

**ARCHAOMETRICAL STUDIES ON PLASTERS OF SOME HISTORICAL
BUILDINGS**

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Approval of the Graduate School of Natural and Applied Sciences.

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ABSTRACT

ARCHAEOMETRICAL STUDIES ON PLASTERS OF SOME HISTORICAL BUILDINGS

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The present study aims to investigate the composition of historical plasters to get information about their material characteristics and their technology. Plaster samples were obtained from four Ankara Citadel houses built in late Ottoman period.

In order to determine the raw material characteristics and mineralogical properties of plasters; chemical analyses, optical observation of cross sections, petrographic analyses of thin sections, elemental analyses by ICP-OES, X-ray powder diffraction analyses for the determination of mineral phases, thermogravimetric analyses and FTIR analyses were carried out. Interpretation of all the analytical examination was used to understand the composition and unique character of plaster samples studied.

Observation of thin sections revealed more plaster layers than those observed in cross sections. Up to twelve layers could be observed with different colours, such as blue, red, yellow, green, white and brown.

Generally, thicknesses of white plaster layers were found to be thicker than the others. In two samples, two black boundaries between plaster layers were identified which could be an indication of the use of asphalt for isolation purposes, like dampness proofing or heat insulation. Soluble salt contents of the plaster samples were in the range 3.04%-9.22%, with an average being 6.62%. The anions identified were Cl^- , SO_4^{2-} . In few samples, PO_4^{3-} , NO_2^- and NO_3^- were found. Binder was found to be lime and gypsum. The amount of binder in terms of total calcium oxide, CaO , was found to be in the range of 33.5-43.6%, with an average being 37.9%. Amount of aggregate was about 62.1% as average. The main minerals identified in plaster samples were calcite and gypsum. Gypsum might be added to increase the strength of the plaster. Beside calcite and gypsum, quartz and pozzolanic activity related mineral, Opal-A, were found in some of the samples. In red plaster layers hematite mineral was also identified. Other colour effective elements were found to be Fe, Sb, Mn, Cu, Cr and Ni. Presence of organic additives was observed but clear identification was not established.

Keywords: pigments, historical plaster, Ankara Citadel houses, ICP-OES, XRD

ÖZ

BAZI TARİHİ BİNALARIN SIVALARININ ARKEOMETRİK YÖNTEMLERLE İNCELENMESİ

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Bu çalışma bazı tarihi binaların sıvalarının malzeme özelliklerini ve teknolojik özelliklerini incelemek amacıyla yapılmıştır. Bu amaçla Ankara Kalesi çevresinde bulunan Osmanlı dönemine ait dört evden sıva örnekleri alınmıştır.

Sıva örneklerinin malzeme özelliklerini ve mineral kompozisyonlarını anlamak için kalın kesit analizleri, ince kesitlerin petrografik analizleri, element analizleri için ICP-OES, mineral tanımlamaları için XRD, termogravimetrik analizler, organik katkı maddeleri ve boya analizleri için FTIR gibi çeşitli kimyasal yöntemler kullanılmıştır. Analitik uygulamaların sonuçları, tarihi yapılarda kullanılan pigment ve sıva maddelerinin niteliği hakkında bilgi edinilmesini sağlamıştır.

İnce kesit analizlerinde, kalın kesit analizlerinde tanımlanan katman sayısından daha fazla katman bulunmuştur. En fazla katman içeren örnekte 12 sıva katmanı sayılmıştır. Katmanların renkleri mavi, kırmızı, yeşil, sarı, beyaz ve kahverenginin farklı tonlarında gözlemlenmiştir. Beyaz katmanların

diğer katmanlara göre daha kalın olduđu belirlenmiştir. İki örnekte ısı yalıtımı amaçlı olduđu düşünölen katran tabakalarına rastlanılmıştır. Tuz testlerinde sıva örneklerindeki kütlece tuz oranınının 3.04%-9.22% arasında deđiştii ve örneklerin Cl^- ve SO_4^{2-} anyonlarını içerdiđi görölmüştür. Bazı örneklerde PO_4^{3-} , NO_2^- ve NO_3^- anyonları bulunmuştur. Yapılan element analizleri sonucunda sıvalarda bağlayıcı olarak kireç ve jips kullanıldıđı, CaO miktarınının 33.5-43.6% arasında deđiştii, ortalama deđerin 37.9% olduđu anlaşılmıştır. Agregata miktarı ortalama 62.1% olarak bulunmuştur. XRD sonuçlarına göre, sıvalarda belirlenen temel mineraller kalsit ve jipstir. Jipsin sıva dayanıklılıđı arttırmak için eklendiđi düşünölmüştür. Ayrıca kuvars ve puzolanik aktiviteyi arttırdıđı bilinen Opal-A mineralleri bulunmuştur. Kırmızı renkli sıvalarda renk veren madde olarak hematit bulunmuştur. Fe, Sb, Mn, Cu, Cr ve Ni renk verici elementler olarak bulunmuştur. Organik madde varlıđı saptanmış ancak tanımlanamamıştır.

Anahtar kelimeler: boya, tarihi sıva, Ankara Kalesi evleri, ICP-OES, XRD

To My Baby, Ada

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CHAPTER 1

INTRODUCTION

Plaster is a material used to cover walls of buildings. Since ancient times humankind had been used different types of plasters for various purposes. Plastering is both a craft and an art, combining many skills. Plastering is known to be older than the ancient Sumerian temples built centuries before Egyptian pyramids.

Historical evidences show that primitive man plastered mud over a framework of sticks and reeds to enclose a protective structure to keep out the elements (Van den Branden, 1971).

The investigation of historic building materials such as plasters and mortars and their technologies are important subject to be studied in the field of archaeometry. Such studies are also important for restoration and conservation disciplines especially for the preparation of compatible repair materials as well as for the area of building science to learn about historical context of the materials science (Caner, 2003).

In this study, plasters of some Ankara Citadel's houses, built during Ottoman period were studied to get information about their material properties.

In the first chapter; the role of plasters in buildings was mentioned. In addition, the history of plasters, their types and their components are given. Besides, the brief history of Ankara is given. Aim of the study was also explained in this introduction chapter.

In the second chapter, plaster samples studied, the Ankara Citadel houses from where plaster samples were taken, and the methods of investigation, the instruments used in the study were explained.

Results of the analyses and discussion were presented in the third chapter.

In the fourth chapter conclusion of the study and suggestions for further studies were mentioned.

1.1 The Role and Importance of Plasters

Plaster is a material used to cover interior surfaces of walls, on ceilings, etc., of the structures or buildings. It is in plastic state. It serves many functions in the structure (Shepelev, 1986; Guelberth & Chiras, 2003).

Stucco is a material used in a plastic state, to form a hard covering for exterior walls or other exterior surfaces of any building or structure (Shepelev, 1986). Throughout this study both the stucco and the plaster will be called as plaster because plaster is most common word used in building material terminology.

Protection of the structure is the main function of the plasters. Plasters are used to bring the walls and ceilings of buildings and other structures to a true surface and to protect them against weathering, such as wetting and drying cycles, freezing and thawing cycles, salt crystallization cycles, due to the changes in weather conditions including temperature, humidity and wind flow (Shepelev, 1986; Caner, 2003). Plasters are made by mixing together one or several kinds of binders, aggregates and water. As they harden, plasters form a solid stone-like body (Shepelev, 1986).

Plaster may also be used for isolation purposes. Especially exterior plasters may have isolation properties. In order to obtain good isolation characteristic, plasters should have high density, low porosity and low water vapour permeability (Esen *et al.*, 2004).

