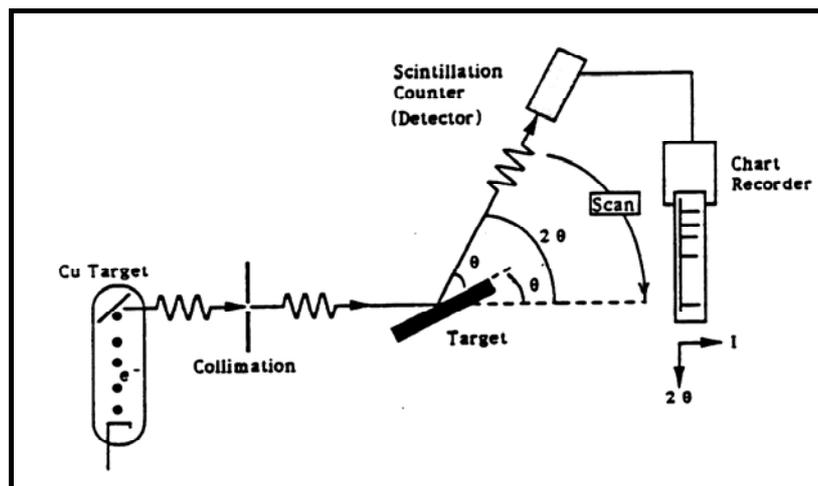
Figure 2.4: Schematic diagram of PXRD

The source consisted of unfiltered Cu K-alpha radiation, generated in a tube operating at 30 kV and 15 mA. Spectra were recorded with 2 theta values ranging from 2 to 50 degrees with a scanning rate of 2 degrees per second. The d-spacing values related with the peak positions in the spectra, were calculated by using the Bragg equation. The mineral compositions of the samples were only qualitatively determined following a search-match procedure by matching the d-spacing values to the minerals that they belong to.

2.3- Fourier Transform Infra Red (FT-IR) Spectroscopy Analysis:

FTIR spectra are obtained by using Bomem Hartmann and Braun MB-102 model FTIR spectrometer with totally 64 scans and 2 cm^{-1} resolution. As a pretreatment method, before taking the spectra, KBr and the samples in powder state were put into an oven at 150 C^o temperature for 24 hours, and after then they were kept in desiccators to cool down. The aim of this pretreatment is to minimize the absorption that may result from the physically adsorbed water molecules in the samples. If a pretreatment does not apply, the O-H vibrations may lead misleading results.

2.4- Thermal Gravimetric Analysis (TGA):

Thermal gravimetric analyses were done between the temperatures 50 and 1000 C^o with a heating rate of 10 C^o per second by using Setaram TG DTA/DSC instrument. The sample mass was varied between 20-30 mg, and alumina holders are used since they are resistant to high temperature applied in the analysis. The dynamic experiments were carried out in nitrogen atmosphere with a flow rate of approximately 80mL per minute.

2.5- Scanning Electron Microscope (SEM)

Scanning electron microscopic views of four representative samples were taken. The powder forms of the four samples; Dm 99 rc, Dm 203 cw.w, Dm 36ck.r, and Dm 42 ck.r were used. Since the ceramics were made of clay, to make them inductive there was a pretreatment. In this pretreatment, the powders stuck on sticky carbon bands were covered with gold. After that the SEM views were taken at different scales of 1 and 10 microns. The surface views were obtained to observe the particles and their sizes.

3. RESULTS and DISCUSSION

3.1- Elemental Characterization by X-Ray Fluorescence (XRF):

Elemental concentrations of the samples measured by means of XRF analyses are given in Table 3.1 and Table 3.2. In table 3.1, elemental compositions of archaeological ceramics are given while in table 3.2 element concentrations of the raw clay samples are tabulated.

From the investigations of the Table 3.1 and Table 1.1, it is observed that calcium (Ca) is the most important element having influence on color, and its amount varies according to the usage of the ceramic. In the cooking pots, the amount of Ca is around 1-2 % and these ceramic samples have color ranging from red to brownish (dark colors). However, in the common wares and amphora, which are used for purposes other than cooking, the concentration of Ca is higher than 4 % (between 4 and 9 %). Among the latter group of ceramics, color occurs lighter than orange, which is pink to white, at the Ca concentrations around 6 and higher. The higher the amount of Ca, the lighter the color is. For example, when it is more than 8 %, as it is in Dm 213, the color appears to be totally white. There are some outliers from this conclusion. Most probably this is related with the firing conditions, such that overfired Dm 37 has 6.18 % Ca but it has black color.

Even though the Ca has the most influence on color, other elements also have importance. To illustrate, Dm 201 and Dm 208 have almost the same Ca amount (5.6 %), Dm 201 has orange color whereas Dm 208 has pink color. The difference between these two samples may be because of that Dm 208 has more Ni while it has less Ti, Cu, and V than Dm 201 has.

When Table 3.1 and 3.2 are compared, that is the comparison between ceramics and raw clays; it is observed that in some of the ceramics amount of Ca is more than the amount of Ca in raw clays. Thus, it can be concluded that in white ceramics, some of which has higher Ca than raw clays, calcite might be added from Dm 128 or the excess Ca came from the micritic calcite coming from the burial environment. Considering the results of the other mineralogical analyses, high concentration of Ca in Dm128 originates from the high amount of calcite in it. Since Dm 128 is almost pure calcite, it is totally different than other local raw clays. On the contrary, in cases where there is less Ca than in raw clays, it may be thought that there was leaching process applied during production. However, SEM analysis is required to see whether the Ca came from the micritic calcite from the burial environment or not.

Furthermore, in some of the ceramic samples the layer formation was observed due to the color differences. In these samples the elements varying in amount are not Ca or Fe. The concentrations of some major elements (Mg, Si, K, etc.) differ to small extent and concentrations of some minor elements (Ni, V, Cu, Zn, Rb, Sr) vary in higher extent in between the different layers of a ceramic sample.

The concentration of iron, Fe, which has a great impact on the color of ceramics, was found to be approximately 4% for all samples. This may be an explanation for the occurrence of the similar colors. In addition, it is known that iron element is found in yellow color in oxidizing environment and in red color in reducing environment. Hence, while the color of the common wares varies in red color, the raw clays, which had been used in the production of these common wares, have yellow color. In Dm 128 clay sample, while the percent concentration of iron element was too low, the calcium is dominant so that color of this clay is white. Moreover, elements like copper (Cu), cobalt (Co), chromium (Cr), titanium (Ti), nickel (Ni), and vanadium (V) have impacts on color according to their concentrations. [31]

Table 3.1: Element concentrations of the archaeological ceramics obtained by XRF analyses.

Element	Mg	Al	Si	K	Ca	Ti	V	Fe	Ni	Cu	Zn	Rb	Sr	Zr	La	Sm
	Concentration															
Sample	%	%	%	%	%	%	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Dm 34 bottom	0.93	6.44	26.28	0.98	1.81	0.51	115.81	4.26	73.84	34.86	73.73	89.09	156.85	183.63	26.42	7.18
Dm 35 in/out	0.98	6.29	30.09	1.89	1.80	0.46	123.41	4.08	39.40	42.04	81.98	122.99	217.57	170.71	23.08	6.28
Dm 36	1.59	6.62	22.87	0.98	5.94	0.42	107.21	3.96	83.34	34.73	51.09	92.77	315.30	150.27	24.14	6.42
Dm 37	0.92	5.53	28.18	1.65	6.18	0.41	106.60	3.81	93.13	23.27	149.41	107.71	329.75	154.64	28.90	4.95
Dm 38 in	0.94	6.29	31.10	1.30	1.49	0.50	130.46	4.15	63.08	37.73	111.14	106.78	155.87	193.72	26.11	7.03
Dm 38 out	0.86	6.48	29.48	1.22	1.51	0.51	105.28	4.23	86.71	43.23	51.22	101.13	166.86	192.71	26.95	7.27
Dm 39 in/out	0.95	6.08	28.88	1.32	1.14	0.48	115.15	4.20	66.33	46.12	59.89	116.31	155.87	180.44	28.57	6.88
Dm 39 out	0.97	6.34	29.23	1.27	1.14	0.50	113.73	4.27	71.25	41.58	72.78	119.13	158.37	183.22	23.24	6.98
Dm 40	1.39	5.90	23.68	1.32	6.24	0.40	107.03	3.60	92.36	16.89	85.16	96.38	321.33	150.59	26.34	5.27
Dm 41 in	0.84	5.79	33.20	0.99	1.45	0.48	100.23	3.93	437.94	39.34	114.86	97.95	179.32	202.15	24.94	6.71
Dm 41 out	0.98	6.03	32.43	0.58	1.64	0.49	114.16	4.19	109.30	38.12	114.25	100.74	194.92	199.05	23.42	6.78
Dm 42	0.81	6.03	32.72	1.11	1.55	0.49	113.12	4.09	117.38	21.81	71.78	87.27	160.86	216.19	29.08	6.67
Dm 43 in	1.02	6.78	25.47	0.91	2.84	0.48	125.00	4.02	98.55	30.99	94.05	92.15	239.51	184.58	25.07	6.22
Dm 43 out	1.10	6.75	27.72	1.13	2.85	0.48	124.34	4.13	98.33	27.62	104.37	91.62	229.24	187.99	25.07	6.50

Table 3.1 (*continued*): Element concentrations of the archaeological ceramics obtained by XRF analyses.

Element	Mg	Al	Si	K	Ca	Ti	V	Fe	Ni	Cu	Zn	Rb	Sr	Zr	La	Sm
							Concentration									
Sample	%	%	%	%	%	%	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Dm 201	0.91	3.43	15.39	1.02	5.63	0.42	114.58	3.95	42.89	49.50	92.07	101.30	384.17	160.64	26.49	5.85
Dm 202	0.69	3.16	26.06	1.21	1.64	0.53	114.65	4.16	66.79	37.21	78.38	79.39	167.30	226.37	28.62	7.64
Dm 203	0.78	3.16	14.64	1.73	7.27	0.40	122.98	3.61	60.26	33.04	82.44	95.11	351.21	160.52	23.81	4.49
Dm 204	0.76	3.10	20.96	3.05	4.80	0.40	126.89	3.73	23.85	39.35	83.73	101.76	345.46	175.96	26.93	4.64
Dm 205	0.68	2.75	20.23	1.57	1.92	0.45	127.25	4.18	-	47.68	86.13	103.23	134.70	190.11	23.01	5.63
Dm 205 out	0.90	4.56	33.17	1.32	1.93	0.44	119.51	3.95	26.57	40.74	131.67	95.93	130.41	182.83	24.89	5.45
Dm 206	1.34	6.92	27.32	1.32	7.36	0.39	110.29	3.86	21.57	29.01	79.89	75.95	326.65	155.98	25.70	3.29
Dm 207	1.30	7.21	37.21	1.25	1.88	0.47	125.62	4.24	7.50	45.36	89.43	103.84	137.86	241.53	30.86	6.35
Dm 208	1.33	7.53	19.02	1.41	5.65	0.38	111.16	3.50	55.85	46.86	88.87	91.58	404.07	156.32	24.46	2.85
Dm 209	1.27	6.82	29.24	1.84	7.12	0.40	107.24	3.82	366.03	17.82	24.40	83.57	300.39	155.63	29.18	4.74
Dm 210	1.65	7.36	26.89	1.53	7.12	0.42	123.28	3.81	41.04	39.90	91.76	78.06	311.84	155.45	29.47	4.27
Dm 211	1.60	7.08	27.29	1.70	7.72	0.41	126.07	3.78	45.48	38.30	87.33	87.35	305.10	154.66	27.55	4.51
Dm 212	0.97	7.40	32.61	1.58	1.30	0.48	110.46	4.08	28.63	43.97	77.16	103.31	167.59	199.36	25.07	6.24
Dm 213	1.37	7.01	25.74	0.89	8.40	0.39	121.51	3.69	50.42	19.92	69.81	54.16	368.08	152.98	25.91	2.91
Dm 214	1.19	7.27	26.84	1.28	6.84	0.40	107.20	3.84	67.03	32.03	71.83	81.67	332.98	156.06	30.10	3.30
Dm 215	1.48	7.49	25.31	1.51	5.81	0.41	106.77	3.87	44.74	35.88	76.69	99.10	327.38	170.27	26.44	4.88
Dm 216	1.82	7.15	25.58	1.12	6.92	0.42	114.95	3.78	77.92	26.91	79.09	97.24	445.08	153.76	29.60	4.50
Dm 217	1.42	7.57	23.51	1.80	5.90	0.42	109.29	3.81	72.60	26.43	83.64	101.68	304.35	166.34	29.59	5.53
Dm 218	0.97	7.87	30.01	1.51	0.99	0.51	123.39	4.16	85.01	44.94	96.64	119.61	161.60	215.06	29.23	7.22
Dm 219	1.16	8.03	17.75	1.62	6.14	0.41	122.27	3.88	49.65	33.92	92.54	138.34	357.42	171.22	27.58	4.30

Table 3.1 (*continued*): Element concentrations of the archaeological ceramics obtained by XRF analyses.