One of the most important benefits of earthen plasters is their protective qualities. Earthen plaster is water resistant which means it resists water movement through it. The surface layer, when wet, tends to retard any further water penetration. Clay minerals consist of tiny flat particles so when moisture comes into contact with an earthen plaster, it may bind to clay mineral particles and forms a bridge between them, causing the clay mineral to expand. In addition, clay minerals are permeable to water vapour (Guelberth & Chiras, 2003).

Plaster also increases the resistance of the structure against fire by improving the thermal performance of the walls by the addition of some convenient materials (Callender, 1982). In order to prepare fire resistant plaster composition, sufficient amounts of naturally occurring phosphate minerals; such as apatite and shale should be added. Also large amounts of exfoliated perlite and/or vermiculite are being incorporated in gypsum plaster or other cementitious mixtures in order to provide walls, partitions, ceilings etc., with coatings which insulate these structures and thus provide fire protection. Both gypsum and Portland cement containing plasters when subjected to high temperatures have a tendency to lose water, which helps to retard the transmission of heat until all of the water is released (Ranney, 1970). Plaster was recognized long ago as a protection against fire. Its value as a fire retardant was demonstrated in many fires that ravaged London during the 13th century. (Van den Branden and Hartsell, 1976).

In addition to the protective function, plaster also improves the appearance of the buildings in terms of texture and colour by hiding the imperfections of rough work on the walls (Guelberth & Chiras, 2003; Houben and Guillaud, 1994).

1.2 A Brief History of Plasters

Plaster is one of the important finishing materials that could be identified in very old buildings such as those of Neolithic site Çatalhöyük and

in the interior walls of the massive pyramids of Giza in Egypt (Cessford, 2001; Guelberth & Chiras, 2003). Çatalhöyük has been described as one of the most important archaeological sites in Turkey. Within the buildings many of the multiple layers of plaster were detected between 0.2–5.0 mm thicknesses (Mortimore *et al.*, 2004).

The Pharaohs of Egypt used plaster surfaces in their palaces and pyramids. It is known that this plasterwork, and the decoration upon it, was applied more than 4,000 years ago. These plaster surfaces still exist in a hard and durable state today. The finest plasterwork accomplished by the Egyptians was made of a plaster produced from calcined gypsum just like the plaster of Paris of the present time (Van den Branden and Hartsell, 1976).

The method of applying plaster was also very similar to the methods used today. The Egyptians plastered on reeds, a method which resembles in every way our method of plastering on lath. Hair was introduced to strengthen the plaster even at this early date (Van den Branden and Hartsell, 1976).

A study of ancient Greek architecture reveals that plaster and stucco work were used by the Greeks at least 2500 years before today. In the ancient Greek language the word “plaster” meant “to daub on” (Van den Branden and Hartsell, 1976).

Apart from the role of plasters in buildings, historical plasters also have information about the production and construction technologies (Sasse and Snethlage, 1996).

1.3 Types of Plasters

Mainly, plasters may be divided into two groups; ancient plasters and artificial plasters.

Ancient or historical plasters can be also named as natural plasters because they are made from natural materials and the final product generally requires very little processing. Natural plasters may be classified into three

basic types as earthen plasters, lime plasters and gypsum plasters (Guelberth & Chiras, 2003).

At the present time, depending on the type of cementing material used, plasters can be distinguished a bit different as clay plasters, lime plasters, lime-gypsum plasters, cement plasters and cement-lime plasters (Shepelev, 1986). The last two types, namely cement plasters and cement-lime plasters can be considered as artificial plasters, because they are produced by industrial processes.

In this study only the natural plasters are studied, thus artificial plasters will not be elaborated.

1.3.1 Mud (clay) Plasters

The simplest and most primitive plasters are based on clay, sand and dung reinforced with chopped straw or other fibrous materials. Such plasters were used in truly vernacular buildings on stone walls and wattle partitions but they were also used in more formal buildings, for example in estate architecture. Mud plaster itself is not resistant to water. Therefore they were often finished with lime wash and they sometimes formed the backing for contemporary or later finishing coats of lime plaster. They have been superseded by more durable and maintainable finishes, but where they survive they are always of historic and archaeological interest (Lee and Larsen, 1994; Davey, 1961; Brown and Clifton, 1978).

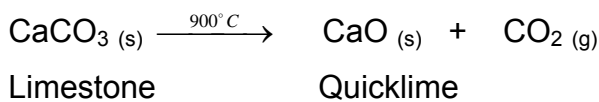
Earthen plasters which are the least processed of all natural plasters are also referred to as mud, adobe or in Europe loam plasters. Earthen plasters can be applied on both interior and exterior walls, and are durable and weather resistant if done right. However the main disadvantage of the mud plaster is its low mechanical property. To increase the strength of the mud plasters one of the three primary components; clay, sand and fibre are added (Guelberth & Chiras, 2003; Davey, 1961; Brown and Clifton, 1978).

1.3.2 Lime Plasters

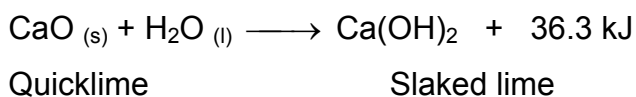
Lime plaster has a long history of use. The first recorded use of lime as an exterior plaster is in Anatolia around 4000 BC. The Romans also used lime to make plasters. In the cold area lime plasters were traditionally applied to stone buildings to protect the mortar from harsh weather and rains (Guelberth & Chiras, 2003).

For artisan and sophisticated buildings of all sorts, for hundreds of years before present century, lime was an essential component of mortars and plasters. Internal plaster, external plaster, roughcast and mortar for building were fundamentally the same material, differing only in the size of aggregate used and the presence or absence of reinforcement such as hair (Lee and Larsen, 1994).

Lime is made by burning or calcining of limestone (calcium carbonate, CaCO_3) in a kiln. When limestone is heated in kilns at the temperatures about 900°C , carbon dioxide is given off. The calcium oxide (CaO) produced is called quicklime or unslaked lime.



Quicklime is then slaked by treating the powdered or lump quicklime with water. Slaked lime is also called lime hydrate or lime putty. (Calcium Hydroxide, Ca(OH)_2).



Pure slaked lime in crystalline form is called portlandite. Portlandite is a hexagonal crystal with a density 2.24 g/cm^3 (Caner, 2003).

The putty is then sieved to remove any unslaked lumps or extraneous material and run into a pit or a tank to mature. For plastering, the mature lime

putty may be mixed with sand to produce coarse stuff or fine stuff or it may be used on its own or diluted with addition of water to produce lime wash. The hardening of each coat of lime plaster relies on the lime setting through carbonation that is the combination with atmospheric carbon dioxide in the presence of water to form calcium carbonate. The carbonation reaction is given below;



This effectively restores the lime plaster to its original calcite state that is chemically identical, although physically usually softer. This chemical process continues for many years even within the finished plaster (Lee and Larsen, 1994).

Types of slaked lime are fat lime or hydraulic lime depending on the amount of impurities in it. If the amount of impurities, expressed as the oxides of magnesium, silicon, aluminium and iron, is less than 5%, the lime is named as fat lime, rich lime or high calcium lime. If the impurities exceed 5%, the lime is no more high calcium lime. It gains hydraulic properties that are setting without the need of carbon dioxide in the air, due to oxides of silicon, aluminium and iron in its composition. Hydraulic limes can be further classified into several sub groups depending on the impurities in it as degree of hydraulicity; feebly hydraulic lime, moderately hydraulic lime and eminently hydraulic lime (Boynton, 1966; Holmes and Wingate, 1997; Caner, 2003).

Hydraulic limes have been evaluated by the Cementation Index theory. Cementation index theory involves some assumptions as to the constitution of hydraulic cementing minerals. Most important assumptions are as follows;

1. In hydraulic limes the hydraulic activity is due to the formation of certain compounds by the reaction of lime and magnesia with silica, alumina and iron.
2. Silica combines normally with the lime in such molecular proportions as to form tricalcic silicate, $3\text{CaO} \cdot \text{SiO}_2$.

- Alumina combines with the lime as the dicalcic aluminate, $2\text{CaO} \cdot \text{Al}_2\text{O}_3$ (Edwin-Eckel, 1928).

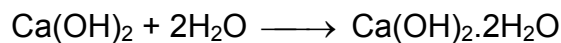
Cementation Index formula may be given as follow; (Boynton, 1966)

$$\text{Cementation Index (C.I.)} = \frac{2.8(\% \text{SiO}_2) + 1.1(\% \text{Al}_2\text{O}_3) + 0.7(\% \text{Fe}_2\text{O}_3)}{\% \text{CaO} + 1.4(\% \text{MgO})}$$

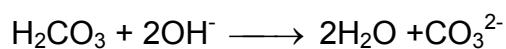
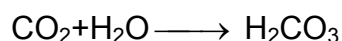
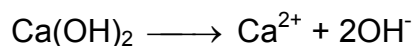
The environmental conditions which influence carbonation reaction are relative humidity, temperature and atmospheric CO_2 (Dheilly *et al.*, 2002, Caner 2003). Humidity directly influences this reaction. On the other hand, it is well known fact that the solubility of CO_2 decreases as temperature increases.

In humid atmosphere the reaction occurs in three sequential steps;

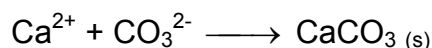
- Physical adsorption of water at the $\text{Ca}(\text{OH})_2$ grain surface



- The dissolution of $\text{Ca}(\text{OH})_2$ into Ca^{+2} and OH^- ions, in addition, the dissolution of CO_2 under the basic pH ($\text{pH} > 10$), yielding CO_3^{-2} ions.



- The precipitation of CaCO_3 (Dheilly *et al.*, 2002, Caner 2003).



Lime plaster, reinforced with hair, may be applied directly to stone or brickwork, to wattle, scratched clay or hacked timber backings such as the

undersides of floor or roof timbers or to timber lathing fixed to straps or studs (Lee and Larsen, 1994).

Lime plaster, typically made of lime and sand, can also be used on interior and/or exterior applications although it is typically applied on exterior walls where it provides excellent protection against the weather, especially rain (Guelberth & Chiras, 2003).

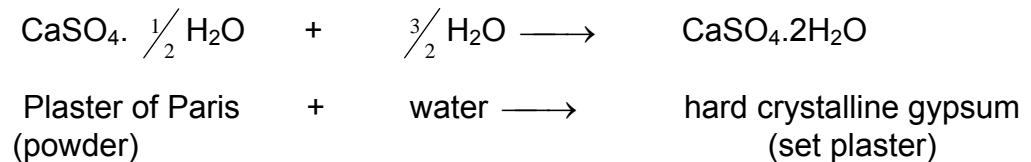
1.3.3 Gypsum Plasters

Gypsum plaster has been used on interior wall and as ceiling finish for thousands of years throughout the world. One of the first uses of gypsum plaster was in Egypt (Guelberth & Chiras, 2003).

Gypsum was used by the Romans in Britain, and then was reintroduced to England in the thirteenth century. There is evidence of its fairly common use thereafter in areas where it occurred naturally. It cannot be asserted categorically, but there is currently no clear evidence that gypsum was used in Scotland before the eighteenth century. Plaster of Paris was probably the first gypsum plaster to be used in Scotland after Roman times (Lee and Larsen, 1994). This is one of the common substances used for plastering. Gypsum occurs as a white or yellowish soft rock. Gypsum is calcium sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) about 20 percent of it is water by weight or about 50 percent by volume. The water is contained in the crystals and is part of their chemical structure. This water of crystallization does not change until it reaches a temperature of 130°C , when it changes into water vapour and it leaves the gypsum. It is this water of crystallization that explains why gypsum is so fire resistant (Van den Branden and Hartsell, 1976).

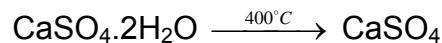
Calcium sulphate plasters are made from gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or from mineral anhydrite (CaSO_4). Plaster of Paris is produced by heating calcium sulphate, CaSO_4 , in mineral form such as gypsum or alabaster to drive off part of its water of crystallization. By calcining the gypsum at a relatively low temperature, usually between 130° and 170° C, for about 3

hours, only about three quarters of the chemically combined water in the gypsum is driven off and a material known as a Plaster of Paris or hemihydrate plaster ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) is formed. The powder obtained from this process forms a rapid-setting, hard plaster when recombined with water and can be used on its own or combined with lime putty or lime plaster (Lee and Larsen, 1994; Davey, 1961).



Gypsum plaster is a more delicate wall plaster. It is rather soft and water soluble and is therefore typically reserved for interior works (Guelberth & Chiras, 2003,).

Another type of gypsum plaster can be produced by burning it at higher temperature. If the gypsum is burned at a temperature of 400°C or above, all the water in the gypsum is driven off and anhydrous calcium sulphate (CaSO_4) is formed (Lee and Larsen, 1994; Davey, 1961).



1.4 Components of Plasters

All plasters have several common features: they all contain a structural component, a binding agent and some form of fibre.

The structural component of plasters, except most gypsum plasters, is sand. Sand provides most of the volume of a plaster and gives a plaster its structure (Guelberth & Chiras, 2003).

1.4.1 Binding Agents

The binding agent bonds the sand particles to one another while the plaster is wet and after it dries or cures. It is the type of binding agent that's used in a plaster that generally gives the material its name. In earthen plaster, it's the clay mineral that performs this function. In lime plasters, lime serves as a binding agent. In gypsum plasters, gypsum is the binder (Guelberth & Chiras, 2003).

In earthen plasters clay mineral serves as a binding agent because of its property of cohesion. Most clay minerals consist of hydrous aluminium silicates, which mean that they contain aluminium silicate with associated water molecules. Being rather sticky, clay mineral binds to the sand and straw in earthen plaster and thus holds the mix together (Guelberth & Chiras, 2003).

Binders or cementing materials fall into two major classes, namely inorganic cementing materials; such as clay mineral, lime, gypsum, cement and soluble glass and organic cementing materials including bitumen, tars and glues. The plasters in use are mostly made of inorganic binders (Shepelev, 1986).

1.4.2 Aggregates

The purpose of using aggregates is to be filling material having natural or artificial origin. The most important functions of aggregates are to make plasters stronger, to save cementing materials and to minimize shrinkage. Depending on the average density, it is possible to distinguish heavy aggregates and lightweight aggregates (Mora *et al.*, 1984; Shepelev, 1986).

The most-used heavy aggregates are natural sand and chips of the coloured rocks. The latter are generally employed for decorative plastering. Lightweight aggregates include pumice, slag, cinder, ash, clay minerals, charcoal, sawdust and chopped straw (Shepelev, 1986).

Properties of lime plasters can be improved by adding various materials, such as casein powder, skim milk, manure and gypsum (Guelberth & Chiras, 2003).

Aggregates make up the bulk of plastering mixes and are composed of inert materials. They are classified as coarse and fine aggregates. All aggregates passing through a 4.6 mm sieve are considered to be fine aggregates and the larger sizes are coarse aggregates (Taylor, 1990).