Element	Mg	Al	Si	K	Ca	Ti	V	Fe	Ni	Cu	Zn	Rb	Sr	Zr	La	Sm
	Concentration															
Sample	%	%	%	%	%	%	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Dm 220	1.29	6.95	22.95	1.26	5.26	0.44	98.39	4.09	56.87	41.88	113.66	101.30	419.22	168.65	26.70	4.99
Dm 221	1.44	8.40	14.71	0.97	4.26	0.47	95.47	4.11	74.68	44.91	94.72	96.68	255.99	168.47	27.38	5.86
Dm 222	1.10	7.17	23.77	-	6.37	0.42	107.52	3.93	55.69	42.05	78.93	104.57	355.83	164.72	28.05	3.78
Dm 223	1.32	7.53	21.95	1.36	5.78	0.42	92.65	3.81	90.46	37.43	85.89	95.32	306.12	166.83	27.65	4.84
Dm 225	0.87	5.01	38.64	1.30	1.47	0.46	91.54	3.64	59.45	27.56	75.29	81.08	172.62	191.45	25.06	6.22
Dm 226	1.12	6.57	27.03	0.34	6.67	0.38	108.05	3.57	42.03	30.57	77.40	91.91	398.14	153.19	26.25	2.89
Dm 227 in	1.18	6.41	27.90	1.42	6.18	0.41	102.60	4.01	105.71	22.57	83.93	90.98	291.59	156.70	21.04	4.15
Dm 227 out	1.04	5.48	25.76	1.48	5.60	0.39	114.76	3.56	74.35	24.30	80.76	97.38	292.23	154.89	26.88	2.94
Dm 228	1.02	8.33	25.14	1.39	2.03	0.49	123.38	4.25	80.17	45.15	80.72	97.22	162.50	187.77	25.34	6.71
Dm 229	0.86	8.47	26.49	1.70	1.70	0.47	109.59	4.24	46.56	48.39	88.65	111.32	158.45	192.21	26.80	6.40
Dm 230	1.24	4.27	32.18	0.86	5.67	0.36	116.25	3.38	53.03	22.85	71.25	78.79	254.36	146.99	22.01	3.33
Dm 231	1.32	6.86	33.97	1.18	4.08	0.44	108.47	3.91	51.70	36.01	83.89	93.85	285.69	183.65	23.54	5.31
Dm 232	0.76	6.57	42.47	1.14	1.98	0.47	96.92	3.60	48.06	33.50	78.99	88.80	168.46	241.36	25.80	6.10
Dm 233	1.27	7.52	24.15	1.34	6.40	0.43	111.42	3.93	79.35	28.85	76.46	105.55	327.05	165.70	25.31	3.88
Dm 235	1.31	7.70	23.86	1.56	4.64	0.45	115.03	4.17	59.36	40.27	94.18	117.22	292.61	167.58	25.25	4.98
Dm 236 in/out	1.27	6.34	28.60	1.13	6.47	0.41	107.32	3.81	52.35	32.60	89.17	89.69	302.33	161.73	26.90	4.08
Mean	1.13	6.40	26.91	1.33	4.29	0.44	112.93	3.93	77.44	35.32	85.06	97.12	263.77	176.46	26.32	5.32
Std. Dev.	0.27	1.41	5.68	0.40	2.36	0.04	9.51	0.23	72.12	8.66	19.59	13.89	89.42	23.33	2.22	1.36

Table 3.2: Element concentrations of the raw clays obtained by XRF analyses.

Element	Mg	Al	Si	K	Ca	Ti	V	Fe	Ni	Cu	Zn	Rb	Sr	Zr	La	Sm
							Concentration									
Sample	%	%	%	%	%	%	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Dm 98	1.02	6.06	32.54	0.88	3.97	0.44	107.65	3.56	74.81	22.68	32.87	91.74	133.35	216.13	24.40	5.96
Dm 99	0.95	6.72	29.66	1.14	2.19	0.49	111.65	3.98	90.55	21.06	56.02	110.24	120.65	210.44	25.39	6.75
Dm 100	1.08	4.78	32.29	0.93	7.18	0.33	83.51	2.95	26.24	12.10	62.28	61.00	335.65	174.96	26.79	4.02
Dm 101	0.85	6.94	24.95	1.03	3.07	0.50	124.24	4.20	71.81	31.40	48.66	115.25	157.09	179.02	23.07	6.92
Dm 102	0.96	5.00	33.12	1.02	6.01	0.37	83.72	3.28	65.76	23.54	23.40	78.50	256.21	183.42	20.72	3.79
Dm 128	0.79	0.79	-	-	33.63	0.10	9.03	1.37	-	-	-	12.17	517.50	54.23	15.94	4.51
Mean	0.94	5.05	30.51	1.00	9.34	0.37	86.63	3.22	65.83	22.16	44.65	78.15	253.41	169.70	22.72	5.33
Std. Dev.	0.11	2.26	3.38	0.10	12.04	0.15	41.29	1.02	23.95	6.89	16.17	38.05	153.51	59.08	3.91	1.39

3.2- Mineralogy by Fourier Transform Infra Red (FT-IR) Spectroscopy:

Spectra obtained by means of the FTIR analyses were given in Figure 3.1 and in Figure 3.2. While in Figure 3.1 the spectra of some common ware samples were shown, in Figure 3.2 the spectra of the clay samples, which were considered to be used in the production of the common wares, were shown.

FTIR spectroscopy was applied for the ceramic samples numbered from Dm 34 to Dm 43. They are the common ware samples whose colors change between red and black and some of whom are in 2 or 3 layers. The samples whose layer separations were possible were named according to the location of the layer in sample, such as bottom, top, inner, outer. In general, all these samples show similar spectra, with small variations. However, since the bands are broad, it is not easy to differentiate these small variations. This is why PXRD method was applied as a further step.

The IR spectra of the layered samples, for example Dm 34c.r.top (taken from the upper inner layer of Dm34) and Dm34c.r.bottom (belonging to the outer bottom layer) does not show any differences. Thus, it can be concluded that there is not much difference observed by FTIR in mineral structure between layers.

Dm 99, 100, 101, 102 and 128 are the clay samples. The IR spectra of these clay samples show a fingerprint similarity, except the clay sample Dm 128. This similarity shows us that Dm 99,100,101,102 clay samples have the same mineral structure. Different from the others Dm 128 is observed to have much more calcite by looking at the sizes of the characteristic peaks of that mineral at 714, 849, 878, 1428, 1452, 1798, 2516, 2580, 2876 and 2983 cm^{-1}. [20] As a result, Dm 128 can be considered as pure calcite. Besides, in the clay samples the specific spectrum of the montmorillonite mineral is clearly seen. In addition, the peaks at 1088 and 1029 cm^{-1} are indicating the presence of montmorillonite mineral.
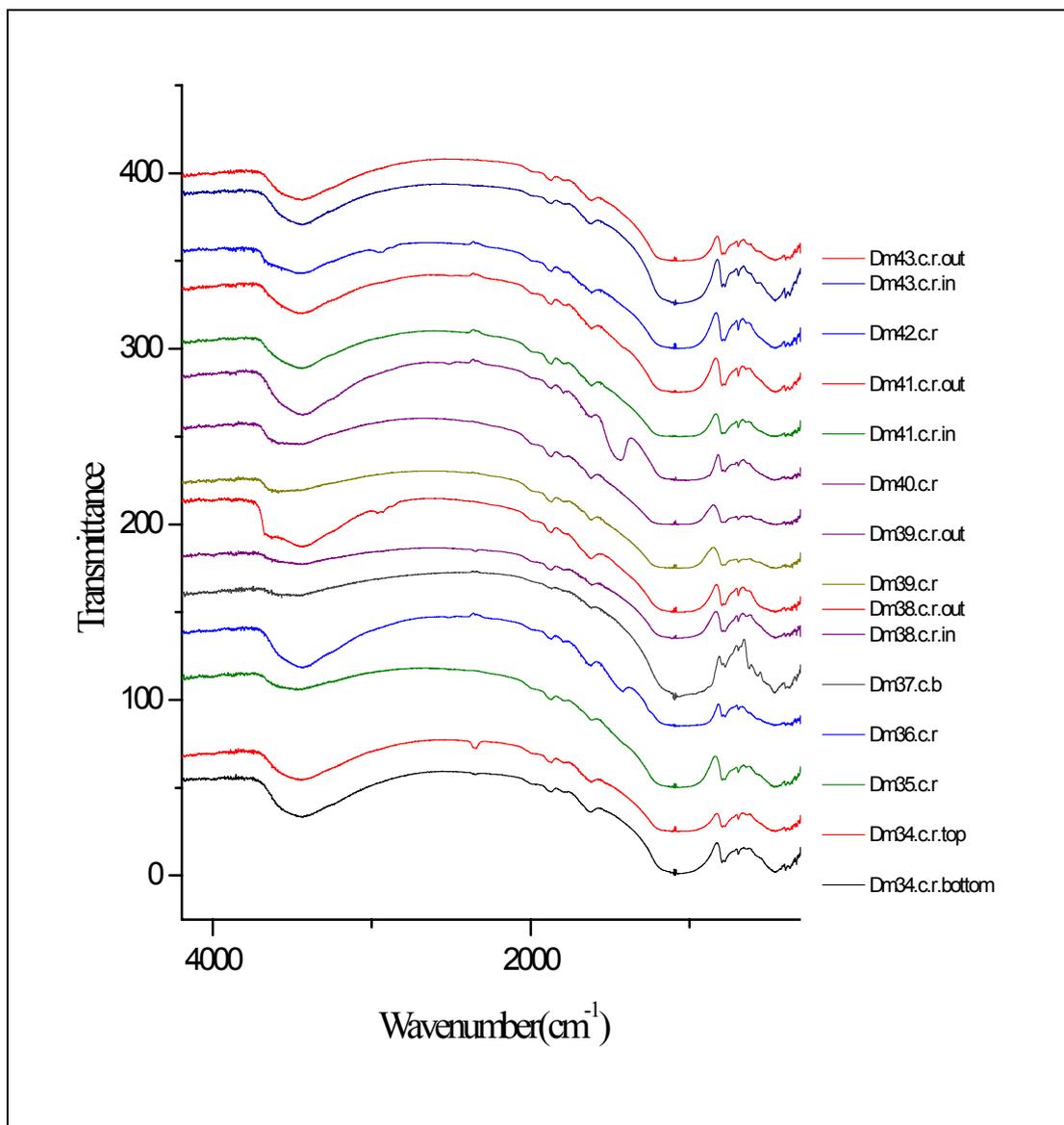
Figure 3.1: FTIR spectra of the archaeological common ware samples

Furthermore, when the spectra belonging to the clays and to the common wares were compared, the functional calcite peak at 1428 cm^{-1} was observed in the clay samples whereas it was not observed in the spectra of the common wares. Taking into the consideration that the structure of calcite is damaged above 800 C^{o}, the high firing temperatures or the high temperatures of usage for cooking could be the reason. In addition, the characteristic double peaks of quartz at 800 and 781 cm^{-1} were observed both in clay and common ware sample spectra.
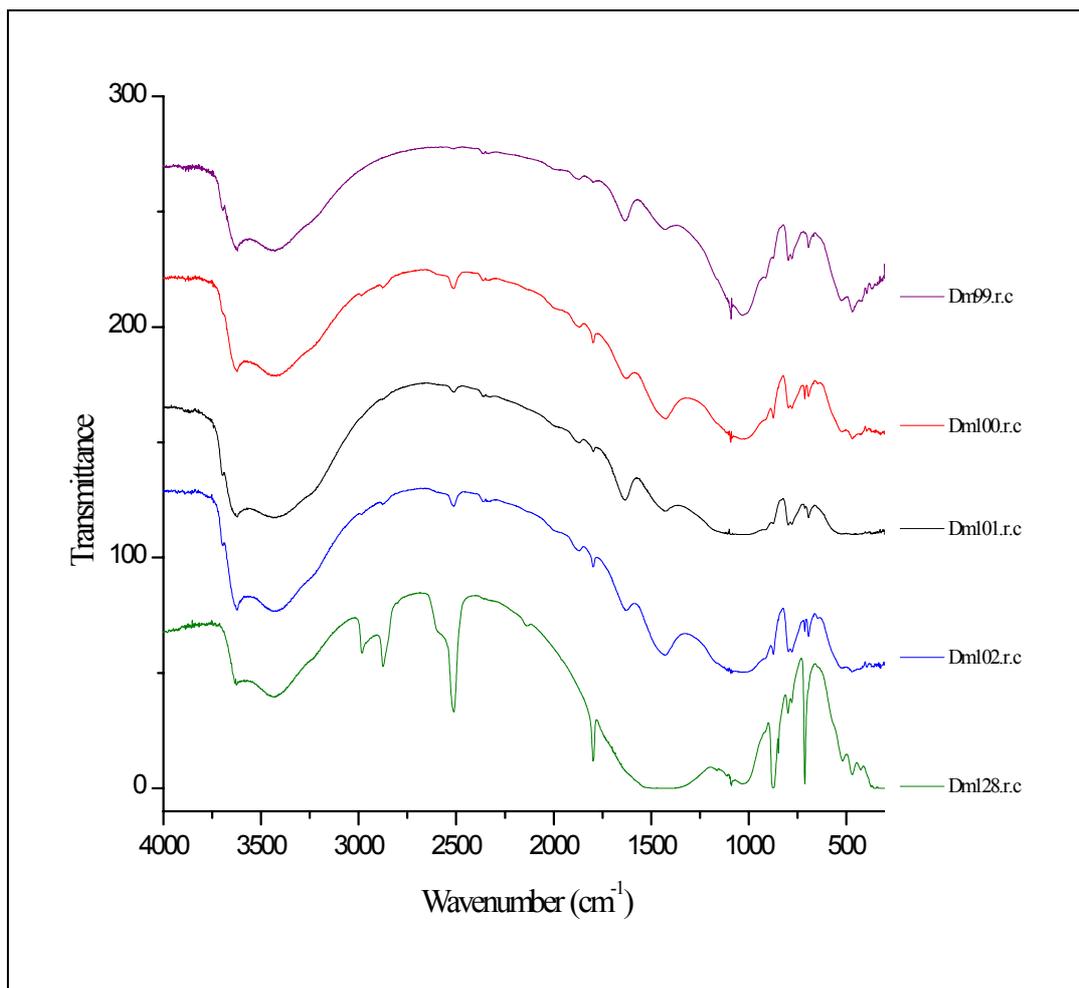
Figure 3.2: FTIR spectra of the clay samples