There are many different types of aggregates used in the production of plasters. These are sand, perlite, vermiculite, granulated pumice, pozzolanic aggregates and so on.

Sand is a fine aggregate formed by the natural disintegration of the rock or it is artificially created by crushing stone or gravel to the required sizes. The two main types of sand are pit sand from inland quarries and river sand obtained by dredging. Sea sand is unsuitable because of the risk of efflorescence due to the presence of salt. Good sand should contain a suitable proportion of large, medium and small sized grains. The reason for this is good filling of the plaster mixtures which can be seen in Figure 1.1 (Taylor, 1990).

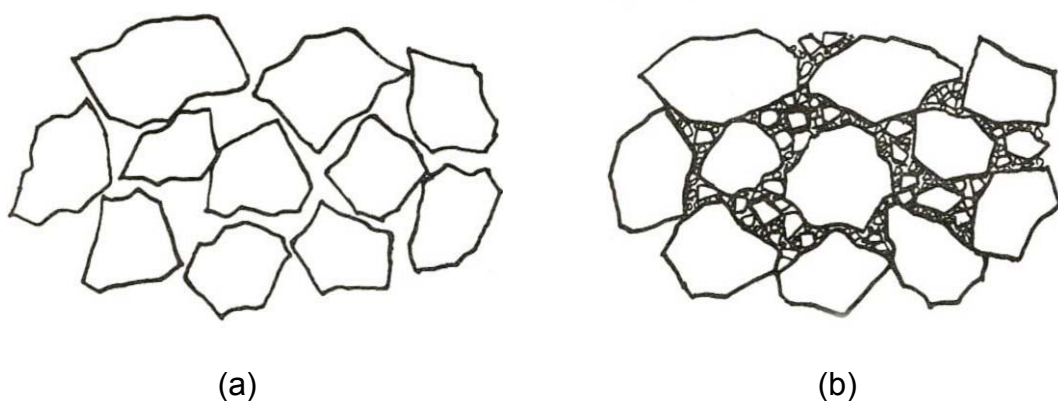


Figure 1.1 Distribution of sand grains (a) Badly graded sand (b) Well graded sand

Expanded perlite is a form of perlite and is lightweight material used in gypsum plaster. Perlite is a natural volcanic glass; it is essentially an amorphous mineral consisting of fused sodium-potassium-aluminium silicate with a small amount of combined water (Taylor, 1990).

Vermiculite is the name given to a group of laminated minerals resembling mica in appearance including small amount of combined water. If the flakes of crude ore are heated quickly to temperatures of 700°C-1000°C, then the contained water between layers turns to steam and forces the layers apart. Vermiculite is chosen for high insulation value and lightness (Taylor, 1990).

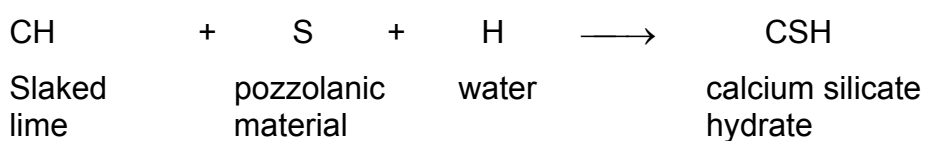
Granulated pumice is another mineral of volcanic origin used in acoustic plaster mixes for its high sound absorption qualities (Taylor, 1990).

Pozzolanic aggregates are defined as fillers or additives, though not cementitious in themselves, contain the compounds such as silica, alumina and iron oxides, which readily react with lime at ordinary temperatures in the presence of water and form stable insoluble compounds with cementing properties. Pozzolanic materials not only lend strength to buildings of other kinds, but even when piers of it are constructed in the sea, they set hard under water (Vitruvius, 1914; Ashurst and Dimes, 1990; Tunçoku, 2001).

Pozzolanic materials may be natural or artificial. Volcanic dust and ash are natural materials showing pozzolanic property. They may also be of biogenic or chemical origin such as diatomaceous earths, siliceous rocks and silica of organic origin such as cherts, flints and opal (Lea, 1970; Diamond, 1976; Dress *et al.*, 1995, Tunçoku, 2001, Caner, 2003).

Opal is the most reactive pozzolanic constituent. It may be present as crystalline form, opal-CT, and X-ray amorphous form of opal-A, which is hydrous silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) (Dress *et al.*, 1995, Tunçoku, 2001, Caner, 2003).

Pozzolanic effect can arise by the reaction between lime and pozzolanic material which can be summarized as follow; (Torracca, 1988)



1.5 Pigments

Humans have been using pigments to produce lasting colours for hundreds of thousands years. The first known examples occur in the Palaeolithic period, approximately 35000 BC, at which time, studies show, our early ancestors used red earth pigments to tattoo their flesh and to decorate the bones of dead. In the middle Palaeolithic period, about 40000 BC yellow ochre, the natural colour, siliceous clay containing hydrated iron oxides, found in the earth in the mountains where there are found certain seams resembling sulphur, was used. Paintings on the walls of caves in France, made about 15000 BC, contain brown, white and yellow pigments (Guelberth & Chiras, 2003; Thompson, 1960; Mora *et al.*, 1994).

The Egyptians began serious colour manufacturing starting from about 4000 BC. They introduced washing of pigments to increase their strength and purity. They also introduced new materials, the most famous of which was Egyptian blue—first produced around 3000 BC. This pigment is calcium copper silicate, $\text{CaCuSi}_4\text{O}_{10}$, made by mixing a calcium salt, carbonate, sulphate or hydroxide, a copper compound, oxide or malachite, and sand which is silica (Barnett, 2005).

Pigments consist of fine powders whose particles are suspended in some medium, typically water and generally fall within in one of two broad categories: natural and synthetic. Natural pigments come from three sources: earth, animals and plants. Synthetic pigments of course are artificially produced, although some are chemically identical to natural pigments (Guelberth & Chiras, 2003).

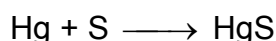
Coloured plasters are obtained by adding colour pigments to an uncoloured material. A pigment is a coloured, finely ground powder of organic or inorganic origin. Pigments are insoluble in water or cementing materials, forming a suspension insusceptible to separation into layers (Shepelev, 1986).

Pigments may be classified into different categories. According to Mora *et al.* (1994) historical pigments can be examined in three parts:

- Mineral (inorganic or earth) pigments which may be natural or artificial
- Organic pigments which may be animal or vegetable origin or they may be synthetic
- Mixed pigments

The colour of natural pigments comes from various minerals. Natural earth pigments frequently derive their colour from the various forms of the mineral iron, which is found in abundance. Different chemical forms of iron produce a stunning range of tones from red through yellow and green to violet (Guelberth & Chiras, 2003). Natural mineral pigments are also found in the ground in the form of oxides, sulphides, carbonates, sulphates etc. more or less crystalline form. (Mora *et al.*, 1994).

Artificial mineral pigments are usually chemical products of well defined composition which have been obtained by dry method or by wet method (Mora *et al.*, 1994). For the preparation of the pigment cinnabar (vermillion), the dry method was the one used by the ancient alchemists and is used by the Chinese at the present time. In the Dutch modification of the Chinese method was carried out, in which 100 parts (by weight) of mercury were combined in an iron pan with 20 parts of molten sulphur to form black amorphous mercuric sulphide (HgS).



The product has to be treated with a strong alkali solution to remove free sulphur and to be washed and ground under water to prepare it as a pigment. The pigment cinnabar also may be produced by wet method which was favoured by English and German producers. The red modification of vermillion (mercuric sulphide) could be made by treating the black sulphide with alkali sulphides. For this purpose, the mercury and sulphur are ground together in the presence of water and toward the end of the grinding operation a warm solution of caustic potash (KOH) is added to complete the transformation. In an improved method, potassium pentasulphide (K₂S₅) is used in place of caustic potash. Vermillion prepared in this way must be

washed and dried to get rid of the soluble sulphur compounds (Gettens and Stout, 1966).

Natural organic pigments are obtained from substances contained in some parts of animals from decoction or maceration of wood, fruits, leaves, bark or roots of plants. The colouring material is produced by evaporation and desiccation (Mora *et al.*, 1994).

Synthetic organic colouring substances may be dyestuffs, derivatives of aniline, phenol, quinines, etc. and although used in the production of coloured fabrics, they are avoided in painting even if, of the best quality, because their resistance to light is definitely inferior to that of the mineral pigments. Humans have been making their own pigments for thousands of years. The Egyptians, for instance, perfected the manufacture of blue pigments and used it to tint glass around the 3rd millennium BC. These people also produced a darker artificial blue, actually a green tinted with cobalt (Mora *et al.*, 1994; Guelberth & Chiras, 2003).

Mixed pigments may contain both mineral and organic material, examples are the lake pigments made by precipitating an organic dyestuff on a colourless base, commonly on oxide or hydrate, so importing its colour to this base (Mora *et al.*, 1994).

A mixture of two or more pigments may be used to obtain desired colour, the amount of each depending on the shade desired (Shepelev, 1986).

Pigments must be ground to a very fine powder. In fact, this fineness largely determines the colouring power of the pigment. The term colouring power refers to the ability of a pigment to maintain its own colour when mixed with a white pigment. The higher the colouring power, the less pigment is needed to obtain a desired shade. A pigment is said to have a good colouring power if the amount of the pigment to be added to the cementing material to obtain desired colour does not exceed 15% by weight (Shepelev, 1986).

The most common colour pigments are as follows:

- Black pigments: carbon black, graphite, manganese dioxide and bone black. Bone black can be obtained by calcining bones in a closed

vessel and refining to remove phosphates and carbonates (Shepelev, 1986; Mora *et al.*, 1994).

- Yellow pigments: ochre and sienna. Ochre contains clay mineral containing hydrated iron (III) oxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Sienna may be raw material (goethite, $\text{FeO}(\text{OH})$) or its burnt form containing Fe_2O_3 , clay mineral and etc. (Shepelev, 1986; Gettens and Stout, 1966).
- Red pigments: iron minium (red ochre or hematite having formula Fe_2O_3), vermilion or cinnabar, HgS , and chrome red ($\text{PbCrO}_4 \cdot \text{Pb}(\text{OH})_2$) (Shepelev, 1986; Gettens and Stout, 1966; Mora *et al.*, 1994).
- Blue pigments: ultramarine blue, Prussian blue and cobalt blue. Ultramarine blue is the natural mineral, called lapis lazuli or lazurite having formula $3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{Na}_2\text{S}$. Prussian blue is the ferric ferrocyanide, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. Cobalt blue is a cobalt aluminate, $\text{CoO} \cdot \text{Al}_2\text{O}_3$ (Shepelev, 1986; Gettens and Stout, 1966; Mora *et al.*, 1994).
- Brown pigments: raw and burnt umber which is similar to ochre but containing a certain amount of manganese dioxide. Deep colour of umber is developed by burning (Shepelev, 1986; Mora *et al.*, 1994).
- Green pigments: chrome green which may be anhydrous chromic oxide, Cr_2O_3 , or hydrated chromic oxide, $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Shepelev, 1986; Mora *et al.*, 1994).
- White pigments: calcium carbonate or chalk, CaCO_3 , gypsum sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and white marble dust (Shepelev, 1986; Mora *et al.*, 1994).

1.6 History of Ankara from Archaeological Perspective

Ankara, the capital city of the Turkish Republic, is located in central Anatolia at the crossroads of main highways connecting east to west and north to south. The prehistoric settlements unearthed in Ankara and its vicinity indicates that the area was continually settled since ancient times (İdil, 1997).

Ankara was the target of attacks during the centuries following the late antique period because of its location at the intersection of the highways connecting the capital with the eastern provinces. The earliest founders of Ankara were Hittites who must have profited from its strategical topography. During that period Ankara was called Ankulla or Ankuwa and the latter is used for the winter residence of the Hittite Kings. The site would have been a fortress and occupied the summit of the hill. There is not much information on the period between the Phrygians and the age of Macedonian king Alexander the Great. Texier thinks the city was founded by the Phrygians in 650 B.C. and received the name Ancyra because the workers found an anchor made of stone in the foundations of the walls. Phrygians must have occupied the site after the Hittites and did not change the appearance of the citadel. Although most of their cities were open in the plain the Phrygians also had fortifications located on hill tops controlling the main routes (İdil, 1997; Sülüner, 2005).

Strabo of Amasia, who lived between 69 B.C and 19 A.D., mentioned Ankara in his "Geographica" as a fortress belonging to the Galatian tribe of Tectosages. He also described it as a polis (Sülüner, 2005). The Tectosages in 278-277 B.C. came to Anatolia and made Ankara their capital. Pliny also speaks of Ankara as a fortress in Galatia saying their cities were mainly composed of some huts and Citadels built at the top of hills. (İdil, 1997; Sülüner, 2005)

The Roman emperor Augustus in 25 B.C. included Galatia under the Roman rule and Ankara became a Roman province. There were twelve settlements in the city and it expanded from the Citadel and its vicinity

towards today's Yenişehir (İdil, 1997). Ankara continued to flourish after the death of Augustus (31 B.C.) and many other public buildings would have been constructed during the Roman rule. The main buildings were; a hippodrome, baths, gymnasium, and theatre. Ankara was also mentioned with the title of metropolis in the official acts (Sülüner, 2005).

During the Byzantine period, Ankara lived through a period of peace until Arab invasion began in 638 A.D. Ankara was attacked again by the Arabs in 776 and 797 but it was not captured. Byzantine emperor Michael III, in 859 A.D., repaired the city walls which had been damaged during Arab invasions (İdil, 1997; Sülüner, 2005).

After the battle of Mankizert in 1071, the Turks dominated Anatolia and the last mention of Ankara is the account of Emperor Alexius Comnenus (1081-1118) and his brother before its capture by the Seljuk Turks (Sülüner, 2005).

Ankara was captured by the Ottomans in 1356 and governed by Ottoman sultan Murad I. During the Ottoman Empire, Ankara was visited by many European travellers. One of them was an unknown painter whose 17th century oil painting (Fig. 1.2) shows the city walls surrounding the town and the buildings surrounded by the city walls. Also the outer city walls surrounding the inner walls and the citadel on the hill are clearly seen in the painting (Fig. 1.2). Many Ottoman houses built in the previous centuries can be seen along the narrow Lanes in the citadel (İdil, 1997; Sülüner, 2005). Mamboury says that the Ottoman walls could have been constructed over the foundations of the Roman walls. Consequently, as in the Ottoman period the Roman wall would have protected the citizens from the bandits as well because there was no outside threat during the Roman period. The walls appear in the engravings of Tournefort (1701) (Fig 1.3.) (Sülüner, 2005).