3.3- Mineralogy by Powder X-Ray Diffraction (PXRD):

Mineral structure of the clay samples were investigated as illustrated in Figure 3.3 obtained from the PXRD analyses. To determine the minerals, 2 theta angles corresponding to the peaks were inserted into the Bragg equation and then d-spacings were calculated. Characteristic d-spacing of the minerals were sought and matched with the d-spacing of the minerals in the samples. As a result, peaks with d-spacings 3.34, 4.26 and 1.82 specific for quartz mineral are observed in the clay samples. The d-spacings of 3.04, 2.29, 1.88 and 2.10 belonging to the calcite mineral and the d-spacings 14.45, 4.48 of the mineral montmorillonite are also present. In

addition, the d-spacings 3.19, 4.04, 3.78, 2.56 of feldspars can be seen in the diffraction pattern of raw clays as in the figure 3.3. [32]
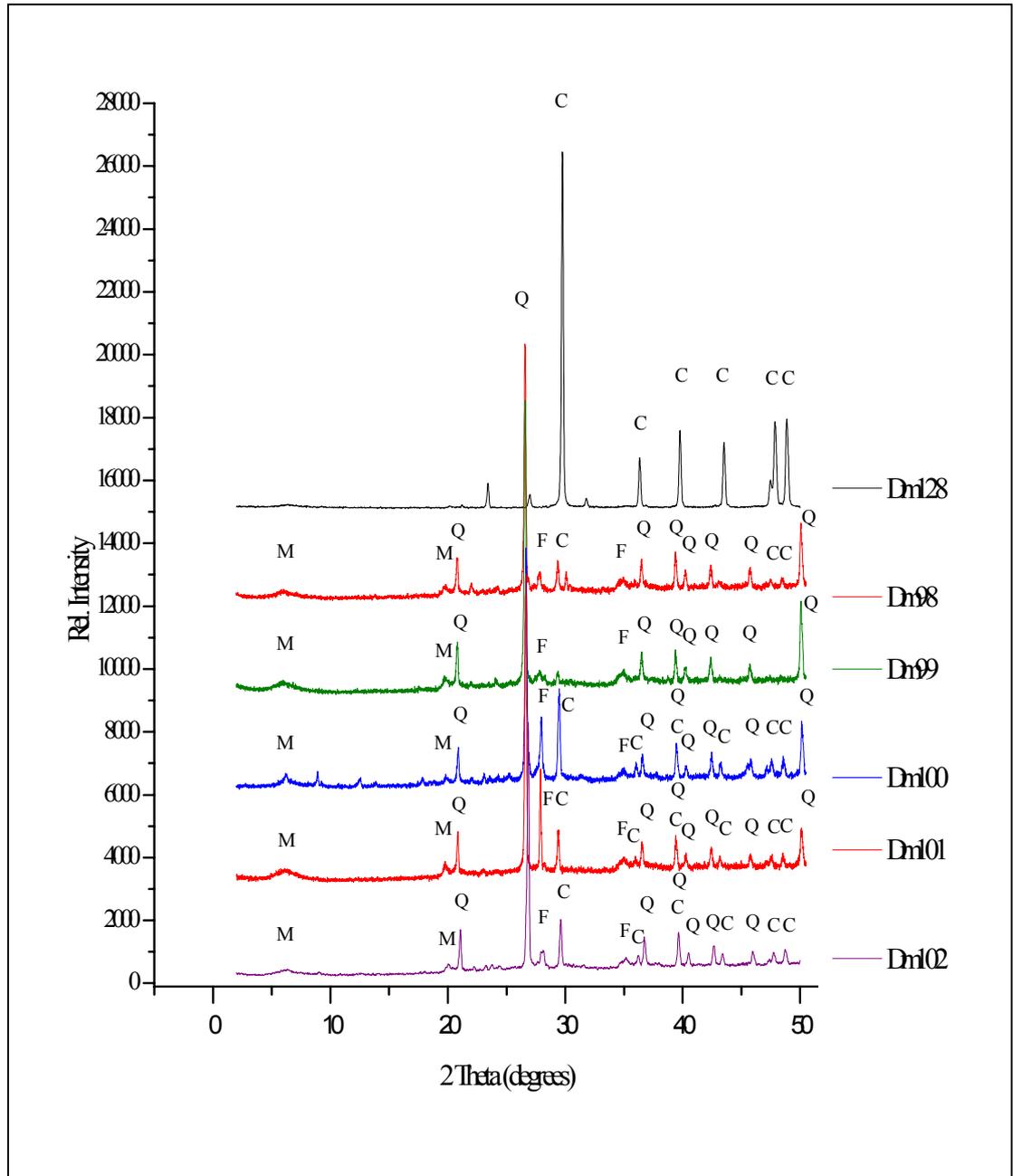
M: Montmorillonite, Q: Quartz, F: Feldspars, C: Calcite
Figure 3.3: 2 theta versus intensity graph of clay samples obtained in PXRD analyses.

The montmorillonite group comprises a number of clay minerals composed of t-o-t (tetrahedral-octahedral-tetrahedral) layers of both dioctahedral and trioctahedral type. [33]

Quartz is a kind of silica minerals. Virtually no solid solution exits between pyroxene and quartz, because of energetics of exchanging cations between octahedral and tetrahedral sites. Fe^{2+}-Mg^{2+} substitution affects the stability of quartz and pyroxene. Since these clays are rich in Fe, quartz is dominant as clearly seen from the diffraction patterns.

Calcite is generally the most common carbonate mineral in clays. It has trigonal (rhombohedral) system. In calcite and its isostructural carbonate, substitution is wide spread among the divalent cations. Calcites associated with dolomite can have several percent Mg^{2+} substitution for Ca^{2+}. [34]

In the Figure 3.3, it can be clearly seen that the PXRD pattern of the sample Dm128 is different than the patterns of other clay samples, Dm 98, 99, 100, 101, and 102. The presence of calcite peaks proves that Dm 128 is almost pure calcite. On the contrary, other raw clays consist of mostly quartz and also feldspars, and montmorillonite minerals. When compared, Dm 100 has more calcite than Dm 98, 99, 101, and 102. In addition, Dm 98 and 99 have the least calcite content. While calcite differs, other minerals seem more or less equal in amount.

The conclusions obtained from PXRD patterns (Figure 3.3) and from FTIR spectra (Figure 3.2) of raw clays are consistent with each other. However, it is rather easy and more convenient to use the PXRD method for mineral determinations for clays since FTIR peaks are broader making them difficult to differentiate. In other words, resolution of PXRD is better, and FTIR can be used as a complementary method.

In figure 3.4, PXRD patterns of pink and white colored common wares and white amphora are given. These are the samples having lighter colors than the ceramic samples having red coloration. In their patterns, the peaks of quartz and

feldspars occur for all samples. In addition, they have peaks of calcite, pyroxene and hematite with different amounts. The peaks with d-spacings of 2.70, 2.52, 3.68 and 1.84 belong to the mineral hematite while pyroxene has peaks at 2.99, 2.95, and 2.90. Among these minerals differing, the most important one is pyroxene, because it is almost an indication for light colored samples. Furthermore, the mineral montmorillonite does not occur in these light colored samples, except in Dm 208 which is observed to be pure.

When all the PXRD patterns of ceramics, two theta versus relative intensity plots, were analyzed as illustrated in Figure 3.4, 3.5 and 3.6, fingerprint similarity is recognized for the light colored (white and pink colored) ceramics including also the amphora having light colors, as shown in Figure 3.4. The similarity occurs at the group of peaks at around two theta of 30°, where there are peaks of pyroxene with d-spacings of 2.99, 2.95, and 2.90. However, there are two samples different than the others in light colored samples, which are Dm219 and Dm208, because they don't have pyroxene peaks. When these two samples observed, it is seen that among the light colored samples just these two ceramics are claimed to be made of pure clay that is without black inclusions. Thus, it can be considered as a proof that the pyroxene in these samples come from an added temper, which is possibly the black sand having mostly pyroxene in it. But another explanation could be that the pyroxene might be formed during firing by the usage of Ca rich clays.

In the previous study with Sinopean amphora, the black sand collected from Demirci was also investigated. The PXRD pattern of it showed that it consists of Augite (mostly), Diopside and Hedenbergite mineral species, all of which are grouped as Pyroxene minerals. In that study, red inclusions were also investigated, and it was observed that they mainly involve Hematite. [3] The mineral hematite does not come out as the origin of red color in our ceramics whereas the pyroxene seems to be an indication of the white color in ceramic samples.

46
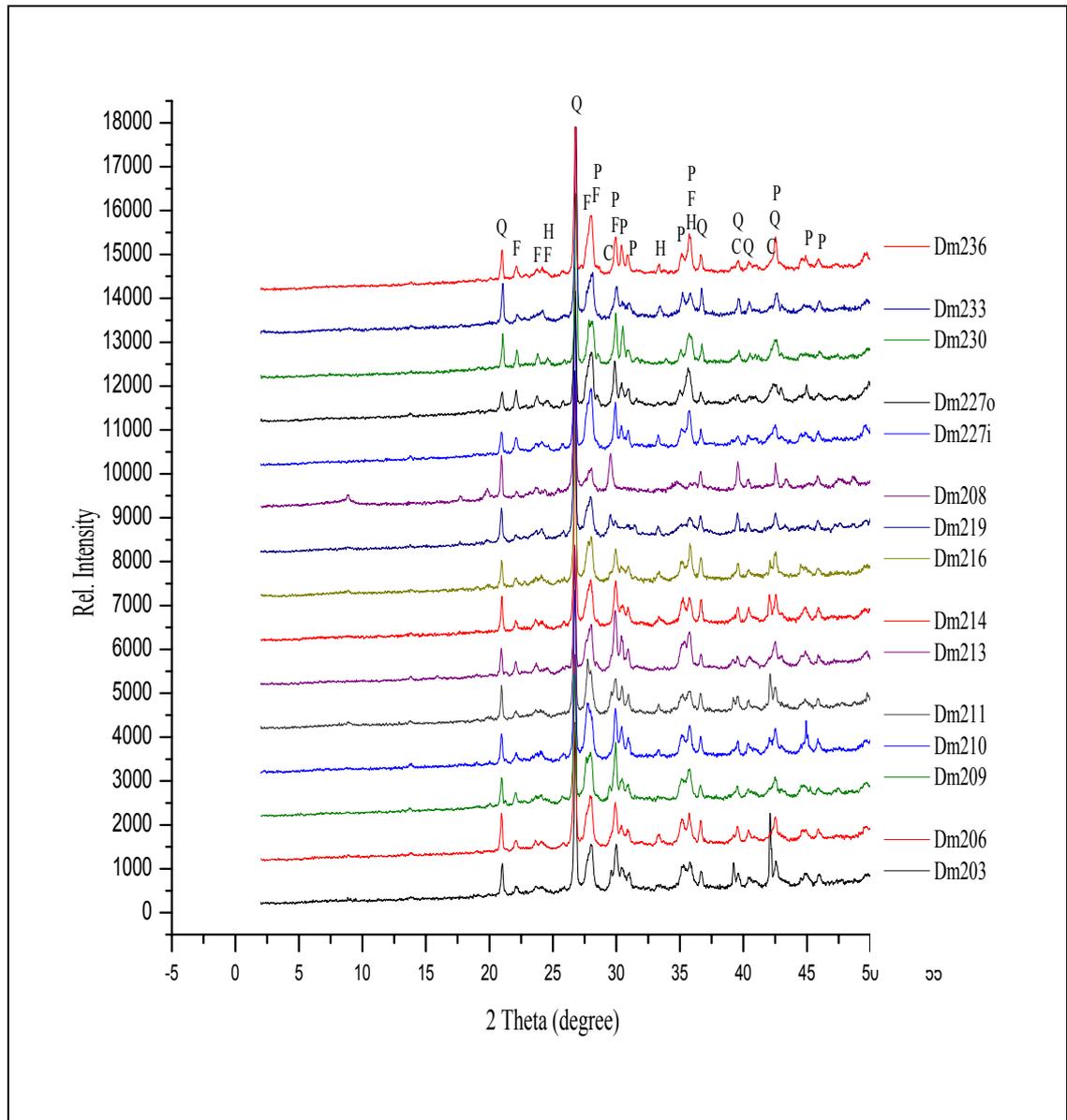
Q: Quartz, F: Feldspars, H: Hematite, P: Pyroxene, C: Calcite