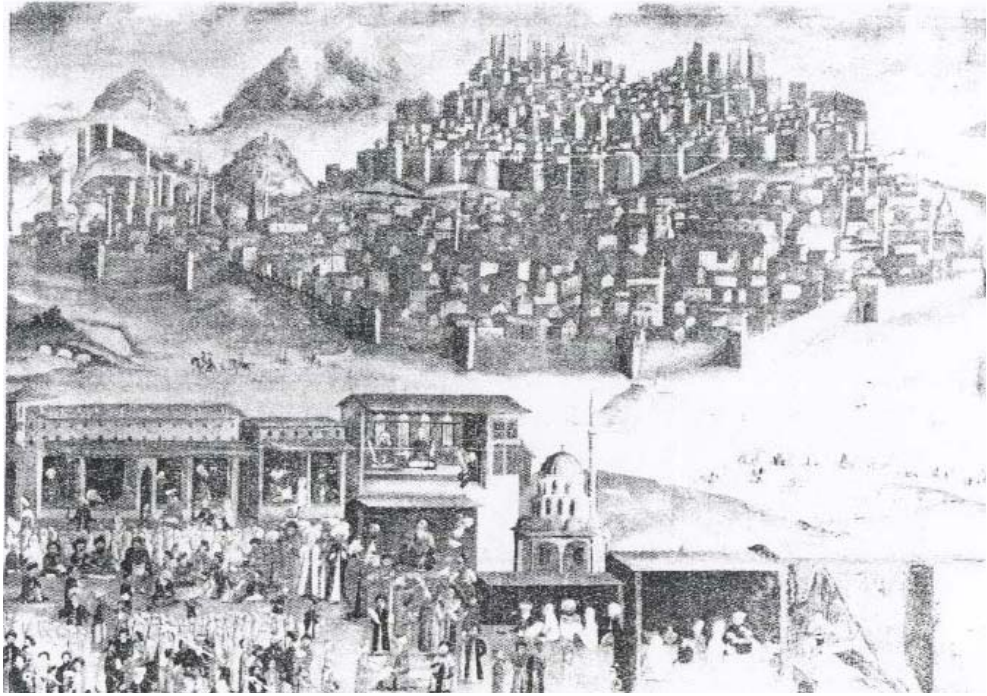


Figure 1.2 Ankara in the 17th century, Rijk Museum, Amsterdam. (Sülüner, 2005)

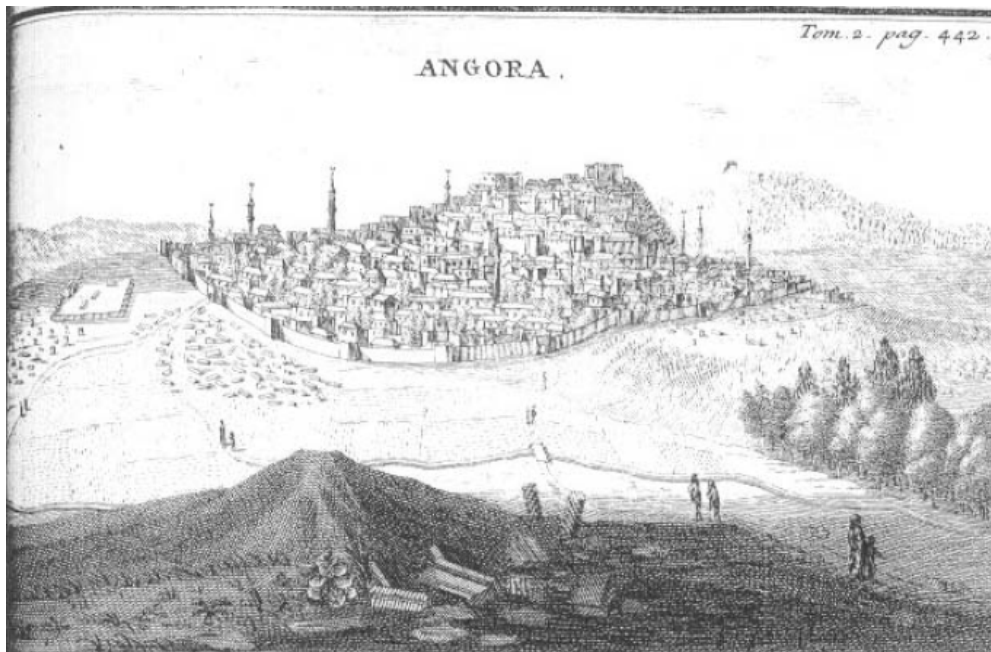


Figure 1.3 An old miniature of Ankara by Tournefort (1701) (Sülüner, 2005)

1.7 Aim of the Study

The aim of this study is to investigate the characteristics of plasters used in the exterior facades of some historical buildings in Ankara Citadel. In addition, results of the investigations will be used to define properties of restoration materials that are compatible with the original ones, since the restoration of historical structures using modern materials may cause serious problems in these structures. Therefore, in order to decide or produce suitable repairing materials, first; it is important to figure out the characteristics of original material.

In the study the components of the plasters, including the binding agent and aggregates used in the plaster and types of pigments were analysed. The composition of plasters especially pigments was tried to be determined. In the analysis, various analytical methods, such as; ICP-OES, FTIR and XRD analyses were performed. In addition to these; semi quantitative wet chemical analysis was also carried out. Interpretation of all the analyses were made to understand the content and unique character of plasters studied.

CHAPTER 2

MATERIALS AND METHODS

Analyses of the plaster include both instrumental methods and visual characterization of the samples belonging to four different houses around Ankara Citadel.

Determination of mineralogical properties and chemical analysis of raw material composition were performed by combined interpretation of some types of analysis such as petrographic analysis of thin sections by optical microscopy, X-ray powder diffraction analyses for the determination of mineral phases, ICP-OES for the element composition of the pigments and FTIR analyses for the determination of binders in plaster samples.

2.1 Description and Nomenclature of the Plaster Samples

Approximately 10 cm² plaster samples were taken from the exterior walls of historical buildings around Ankara Citadel. Samples were collected by considering some important points. The first one having prime importance is defining the place for sampling. In order to collect representative samples, it is important to take care of sampling from the architectural components of upper structures. In addition, the samples were collected from regions which are protected against the effects of sun or rain.

The nomenclature of the samples was needed to simplify the representation of experimental results. The nomenclature of the samples was done as follow.

The first letter shows the lane on which the house had been built and the first number shows the number of entrance gate and the following second number is layer number of the plaster. For example the code of “E-7.1” represents the first layer of sample taken from the house in Eylül Lane having the entrance gate number 7.

For the nomenclature of cross section and thin section analyses the last number of previous code is removed hence all layers of one house can be seen in one cross section or thin section sample. For example the code E-7 represents the thin section of the plaster layers taken from the house in Eylül Lane.

2.1.1 Samples of Eylül Lane

The samples from this house (Fig. 2.1 a, b) are described below:

Code: E-7.1

Period: Ottoman

Place: Eylül Lane, No:7, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layer with an average thickness of 102 μm and looks green

Code: E-7.2

Period: Ottoman

Place: Eylül Lane, No:7, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layer with an average thickness of 173 μm and looks white

Code: E-7.3

Period: Ottoman

Place: Eylül Lane, No:7, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layer with an average thickness of 61 μm and looks red



Figure 2.1 General views of Eylül Lane House

2.1.2 Samples of Sarıca Lane

The samples from this house (Fig. 2.3 a, b) are described below:

Code: S-26.1

Period: Ottoman

Place: Sarıca Lane, No: 26, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layer with an average thickness of 55 μm and looks yellow and with an average thickness of 118 μm and looks white

Code: S-26.2

Period: Ottoman

Place: Sarıca Lane, No: 26, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layer with an average thickness of 156 μm and looks blue and with an average thickness of 155 μm and looks white

Code: S-26.3

Period: Ottoman

Place: Sarıca Lane, No: 26, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layer with an average thickness of 569 μm and looks white

Code: S-26.4

Period: Ottoman

Place: Sarıca Lane, No: 26, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layer with an average thickness of 110 μm and looks blue

Code: S-26.5

Period: Ottoman

Place: Sarıca Lane, No: 26, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster, including four layers, looks white having thicknesses orderly 141 μm , 102 μm , 100 μm and 61 μm .