Figure 3.4: The PXRD patterns of pink and white colored common wares and white amphora

In the figure 3.5, PXRD patterns of some red colored common wares are given. In these patterns, the peaks of quartz, feldspars, and calcite are observed for all samples. However, the peaks of montmorillonite, hematite and pyroxene occur only in some. Even though for some samples the pyroxene peaks at around two theta of 30° is observed, these peaks are not as intense as for the light colored samples. In the red colored samples, hematite peaks are more intense than in light colored ones.
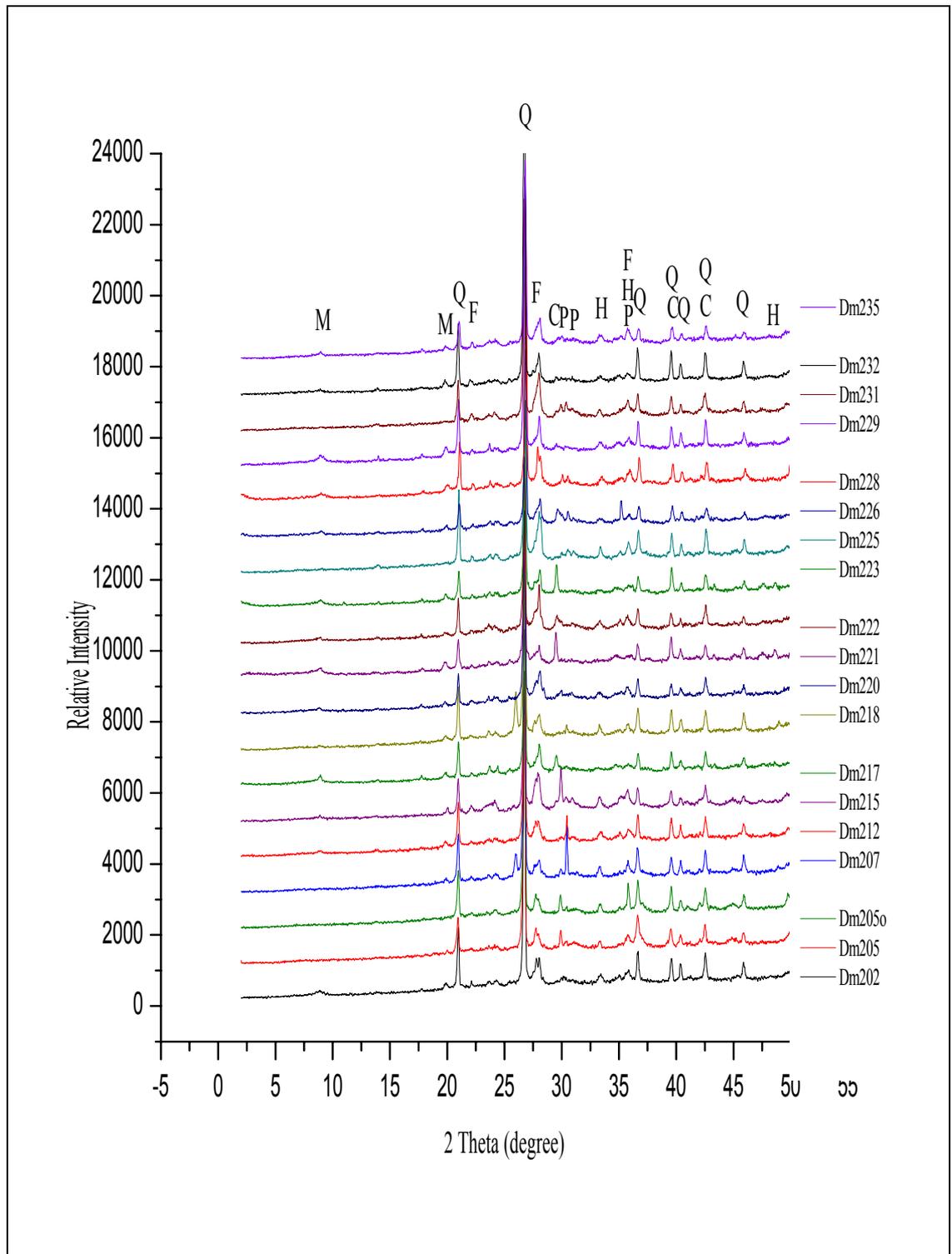
M: Montmorillonite, Q: Quartz, F: Feldspars, H: Hematite, P: Pyroxene, C: Calcite

Figure 3.5: The PXRD patterns of some red colored common wares
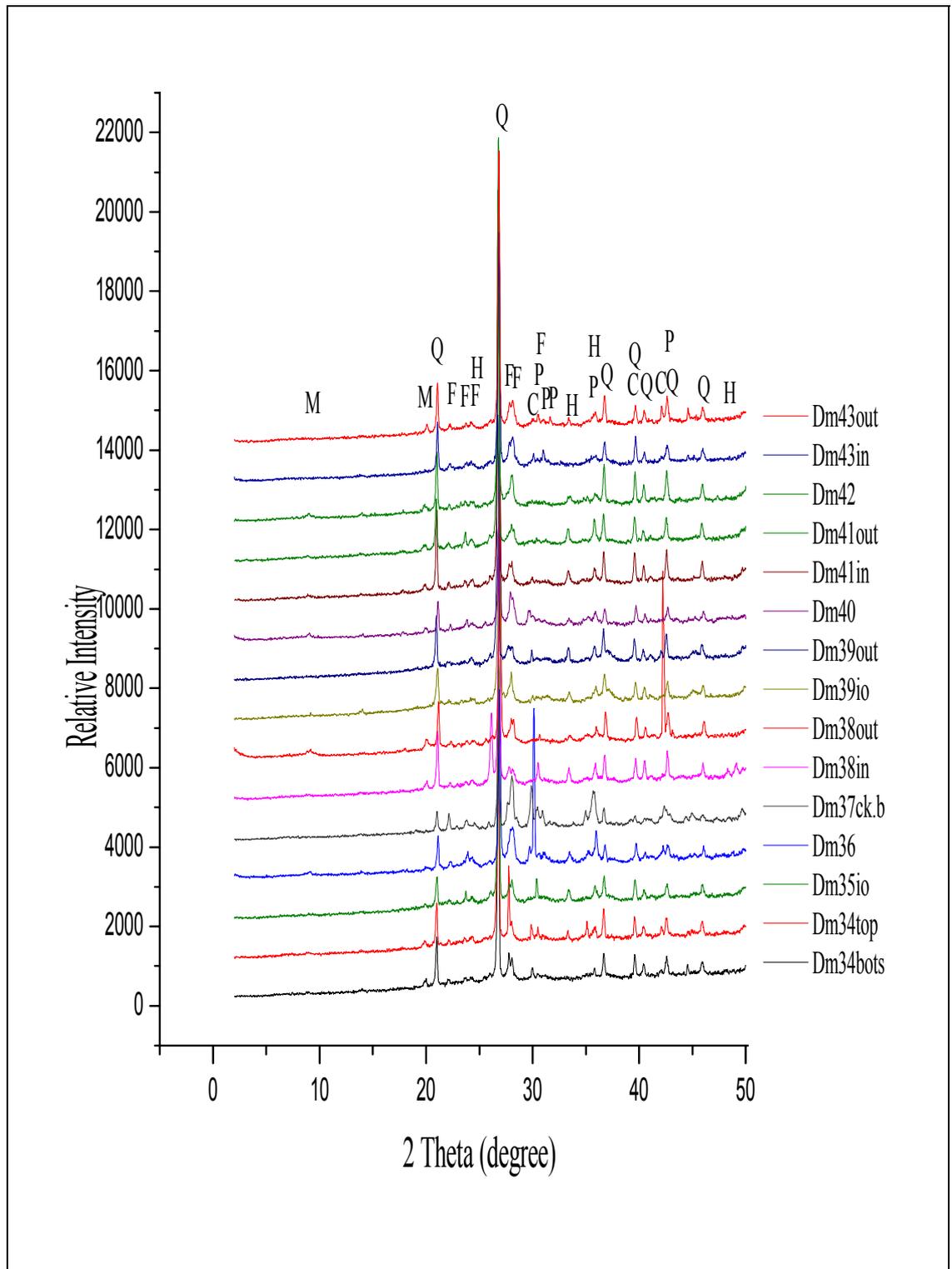
M: Montmorillonite, Q: Quartz, F: Feldspars, H: Hematite, P: Pyroxene, C: Calcite

Figure 3.6: The PXRD patterns of some red and layered common wares

In the Figure 3.6, PXRD patterns of some red and layered common wares, and a black colored ceramic (Dm37) are shown. In most of these samples, layers are observed due to different coloration. When possible these samples were separated into its layers prior to the experiments. The peaks of quartz and feldspars occur in all patterns. However, the presence and intensity of the peaks for montmorillonite, hematite, pyroxene and calcite vary.

As a difference from the light colored samples, these red and layered samples do not have or have very little peaks of pyroxene, except Dm 37. The black sample Dm 37c.b shows similar pattern with the light colored ones. Even though it has black color, its pattern resembles the patterns of the light colored ones since it has recognizable peaks of pyroxene.

When the variations in between two layers of a sample is investigated, it is seen that while different layers of some samples (Dm 41in and Dm 41out) show almost same patterns, some of them (Dm 43in and Dm43 out) show slight differences, and some (Dm 38in and Dm 38out, Dm 34top and Dm 34 bottom) has recognizable different peaks.

The Figure 3.7 shows the PXRD patterns of two red colored amphoras, Dm 204 and Dm 201. In both patterns, the peaks of quartz, feldspars, pyroxenes, hematite, montmorillonite and calcite are observed. The intensities, related with the amount of minerals, of the peaks of pyroxene and hematite are almost the same. Moreover, the montmorillonite and calcite peaks are very small. Although they have recognizable pyroxene peaks (but still smaller than the light coored ones have), they are red in color.
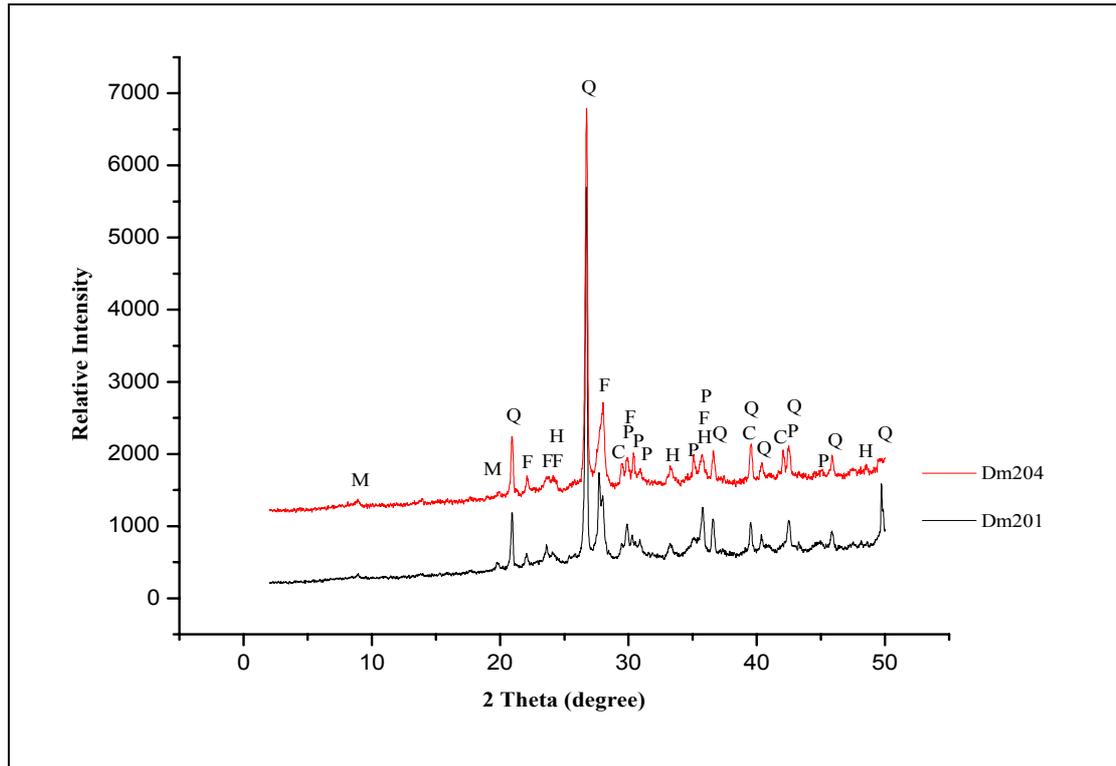
M: Montmorillonite, Q: Quartz, F: Feldspars, H: Hematite, P: Pyroxene, C: Calcite

Figure 3.7: The PXRD patterns of red colored amphora

By investigating all the PXRD patterns, it can be concluded that the differentiation is possible according to the clay type used. The PXRD patterns for the pink and white colored ceramics are easy to recognize and differentiate from the PXRD patterns of red colored ceramics. The patterns of the red ones do not have the similar peak groups with the light colored ones. These are the peaks at two theta of 30° belonging to pyroxene whether it comes from black sand added as temper or is formed during firing by usage of Ca-rich clays.

In addition, the presence or absence of montmorillonite peaks gives an idea about the firing temperature. Since the raw clays used have montmorillonite in them, we expect ceramics to have this mineral also. However, in some ceramics, especially the light colored ones, there is no peak of montmorillonite. It is known that montmorillonite starts to lose its crystallinity above 700 °C, and between 950 and 1000 °C it is used up in chemical reactions. As a result, it can be concluded that the samples having patterns without montmorillonite peaks had been fired at

temperatures higher than 950 ^{o}C whereas the ones with montmorillonite peaks in their PXRD patterns had lower firing temperatures.

3.4- Reaction Observations by Thermal Gravimetric Analysis (TGA):

The differential of the weight of the samples during the temperature increase throughout the thermal gravimetric analyses (TGA) are shown in Figure 3.8. The peak observed around 800 C^{o} is a result of the calcination reaction occurring due to the change in the temperature. The size of this curve changes with the change of the amount of calcite mineral in the samples. Thus, the integral area of this curve would give an idea for the amount of calcite. As it is clearly seen from figure 3.8, the amount of calcite is higher in Dm 128 clay than in the others.

Calcination: $CaCO_3 \rightarrow CaO + CO_2(g)$ ~ 800 ^{o}C
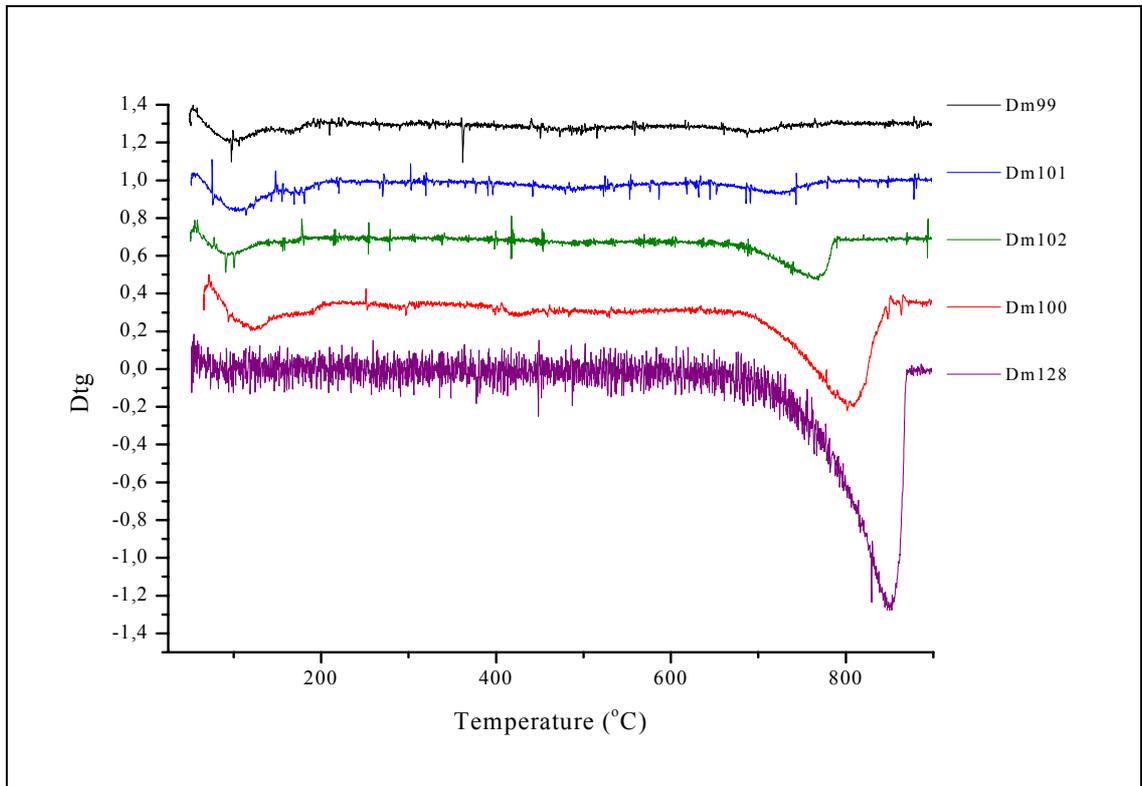
Figure 3.8: Temperature versus differential of weight (Dtg) graph for clay samples obtained by the TG analyses.

3.5- Scanning Electron Microscope (SEM)

Scanning electron microscopic views of four representative samples were shown in the following figures. The surface views were obtained to observe the particles and their sizes.

In the following figures, it is observed that particle sizes vary from 1 to 10 micron scale. However, for the vitrification investigations thin sections should be used during the analysis instead of the powder forms of samples.

Figure 3.9: SEM views of Dm 99 rc at 1 and 10 micron scales, respectively.
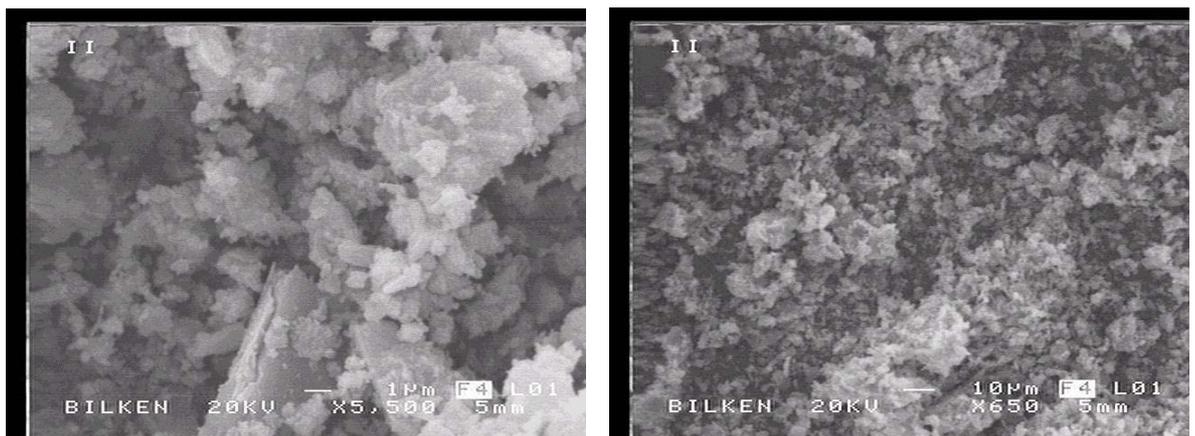
Figure 3.10: SEM views of Dm 203 cw.w at 1 and 10 micron scales, respectively.

Figure 3.11: SEM views of Dm 36 ck.r at 1 and 10 micron scales, respectively.
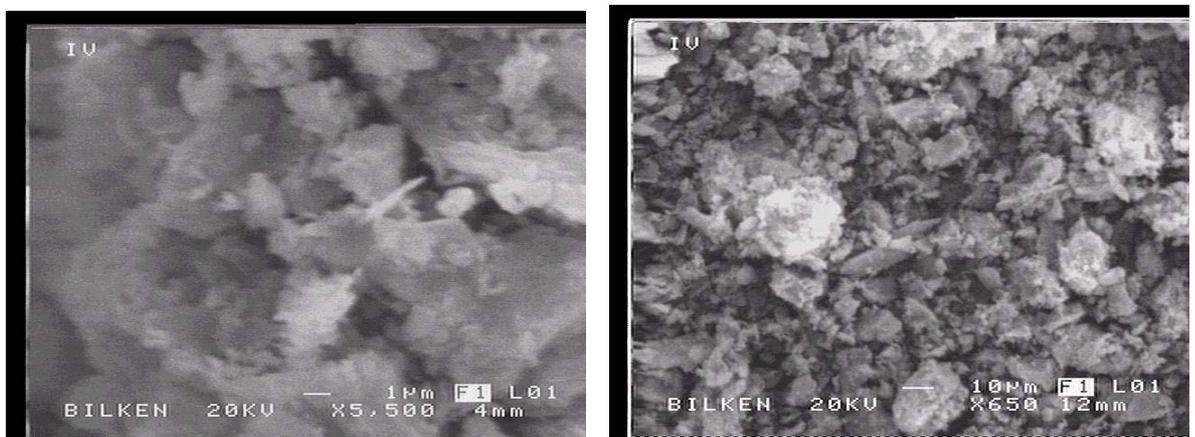
Figure 3.12: SEM views of Dm 42 ck.r at 1 and 10 micron scales, respectively.

From the SEM views, not much results were obtained in this study because the samples were grinded in a mortar. If these analysis were done by using thin sections, more results could be obtained. An improved SEM instrument combined with a XRF instrument would be the best for this kind of petrographical analysis.

3.6- STATISTICAL INTERPRETATION

3.6.1- Principal Component Analysis (PCA)

PCA were done by taking the raw clay and common ware samples as objects and element concentrations as variables. By PCA grouping of the similar samples can be done. It is easier to differentiate points grouped on a plot rather than dealing with the comparison of thousands of numerical data. For the application of PCA, Statistical Analysis Software (SAS) was used. It is a software package that you can run in unix by writing a code. The concentration of each element for each sample is used as raw data. PCA is a complementary method widely used in applied spectroscopy to interpret the results easily. The data obtained from the XRF analyses are used for provenance determinations in literature also. [35, 36]

To run the SAS, the data is written in the matrix form and then program gives the principal components by using the eigenvalues. As a result, similar samples found closer in distance forming groups in the graphs. Graphs are the two dimensional projection of the sample variations.

The Table 3.3 shows the principal components from the first PCA for including only Demirci samples. In the Figure 3.13, principal component 1 versus principal component 2 graph obtained by running the SAS for PCA for the samples excavated at Demirci is given. It is clearly seen that ceramics that had not been used for cooking and ceramics that had been used as a cooking pot can be clearly differentiated as Group 1 and Group 2. So we can conclude that depending on the purpose of usage even ceramics from the same origin can be differentiated as groups by the PCA method. This is most probably the result of the added temper to strengthen the raw clay used for the production of these ceramics.

Furthermore, the samples taken from different layers of the same ceramic sample are found to be very close indicating almost the same elemental composition between the layers of a ceramic.