Code: S-26.6

Period: Ottoman

Place: Sarıca Lane, No: 26, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layer with an average thickness of 125 μm and looks green



Figure 2.2 General views of Sarıca Lane House

2.1.3 Samples of Yeniyıldırımlar Lane

The samples from this house (Fig. 2.5 a, b) are described below:

Code: Y-3.1

Period: Ottoman

Place: Yeniyıldırımlar Lane, No: 3, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layer with an average thickness of 32 μm looking brown and fine plaster layer with an average thickness of 189 μm looking blue

Code: Y-3.2

Period: Ottoman

Place: Yeniyıldırımlar Lane, No: 3, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layer with an average thickness of 76 μm and looks yellow

Code: Y-3.3

Period: Ottoman

Place: Yeniyıldırımlar Lane, No: 3, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layer with an average thickness of 76 μm and looks yellow

Code: Y-3.4

Period: Ottoman

Place: Yeniyıldırımlar Lane, No: 3, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layer with an average thickness of 226 μm , looks white and fine plaster layer with an average thickness of 298 μm , looks greyish white

Code: Y-3.5

Period: Ottoman

Place: Yeniyıldırımlar Lane, No: 3, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layer with an average thickness of 141 μm and looks green



Figure 2.3 General views of Yeniıldırımlar Lane House

2.1.4 Samples of Öksüzler Lane

The samples from this house (Fig. 2.7) are described below:

Code: O-13.1

Period: Ottoman

Place: Öksüzler Lane, No: 13, Ulucanlar Quarter

Type: Exterior plaster

Visual Features: Fine plaster layers with an average thickness of 125 μm and looks red and with an average thickness of 125 μm and looks white



Figure 2.4 General view of Öksüzler Lane House

2.2 Determination of Raw Material Properties

Raw material properties of plasters were examined by determination of the ratio of the binder and aggregate parts of the plasters, qualitative analysis of the soluble salts by spot tests and examination of pozzolanic activity of the fine aggregates which means smaller than 125 μ .

2.2.1 Determination of the Binder and Aggregate Ratio by Volumetric Method

The ratio of the binder and aggregate parts of the plasters was determined by the analysis of Ca^{2+} in the binder part by using complex formation titration. For this purpose 0.01 M standard EDTA solution was used.

For the test, definite amount of powdered plaster sample was weighed accurately for each sample. The amounts of the samples taken are given in Table 2.1. After that, weighed samples were treated with 5 ml of 2% acetic acid solution. All samples were left for 5 days in order to get dissolution of the calcium compounds. After the dissolution of the calcium compounds, volume was made 100 ml with distilled water. Then these solutions were taken and pH values of the solutions were adjusted to 12-13 using few drops of 10% NaOH solution. Calcon was used as indicator. Calcon indicator was prepared by dissolving 0.02 gr calcon in 100 ml ethyl alcohol. The final solution was titrated with 0.01 M EDTA solution, until a pink colour became permanently blue. (Black, 1965)

The detailed procedure of the test and chemical reactions are given in Appendix 1.

Table 2.1 The amounts of powdered samples taken for determination of the binder and aggregate ratio by EDTA titration

Sample	Weight (g)
E-7.1	0.0989
E-7.2	0.1147
E-7.3	0.1002
S-26.1	0.0964
S-26.2	0.0962
S-26.3	0.0975
S-26.4	0.0941
S-26.5	0.0941
S-26.6	0.0731
Y-3.1	0.1052
Y-3.2	0.1049
Y-3.3	0.1030
Y-3.4	0.1012
Y-3.5	0.1017
O-13.1	0.0914

2.2.2 Determination of Soluble Salt Content in Plasters by Electrical Conductivity Measurements

The amount of soluble salt in the plaster samples, as percent by weight was determined by the measurement of electrical conductivity. For this purpose, powdered plaster samples were dried in an oven at 40°C for 24 hours. From each sample 1 g was taken and mixed with 50ml distilled water. The mixtures were left closed for settlement of suspended particles for 24 hours and then filtered. The measurements of electrical conductivity of each salt extract solution were done by a conductometer of Metrohm AG Herisau, Kondoktometer E382.

Percent salt in the plaster sample was calculated using the following equations (Black, 1965);

$$EC = [(0.0014 * R_{std}) / (R_{ext})] \text{ (mhos cm}^{-1}\text{) where;}$$

EC: electrical conductivity

R_{std} : the cell resistance with standard solution (0.01 N KCl)

R_{ext} : the cell resistance with extract solution

$$\% \text{ salt in the sample} = [A * V_{ext} / 1000] * [100 / W_s] \quad \text{where;}$$

A : salt concentration (mg/L) = 640 * EC (mmhos cm⁻¹)

V_{ext} : volume of the extract solution (ml)

W_s : Weight of sample (mg)

2.2.3 Qualitative Analysis of the Soluble Salts by Spot Tests

For the determination of the soluble salt content, powdered plaster samples were dried in an oven at 40°C for 24 hours. Then 0.25 g was taken from each sample and put in the 50 ml distilled water and shaken well. The solution was left closed for settlement of undissolved (suspended) particles for 24 hours and then filtered. The filtrate was later concentrated by evaporation of excess water in oven at 40°C for 6 hours. The remaining concentrated solution was analysed. In the analysis anions were determined using the methods given for spot tests (Feigl, 1958; Teutonico, 1988). The most common soluble salts in the porous building materials are sulphates, chlorides, nitrates, nitrites and phosphates of sodium, potassium and magnesium elements. In order to indicate their presence spot test were performed.

2.2.3.1 Determination of Anions

In the analyses common anions of the soluble salts, which are PO_4^{3-} , SO_4^{2-} , Cl^- , NO_2^- , NO_3^- and CO_3^{2-} , were determined. For this purpose spot tests were performed. Procedures of the tests used in the analysis are given in Appendix 2.

2.2.4 Examination of Pozzolanic Activity of the Fine Aggregates

Pozzolanic activity shows the abundance of pozzolanic materials in the aggregates and it is related with the durability of the building materials. Pozzolanic activity of the aggregates of some plaster was determined by using two methods; Luxan method (1989) and the method given in TS EN 196-5 (2002).

For the test given in TS EN 196-5, accurately weighed fine aggregates were used.

The aggregates were put in containers filled with 30 ml saturated $\text{Ca}(\text{OH})_2$ solution and covered. One container was filled with only $\text{Ca}(\text{OH})_2$ solution to be used as blank. All containers were left covered for ten days. Then, 10 ml of solution was taken out from each container and titrated with 0.01 M EDTA standard solution (Black, 1965).

The differences in concentration of Ca^{2+} ion between the sample solutions and blank solution can be obtained from the results of titration. Since pozzolanic active aggregate reacts with Ca^{2+} ion, the differences in the concentration of Ca^{2+} ion gives some information about the pozzolanic activity of the aggregates for ten days of reaction period.