Table 3.3: Principal Components from the output of PCA for Figure 3.13

Sample	Prin1	Prin2	Prin3
Dm34t	1 .93215	-1 .55249	-1 .06232
Dm34b	2 .52135	-0 .35495	0 .45529
Dm35io	2 .01173	1 .25484	-1 .36573
Dm36	-1 .47637	0 .17552	0 .88748
Dm 37	-1 .25446	1 .06983	-0 .69429
Dm 38i	3 .16269	0 .72859	-0 .30395
Dm 38o	2 .97232	-0 .52207	0 .63798
Dm 39io	2 .79162	0 .68975	0 .18390
Dm 39o	3 .10462	0 .24736	-0 .24716
Dm 40	-2 .53008	-0 .21222	0 .07480
Dm 41i	2 .59588	-1 .91824	1 .15622
Dm 41o	2 .72005	-0 .73474	0 .35534
Dm 42	2 .41737	-1 .82987	0 .84409
Dm 43i	1 .25880	0 .01961	0 .17016
Dm 43o	1 .45960	0 .10081	0 .29580
Dm 98rc	0 .58916	-3 .24460	0 .32719
Dm 99rc	2 .33945	-1 .53041	0 .57136
Dm 100rc	-4 .60113	-4 .20942	-0 .24966
Dm 101rc	2 .42618	-0 .08835	-0 .28272
Dm 102rc	-2 .65250	-4 .48835	-0 .89041
Dm 201	-0 .61576	1 .57892	-2 .21507
Dm 202	3 .44085	-1 .22722	-1 .12135
Dm 203	-1 .94428	0 .70779	-3 .77410
Dm 204	-0 .68746	1 .97580	-4 .31728
Dm 205	2 .43073	0 .56321	-3 .64863
Dm 205o	1 .74268	-0 .12110	-1 .61813
Dm 206	-2 .90096	0 .04865	0 .20919
Dm 207	3 .21999	0 .68303	1 .69598
Dm 208	-3 .03887	1 .55161	-0 .44898
Dm 209	-2 .34825	-1 .32696	1 .71105
Dm 210	-2 .20966	1 .78591	1 .07868
Dm 211	-2 .14940	1 .75545	0 .38997
Dm 212	2 .49927	0 .02959	0 .21841
Dm 213	-4 .03819	-0 .82684	0 .50354
Dm 214	-2 .56212	0 .36686	0 .99843
Dm 215	-1 .55223	1 .03410	0 .82201
Dm 216	-3 .03387	1 .44539	1 .91208
Dm 217	-1 .46128	1 .36787	1 .03263
Dm 218	3 .81972	1 .50117	1 .02010
Dm 219	-0 .99580	3 .20286	-0 .16389
Dm 220	-1 .01092	1 .75607	0 .66992
Dm 221	-0 .09035	1 .80618	1 .89063
Dm 222	-1 .43127	1 .26696	0 .49278
Dm 223	-1 .58982	0 .67743	1 .16002
Dm 225	0 .99194	-3 .24179	-0 .19291
Dm 226	-3 .19211	-0 .65153	0 .36095
Dm 227i	-1 .70237	-0 .78832	-0 .42519
Dm 227o	-2 .37790	-0 .14184	-1 .10697
Dm 228	2 .55001	1 .14656	0 .61220
Dm 229	2 .68326	1 .46040	0 .47571
Dm 230	-3 .01075	-2 .32988	-1 .52289
Dm 231	-0 .09013	-0 .54316	0 .57745
Dm 232	2 .14412	-3 .22115	0 .67086
Dm 233	-1 .54919	0 .83710	0 .47416
Dm 235	0 .13236	2 .23837	0 .35267
Dm 236	-1 .86042	0 .03187	0 .36257
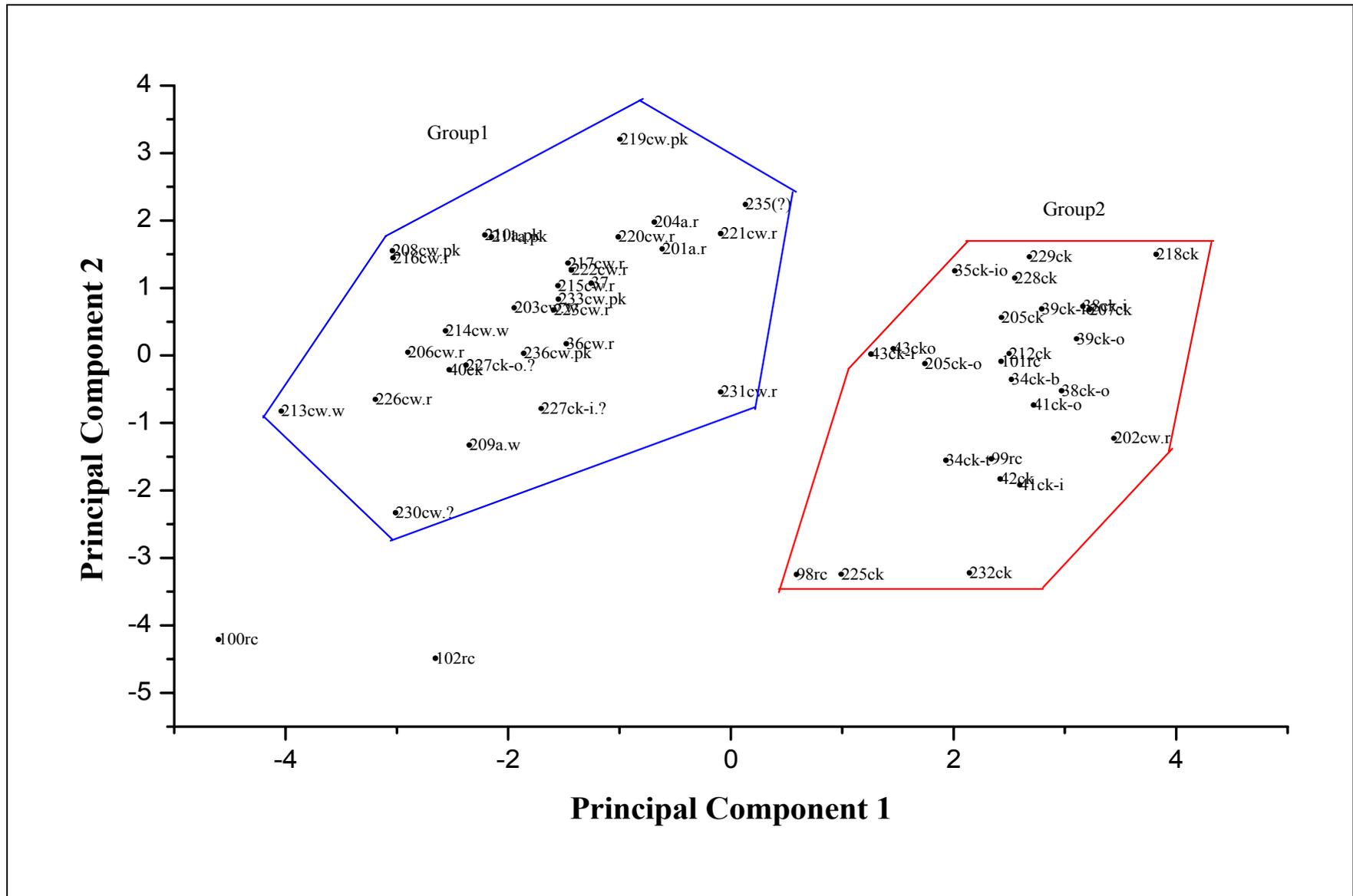
Figure 3.13: Principal component 1 versus 2 obtained from SAS program.

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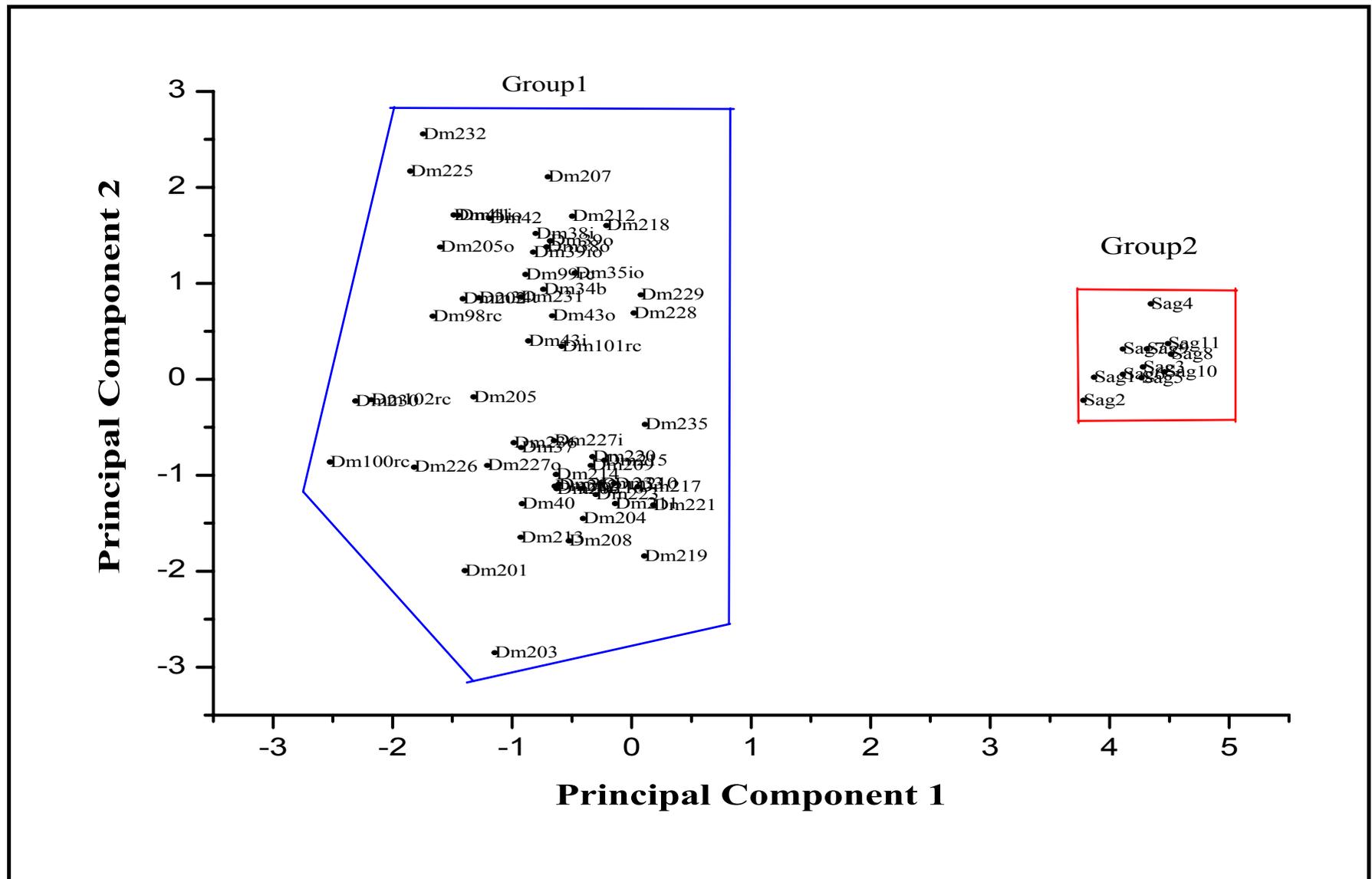
Figure 3.14: Principal component 1 versus 2 obtained from SAS program.

PCA is not only used for gouping of samples from one origin but also by applying to samples from different origins provenance studies can be done. Sometimes ceramics from different provenances may look similar in shape and appearance. To see whether it is possible to differentiate between these kinds of samples, PCA was applied in this study for samples having same morphological properties of same period, but differ in location. For this reason, elemental concentrations of ceramic samples excavated at different regions of Turkey but having same shapes of a period was used altogether. A group consists of the samples from Northern part of Turkey whereas the other group consists of some samples from Southern part of Turkey. These are from Demirci and Sagalassos excavations, respectively.

In the Figure 3.14, principal component 1 versus principal component 2 graph obtained by running the SAS for PCA for the samples excavated at both Demirci and Sagalassos are given. The elemental compositions of the Sagalassos ceramics were obtained from the experimental (bulk analysis) data reported in 'Sagalassos IV Report on the Survey and Excavations Campaigns of 1994 and 1995', which was edited by M. Waelkens and J. Poblome, on page 514. [37] The element concentrations for Sagalossos ceramics are tabulated in the Table 3.4.

It is important to run the SAS for PCA by including the data of Sagalassos, because Sagalassos is located also in Turkey (but in the Southern part) and the period of production for some of the ceramic samples of Sagalassos are the same with the production period of Demirci ceramics.

As a result, it is clearly seen from the Figure 3.14 that Demirci and Sagalassos ceramic differ into two distinct groups according to the locations. Even though the period of production is same for some of Sagalassos and Demirci ceramics, and also they have similar shapes and morphologies, production center determines the characteristic properties of the ceramics since the raw clays used during production varies for different locations.

Table 3.4: The element concentrations for the Sagalossos ceramics

Sample Assemblage	Concentration (%)									
	Si	Al	Fe	Mn	Mg	Ca	Na	K	Ti	P
1	24.92	8.16	5.55	0.09	3.85	5.72	0.62	2.42	0.70	0.10
2	24.19	7.94	5.67	0.08	3.81	6.45	0.72	2.16	0.71	0.14
3	24.43	8.55	5.74	0.08	4.17	5.80	0.73	2.22	0.75	0.10
4	25.37	8.64	5.88	0.08	3.97	4.34	0.75	2.32	0.77	0.09
5	24.16	8.71	5.76	0.06	3.99	6.10	0.73	2.21	0.75	0.09
6	24.36	8.44	5.55	0.08	4.02	5.75	0.74	2.33	0.74	0.14
7	24.11	8.58	5.69	0.07	3.94	5.00	0.79	2.26	0.74	0.12
8	24.33	8.52	5.94	0.08	3.98	5.67	0.79	2.33	0.78	0.11
9	24.60	8.38	5.82	0.08	4.17	5.29	0.78	2.29	0.75	0.12
10	24.40	8.45	5.88	0.07	4.09	6.06	0.84	2.34	0.76	0.12
11	24.62	8.67	5.93	0.07	4.14	5.40	0.72	2.25	0.77	0.10

3.5.2- Cluster Analysis

Cluster analysis is another widely used method as a classification tool. In this analysis, a hierarchical tree plot is obtained. It begins with each object in a class by it self and finally all objects are joined together by relaxing the criterion of similarity. In these plots, the vertical axis denotes the linkage distance. Similar samples forms clusters reflected in the hierarchical tree as distinct branches. As the result of a successful analysis with the joining method, one is able to detect clusters (branches) and interpret those branches. For this analysis Statistical Analysis Software is used as in the PCA method.

In the following tables, Table 3.5 and Table 3.6, output of the cluster analysis obtained by a SAS run is tabulated. By using these outputs tabulated, the cluster history including the samples joined into clusters and the linkage distances, the hierarchical tree was plotted as shown in Figure 3.15. In this dendogram, there are groups occuring as braches. From left to right subgroups are such that:

As a first group, all Sagalassos samples (from Sag1 to Sag 11) form a cluster. Demirci samples vary from Sagalassos samples. All of the Demirci samples are located on the right of Sagalassos samples in the dendogram. The brach including Dm 235, 222, 233, 217, 40, 36, 220, and 223 forms the second group. In this second group, six out of eight samples are common wares having red color, except one.One of the two outliers is a fragment of a cooking pot with soft surface and the other one is an unknown type, either a common ware or a cooking pot.

Dm 227o, 213, 210, 214, 206, 211, 226, 215, 216, 227i, 236, 37, and 209 appear as the third group. In this group, ten out of thirteen samples have light colors (pink and white). Other three have orange, red and black color. Seven samples of this group are common wares, three are amphora, and one is cooking pot and two other are unknown type.

The fourth group starts with Dm 43i and ends with Dm 100rc from left to right. Seventeen out of twenty five samples are cooking wares, five are raw clays, and three are common wares. The ceramics in this group are all red except one.

All others on the right form the last group. In this group Dm 207, 225, and 232 seem like another subgroup since they are all cooking pots. The other seven are; four common wares, two amphoras, and a cooking pot. Dm 208 and 219, which are the only light colored pure common ware samples, come together in a branch.

As a result, it can be concluded that the first Sagalassos group and all other groups which are Demirci samples differs according to the location. Further observations show that there are also subdivisions in Demirci group acoording to color and function of the ceramic with some outliers. For example, the second and third group together seems as the group of common wares and the other groups in

Demirci samples are mostly cooking wares. Furthermore, common wares of Demirci are also subdivided according to their colors. The second group consists of red colored commonwares while the third group consists of light colored common wares.

All the raw clay samples are found in between the cooking wares, far from the common wares. Thus, it can be concluded that during the production of common wares materials other than the raw clays had been used. Addition of a temper, whether black sand or Ca-rich clays, can be the reason for that.

In addition to the investigation of different types, samples separated into two layers are investigated. In some samples (e.g. Dm 34, Dm 39), two layers of a sample come together at a first branching meaning that they are the most similar ones. However, sometimes two layers of a sample do not combine at a first branching.

The last group seems like the group of outliers, but there are still subgroups such as Dm 208 and Dm 219 which have similar characters. In addition, there are only two red colored amphora and they are in this last group, not separated far away.

It is more difficult to work out the clusters in cluster analysis than to differentiate the groups in PCA. The interpretation of the data in the cluster analysis requires more experience or improved graphic softwares for the dendogram plots. However, as a result, one can still easily recognize that Sagalossos wares form a cluster as a branch in the left side and Demirci wares on the right side, as shown in the dendogram in Figure 3.15.

Table 3.5: The SAS System The CLUSTER Procedure
Average Linkage Cluster Analysis

```
            Eigenvalues of the Covariance Matrix
         Eigenvalue     Difference     Proportion     Cumulative

  1     27.8480895     23.7587187        0.7806         0.7806
  2      4.0893708      1.2533596        0.1146         0.8952
  3      2.8360112      2.0632588        0.0795         0.9747
  4      0.7727524      0.6625924        0.0217         0.9963
  5      0.1101600      0.0901239        0.0031         0.9994
  6      0.0200360      0.0197352        0.0006         1.0000
  7      0.0003008                       0.0000         1.0000


Root-Mean-Square Total-Sample Standard Deviation = 2.257582
Root-Mean-Square Distance Between Observations   = 8.447097



                    Cluster History
                                            Norm    T
                                            RMS     i
  NCL      --Clusters Joined---    FREQ     Dist    e

   66     Sag3        Sag6           2      0.0356
   65     Sag9        Sag11          2      0.0395
   64     CL66        Sag8           3      0.0448
   63     Sag5        Sag10          2      0.0486
   62     Dm39io      Dm39o          2      0.0527
   61     CL64        CL63           5      0.0556
   60     Dm41i       Dm42           2      0.0689
   59     Dm222       Dm233          2      0.0715    T
   58     Dm210       Dm214          2      0.0715
   57     Dm206       Dm211          2      0.0725
   56     Dm43i       Dm101rc        2      0.0772
   55     Dm38o       CL62           3      0.0799
   54     Sag7        CL65           3      0.0821
   53     CL61        CL54           8      0.0937
   52     CL60        Dm41o          3      0.0974
   51     Dm227i      Dm236          2      0.0998
   50     Dm36        Dm220          2      0.1034    T
   49     Sag1        CL53           9      0.1034
   48     CL57        CL58           4      0.1062
   47     Dm217       CL59           3      0.1182
   46     Dm35io      Dm99rc         2      0.1239
   45     Dm37        CL51           3      0.1276
   44     CL49        Sag2          10      0.1364
   43     CL46        CL55           5      0.1468
   42     Dm102rc     Dm230          2      0.1519
   41     Dm215       Dm216          2      0.1542
   40     CL50        Dm223          3      0.1596
   39     Dm34t       Dm34b          2      0.1625
   38     Dm228       Dm229          2      0.1705
   37     Dm208       Dm219          2      0.1804
   36     CL48        Dm226          5      0.182
   35     Dm100rc     CL42           3      0.1873
   34     CL52        Dm205o         4      0.1915
```

Table 3.5 (*continued*) : The SAS System The CLUSTER Procedure
Average Linkage Cluster Analysis

```
                     Cluster History
                                              Norm    T
                                              RMS     i
    NCL     --Clusters Joined---      FREQ    Dist    e

    33     Dm40        CL47            4      0.1944
    32     CL45        Dm209           4      0.1989
    31     CL40        CL33            7      0.2029
    30     Dm98rc      Dm231           2      0.205
    29     CL43        Dm38i           6      0.2097
    28     CL44        Sag4           11      0.2117
    27     CL29        Dm218           7      0.2189
    26     CL31        Dm235           8      0.2299
    25     Dm201       Dm203           2      0.2356
    24     CL36        Dm213           6      0.2375
    23     CL39        Dm43o           3      0.2446
    22     CL34        Dm212           5      0.2473
    21     CL24        CL41            8      0.2508
    20     CL56        CL38            4       0.262
    19     CL23        CL20            7      0.3101
    18     CL21        Dm227o          9      0.3162
    17     CL32        CL18           13      0.3252
    16     Dm207       Dm225           2      0.3264
    15     CL22        CL30            7      0.3441
    14     Dm204       Dm205           2      0.3989
    13     CL27        CL15           14      0.4486
    12     CL26        CL28           19      0.4805
    11     CL19        Dm202           8      0.494
    10     CL37        Dm221           3      0.4975
     9     CL12        CL17           32      0.5678
     8     CL16        Dm232           3      0.569
     7     CL13        CL35           17      0.6444
     6     CL11        CL9            40      0.6533
     5     CL25        CL10            5      0.6823
     4     CL5         CL14            7      0.8207
     3     CL6         CL7            57      0.9555
     2     CL3         CL4            64      1.3624
     1     CL2         CL8            67      1.7505
```

Table 3.6 : Two-Cluster Solution\ by cluster

Sample	CLUSTER	CLUSNAME	sample	CLUSTER	CLUSNAME
Sag3	1	CL2	Dm215	1	CL2
Sag6	1	CL2	Dm216	1	CL2
Sag9	1	CL2	Dm223	1	CL2
Sag11	1	CL2	Dm34t	1	CL2
Sag8	1	CL2	Dm34b	1	CL2
Sag5	1	CL2	Dm228	1	CL2
Sag10	1	CL2	Dm229	1	CL2
Dm39io	1	CL2	Dm208	1	CL2
Dm39o	1	CL2	Dm219	1	CL2
Dm41i	1	CL2	Dm226	1	CL2
Dm42	1	CL2	Dm100rc	1	CL2
Dm222	1	CL2	Dm205o	1	CL2
Dm233	1	CL2	Dm40	1	CL2
Dm210	1	CL2	Dm209	1	CL2
Dm214	1	CL2	Dm98rc	1	CL2
Dm206	1	CL2	Dm231	1	CL2
Dm211	1	CL2	Dm38i	1	CL2
Dm43i	1	CL2	Sag4	1	CL2
Dm101rc	1	CL2	Dm218	1	CL2
Dm38o	1	CL2	Dm235	1	CL2
Sag7	1	CL2	Dm201	1	CL2
Dm41o	1	CL2	Dm203	1	CL2
Dm227i	1	CL2	Dm213	1	CL2
Dm236	1	CL2	Dm43o	1	CL2
Dm36	1	CL2	Dm212	1	CL2
Dm220	1	CL2	Dm227o	1	CL2
Sag1	1	CL2	Dm204	1	CL2
Dm217	1	CL2	Dm205	1	CL2
Dm35io	1	CL2	Dm202	1	CL2
Dm99rc	1	CL2	Dm221	1	CL2
Dm37	1	CL2	Dm207	2	CL8
Sag2	1	CL2	Dm225	2	CL8
Dm102rc	1	CL2	Dm232	2	CL8
Dm230	1	CL2			

Table 3.7: Five-Cluster Solution

CLUSTER=1	
sample	CLUSNAME
Sag3	CL6
Sag6	CL6
Sag9	CL6
Sag11	CL6
Sag8	CL6
Sag5	CL6
Sag10	CL6
Dm222	CL6
Dm233	CL6
Dm210	CL6
Dm214	CL6
Dm206	CL6
Dm211	CL6
Dm43i	CL6
Dm101rc	CL6
Sag7	CL6
Dm227i	CL6
Dm236	CL6
Dm36	CL6
Dm220	CL6
Sag1	CL6
Dm217	CL6
Dm37	CL6
Sag2	CL6
Dm215	CL6
Dm216	CL6
Dm223	CL6
Dm34t	CL6
Dm34b	CL6
Dm228	CL6
Dm229	CL6
Dm226	CL6
Dm40	CL6
Dm209	CL6
Sag4	CL6
Dm235	CL6
Dm213	CL6
Dm43o	CL6
Dm227o	CL6
Dm202	CL6

CLUSTER=2	
sample	CLUSNAME
Dm39io	CL7
Dm39o	CL7
Dm41i	CL7
Dm42	CL7
Dm38o	CL7
Dm41o	CL7
Dm35io	CL7
Dm99rc	CL7
Dm102rc	CL7
Dm230	CL7
Dm100rc	CL7
Dm205o	CL7
Dm98rc	CL7
Dm231	CL7
Dm38i	CL7
Dm218	CL7
Dm212	CL7

CLUSTER=3	
sample	CLUSNAME
Dm208	CL5
Dm219	CL5
Dm201	CL5
Dm203	CL5
Dm221	CL5

CLUSTER=4	
sample	CLUSNAME
Dm207	CL8
Dm225	CL8
Dm232	CL8

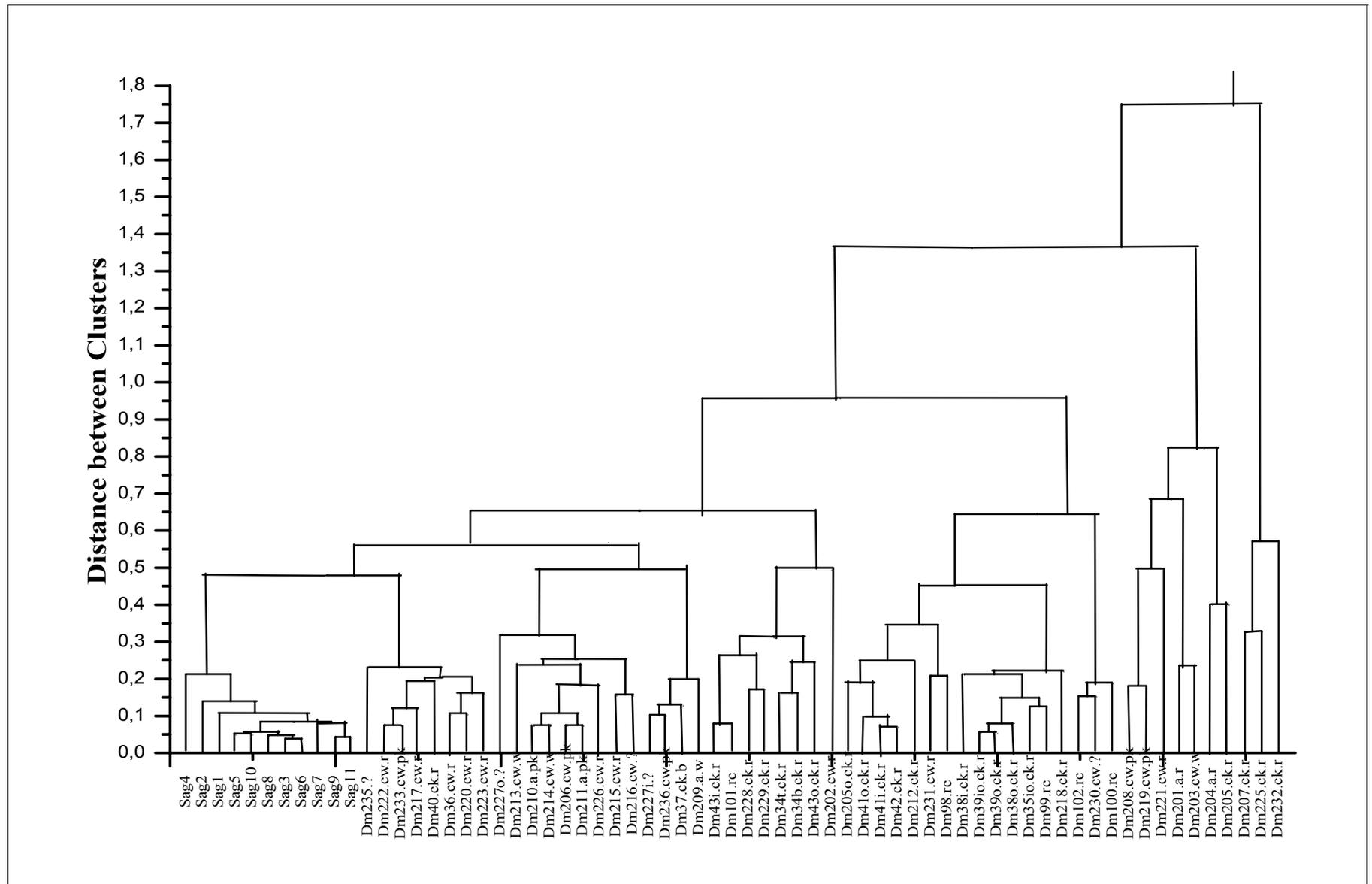| CLUSTER=5	
sample	CLUSNAME
Dm204	CL14
Dm205	CL14

Figure 3.15: Dendogram obtained by Cluster Analysis

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4. CONCLUSIONS

Chemical characterization of the clays taken from Demirci and of the common wares and potteries found by the archaeological excavations in Demirci region were made by the XRF, PXRD, FTIR, and TGA methods. Besides the spectroscopic and thermographic analysis, statistical methods were applied as a complementary study. The statistical methods, PCA and Cluster Analysis were done in order to interpret the data obtained by XRF analysis.

From the investigations of the elemental concentrations of Demirci samples, it is claimed that calcium (Ca) is the most important element having influence on color. When the concentration is higher than 6 %, light colors pink to white is observed. However, when its amount is less, reddish color is observed.

Among the clay samples, amount of Ca in Dm 128 was found to be much higher than in the other raw clays. By further chemical analysis it is found to be almost pure calcite. Thus, it is thought that this calcite-rich clay, taken from the archaeological kiln from the excavation field, had been taken from a lime source and used in a technique.

By FTIR spectroscopy, the presence of montmorillonite, feldspars, quartz, and calcite was observed. The spectra obtained were similar. By the comparison of the FTIR spectra of the clays and the common wares, it is observed that there are calcite peaks in clay samples but not in the spectra of common wares. As a result of this, it is concluded that firing temperature of the clay originated common wares is thought to be higher than the calcination temperature, 800 C$^{\circ}$.

In the FTIR spectra of some layered samples there was no distinction between two layers of a sample; however, element concentrations obtained from the XRF data show variations sometimes. According to this observation, it can be concluded that there occurs an elemental migration during firing.

From the PXRD experiments, the patterns obtained show different characters for the light colored (pink and white) and the red colored ceramic samples. By investigating all the PXRD patterns, it can be concluded that the differentiation is possible according to the clay type used during production. The PXRD patterns for the pink and white colored ceramics are easy to recognize and differentiate from the PXRD patterns of red colored ceramics. The light colored ceramics have pyroxene while the others not. The pyroxene may come from black sand added as temper or might be formed during firing when Ca-rich clays used as raw materials.

In addition, the presence or absence of montmorillonite peaks gives an idea about the firing temperature. Since in some ceramics, especially the light colored ones, peaks of montmorillonite are absent, it can be concluded that the samples having patterns without montmorillonite peaks had been fired at temperatures higher than 950 ^{o}C, at which montmorillonite deforms.

The conclusions obtained from PXRD patterns and from FTIR spectra are consistent with each other. However, it is rather easy and more convenient to use the PXRD method for mineral determinations for clays since FTIR peaks are broader making them difficult to differentiate whereas the resolution of PXRD is better.

TGA was only applied for the raw clays and it is used to observe the calcination reaction at around 800 ^{o}C. From TGA, it is clearly observed that the amount of calcite is higher in Dm 128 clay than in the others.

Statistical methods were used in this study to see whether the chemical analysis can be used for classification of ceramic samples. In this study, analyses were done

within Demirci samples and also by including samples from another location, Sagalassos.

By the PCA method, it is seen that even ceramics from the same origin can be differentiated as groups depending on the purpose of usage. This is most probably available because of the added temper to strengthen the raw clay used for the production of these ceramics.

In addition, the PCA with ceramics from different locations, Demirci and Sagalassos, shows that ceramics differ into groups according to the regions. Although the period of production, shapes and morphologies are same for some of Sagalassos and Demirci ceramics, production place determines the characteristics of the ceramics since the raw clays used during production varies for different locations.

Cluster Anaysis gives similar results as PCA. Also by this method, classification of samples according to the location is possible. Furthermore, there are subdivisions within Demirci group according to color and function of the ceramic, except some outliers. Moreover, common wares are also subdivided according to their colors.

Also, the raw clay samples are found in between the cooking wares, far from the common wares in the dendogram. Thus, it can be considered as a proof that during the production of commonwares materials other than the raw clays had been used. Addition of a temper, whether black sand or Ca-rich clays, can be the reason for that.

When the two statistical methods used in this study are compared, both of them give consistent results. The classification of samples, according to both the functionality and the location, is easy and possible by using the elemental concentrations obtained via chemical analysis with these complementary statistical methods. However, PCA is found to be better since it provides groupings easy to recognize on a plot rather than a dendogram.

As a result, the chemical methods used in this study can be applicable for classifications and characterizations. Statistical interpretations show that there is a clear distinction between the ceramics from Demirci and Sagalassos. These are the locations totally separated from each other, one region is in the north and the second region is in the south of Turkey. However, sometimes there are trade routes making the cases complicated. Because of the importations and exportations, the distinctions among the ceramics may not be as clear as in this case. For example, investigating the classifications among the ceramics from Demirci and Colchis is expected to be more complicated than in this study.

In addition, during this kind of studies multidisciplinary methods, including chemistry, archaelogy and petrography, will be the best way for better interpretations. As in this study, to find out the classes resulted from chemical analysis one should invoke the knowledge gained from the archaelogical observations. Furthermore, petrogaphic studies are required to be able to say where some elements in the samples are originated. To illustrate, to be able to find out whether the calcium is originated from the burial environment, the micritic calcite should be saught by the application of improved petrographic methods.

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APPENDIX

Sample Dm 201:

It has red and brown inclusions. There are also black inclusions which are smaller in size and more in exterior but bigger inside. Interior section has lighter color.

Sample Dm 202:
This sample is a small fragment compared to others which makes it hard to classify. It has both black, white and red inclusions.

Sample Dm 203:

This sample is white in color and it has very small black inclusions and big brownish red inclusion both inside and outside. There is no layer formation but slight pink color observed in down parts.

Sample Dm 204:

No layer formation observed in this sample. There are small black inclusions and also small white and red inclusions but less in amount.

Sample Dm 205:

There are layers in this sample: red outer and gray interior sections. This sample is divided into its layers for the analysis. There are many big white and black inclusions, and also red inclusions but less.

Sample Dm 206:

The sample is whitish in color but it has very small black inclusions. It also has big red and small white inclusions but less. Interior section is in pink.

Sample Dm 207:

It has brick-red color. Interior layer is gray in color. Blackening at the bottom due to usage for cooking. There are many inclusions generally black but also white and red.

Sample Dm 208:

It has orage-red color. There is layer formation observed in the cross section.

Sample Dm 209:

This sample is white whitout layers in color but it has big sized black inclusions. There are also very small red inclusions.

Sample Dm 210:
This sample is white in color, but also it has degradation of color to pinkish. It has a lot of big black inclusions.

Sample Dm 211:
This sample is white in color. There is a coloration from white to pink and inside is pink. There are black inclusions in different sizes but also there are small red inclusions less than the black ones.

Sample Dm 212:
This is a red colored ceramic. It has black interior which seems like something cooked inside. It has very small but many black, red and white inclusions.

Sample Dm 213:
This is mostly white in color. There are a lot of small, but also some big black inclusions.

Sample Dm 214:
This sample is white. It has very small black inclusions and big red inclusions but they are less.

Sample Dm 215:
This sample has orange-red color. There are less and small inclusions.

Sample Dm 216:
This is a sample with handle part. It has reddish color. There are a lot of black inclusions and some red inclusions.

Sample Dm 217:
This sample is orange-red in color. It has very small black inclusions.

Sample Dm 218:
This is a red sample. It has white calcerous formations on it indicating usage with water. But while not to get missleading results, this white portion did not included while grinding.

Sample Dm 219:
This sample has pinkish color. It is observed to be made of a pure clay. It has no inclusion.

Sample Dm 220:
This sample is red in color and seems to be made of almost pure clay. However, it has very less red, black and white inclusions.

Sample Dm 221:
This sample has orange-red color. There are small black, white and brownish inclusions, but not much.

Sample Dm 222:
This sample is red sample. It is part of body with handle. There are a lot of big black, white and red inclusions in the handle part, but in the body there are less inclusionsthan in the handle, but still much. Sample portion grinded for the analysis was taken from the body not the handle part.

Sample Dm 223:
This is a circular bottom of a plate. It is orange in color. There are big brown inclusions, and some small black inclusions.

Sample Dm 225:
This sample has brownish-red color. There are a lot of small white and less black, and also some red inclusions.

Sample Dm 226:
This is a red colored sample. It has small and middle sized black inclusions.

Sample Dm 227:
This sample has two layers. The exterior layer has gray color and it has small black inclusions. The interior layer has color in between white, yellow and pink, and it has small black and red inclusions.

Sample Dm 228:
This is sample is red in color but its bottom has dark brown firing signs. It has a lot of black inclusions, some red and also some white inclusions.

Sample Dm 229:
This is orange-red in color. There are big black, red and white inclusions.

Sample Dm 230:
This sample has greenish surface and black-gray inside, indicating problem of firing conditions. There are black inclusions and white porous formations inside.

Sample Dm 231:
This sample is orange-red in color. It has middle sized black inclusions.

Sample Dm 232:
This sample is orange-red in color. It has less black inclusions, and also has some red and white inclusions.

Sample Dm 233:
This is made of almost pure pinkish colored clay. There are some black and red inclusions, but they are small and less.

Sample Dm 235:
This is orange in color. There are some middle sized black inclusions and also some brown, white, greenish inclusions but they are less.

Sample Dm 236:
This sample has layer formation but the exterior layer is too thin to be separated. The exterior layer is gray while the interior is pinkish. There are a lot of middle sized black inclusions in the interior layer.

Sample Dm 34:
This sample has two layers. It has gray-black interior and red exterior. It has a lot of black inclusions and also some red and white inclusions.

Sample Dm 35:
This is a handle connected to a body. It has three layers. The interior is violet, the middle layer has re dcolor and the outer layer is violet-red in color. There are black, red, and white inclusions.
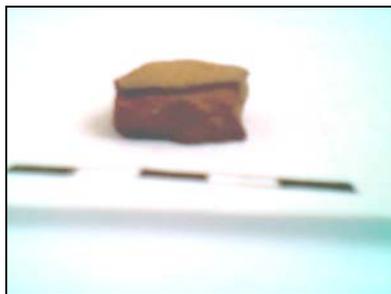
Sample Dm 36:
This is a handle without any layers. There is a lot of black inclusions, and some white and red inclusions less in amount.
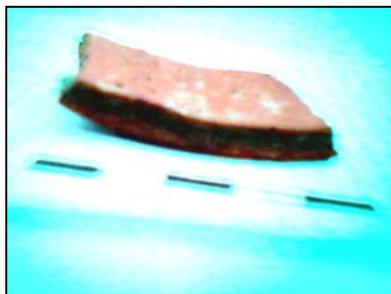
Sample Dm 37:
This is a very small fragment. It is almost pure black with very fine grains. There is a very thin yellow layer, may be from burial environment.

Sample Dm 38:
This is a small fragment, too. There is layer formation. The interior layer has pinkish red color while the exterior is brownish red. There are some black and white inclusions.
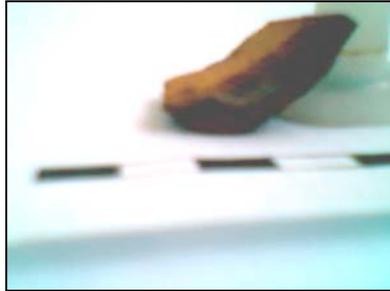
Sample Dm 39:
This is a red sample with layers. The interior is violet (brownish red) while the exterior has red color. There are small but much black inclusions.

Sample Dm 40:
This is an orange-red sample without any layers. It seems to be made of pure clay but with added big black inclusions.
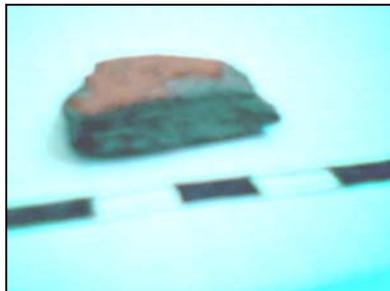
Sample Dm 41:
This is a sample with two layers. The interior is violet-red while the exterior is orange-red. It has small and less black inclusions.

Sample Dm 42:
This is a red fragment without layer formation. It has a lot of middle and small sized black inclusions, and also has some white inclusions.

Sample Dm 43:
There are three layers in this sample. The interior is black-gray, the very thin bottom layer is red and the top layer is pinkish gray in color. There are a lot of black inclusions.