In the study of Luxan *et al.*, 1989, the consumption of $\text{Ca}(\text{OH})_2$ in the solution was measured by a decrease in electrical conductivity. In this study, the consumption of $\text{Ca}(\text{OH})_2$ was converted to drop in electrical conductivity by the simple equation given below; (Black, 1965, Caner, 2003)

Total concentration of soluble salts, usually expressed as electrical conductivity (EC) in units of mmho/cm or dS/m (1mmho/cm = 1 dS/m)

Total cation concentration, milliequivalent per liter= 10 x (the electrical conductivity in mmho)

Where total cation concentration corresponds to concentration of Ca^{2+} ion consumed.

2.3 Mineralogical Properties of Plasters

Mineralogical and textural analyses of the samples were carried out by cross section and thin section examinations, X-Ray powder diffraction and FTIR analyses.

2.3.1 Cross Sections and Examinations

Plaster samples were placed into plastic molding boxes of about 1.5 cm x 3 cm x 1 cm in order to harden them for the preparation of thin sections. Then they were hardened in the polyester resin (Sodemi Resin HG 59) mixed with accelerator and hardener. After the samples were hardened, they were removed from boxes and cut into slices. Then the slices were examined and their images were taken by a Leica microscope.

The images and the results of the cross section examinations were given in Chapter 3.2.1.

2.3.2 Thin Sections and Optical Microscopy

Plaster samples were placed into plastic molding boxes of about 1.5cm x 3cm x 1cm in order to harden them for thin section analysis. Plaster samples were hardened in the polyester resin (Sodemi Resin HG 59) mixed

with accelerator and hardener. After the samples were hardened, they were removed from boxes and cut into slices as thin as possible. These thin slices were fixed on microscope slides and then they were reduced to 30 μ thickness for analyses.

Thin sections of the samples were examined under polarizing microscopes of Leica DM EP equipped with photographic attachments. Mineralogical properties of binder and aggregates and also morphological properties of plaster samples like the number of layers, size and distribution of the particles in these layers were examined.

The images and the results of the thin section examinations were given in Chapter 3.2.2.

2.3.3 X-Ray Powder Diffraction (XRD) Analysis

X-Ray diffraction analyses were performed on powdered plaster samples. Before the analyses, layers of plasters were separated and each part was ground in an agate mortar.

X-ray powder diffraction is a traditional tool to detect and/or determine crystalline phases and mineral pigments such as iron oxides. Aside from the mere presence of goethite or hematite, certain information on the crystallinity of these phases can be obtained and related to the pigment genesis or provenance (Hradil *et al.*, 2003).

There were totally four plaster samples taken from houses. Three of them include more than two layers. The fourth one has only two layers. The first sample, taken from Eylül Lane, No: 7, has three layers and each layer could be separated. The second sample from Sarıca Lane No: 26 has many layers and it could be separated into six different parts. The sample from Yeniyıldırımlar Lane No: 3 has also many layers and it could be separated into five different parts. Lastly the sample, taken from Öksüzler Lane, No: 13, has two layers and they could not be separated.

The instrument used for XRD analyses was a 100 kV Philips twin tube (PW/1050) X-ray diffractometer. Analyses were done by using CuK α radiation with Ni filter, adjusted to 40kV and 40mA. The XRD traces were recorded for 2 θ values from about 3° to 70°.

XRD analyses of the samples have been done in two ways. First the powdered samples without any treatment were analysed. Secondly all ground samples were treated with 2% aqueous solution of acetic acid to dissolve all CaCO₃ content. After CO₂ gas evolution ceased, the mixture was centrifuged. The liquid part was decanted. After decantation the remaining residue washed with distilled water several times by centrifuging. After several centrifuging and decantation, sample tubes were dried in an oven at about 40°C. The dried sample was taken out of the tube and analysed. XRD analysis was carried out in the Department of Metallurgical and Materials Engineering, METU.

The trace and the results of the XRD analyses of untreated and treated samples were given in Chapter 3.2.3.

2.3.4 Fourier Transform Infrared (FTIR) Analysis

Infrared spectrometry is a capable method for the application of qualitative and quantitative determination of molecular species of all types. The applications of infrared spectrometry can be divided into three major categories according to the infrared spectral region, which are far, near and mid-infrared regions. Mid-infrared spectrometry is a useful method for determining the structure of organic and biochemical species (Skoog *et al.*, 1998).

Sample handling is the most difficult part of an infrared spectrometric analysis. KBr pelleting is one of the popular techniques for handling solid samples. In this study, in order to pelleting, powdered samples treated with 2% acetic acid solution were used. For this purpose; a milligram of the finely ground powder from each sample was mixed with about 100 mg of dried

potassium bromide powder. Mixing was carried out with a mortar and pestle. The mixture was then pressed in a special die at approximately 10,000 pounds per square inch to yield a transparent disk (Marel and Beutelspacher, 1976). The analyses were carried out in FTIR laboratory of Chemistry Department, METU.

The trace and the results of the FTIR analyses were given in Chapter 3.2.4

2.4 Chemical Properties of Plasters

Element composition of the powdered plaster samples was determined by using Inductively Coupled Plasma - Optic Emission Spectrometry and other chemical properties were examined by thermogravimetric analysis.

2.4.1 Inductively Coupled Plasma - Optic Emission Spectrometry (ICP-OES)

In order to perform chemical analysis the same plaster layers used in the XRD analyses were used. The elements analysed are Ca, Si, Al, Fe, S, Sb, Cr, Mn, Ni and Cu. Some of these elements, such as Ca, Si, Al and Fe can be considered as matrix elements. Other elements are considered to be colour forming elements such as Sb, Cr, Mn, Ni and Cu.

Inductively coupled plasma optical emission spectrometry (ICP-OES) is widely used method for elemental analysis of inorganic samples. The simultaneous, multi-element nature of the technique allows the determination of a large number of elements under the same working conditions in a very brief time period as all elements present in the radiation source emit their spectrum at the same time (Trevizan *et al.*, 2006; Ojeda and Rojas, 2007).

ICP-OES has gained worldwide acceptance as a versatile analytical technique for many types of samples. The technique is characterized by low background emission hence superior detection limits, high temperature leading to few chemical interferences and wide linear response range (Ojeda and Rojas, 2007). Therefore it is chosen for the elemental analyses of this study.

The working principle of the ICP-OES is as follow. Sample is generally introduced as a solution and is nebulised to form a fine aerosol, which is transported into the centre of the plasma where it rapidly undergoes dissolution, vaporization to molecular level and dissociation into atoms; some of the atoms are ionised. Both atoms and ions become excited in the plasma and, as they revert to their ground state in the tail flame, they emit light; in ICP-OES their characteristic emission is measured using an optical spectrometer (Ojeda and Rojas, 2007). The instrument used in the analyses is Perkin Elmer Optima 4300DV with an Echelle polychromator using an S-CCD (Segmented Charge Couple Device) array detector system. Detection limits of the instrument are in the range of $\mu\text{g/L}$. Analyses were performed in the METU Central Laboratory.

The results of the ICP-OES analyses were given in Chapter 3.2.5.

2.4.2 Thermogravimetric Analysis

Differential thermal analysis is a technique of recording the difference in temperature between a substance under study and a reference material as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. The record obtained is called the differential thermal analysis or DTA curve. If the substance is thermally active in the temperature range used, the curve shows a series of peaks, the position of which is determined by the chemical composition and crystal structure of the substance and the area of which is related to the energy involved in the reaction occurred (Mackenzie, 1970).

The instrument used for analyses was a Setaram Labsys which is simultaneous thermogravimetric analyzer and differential thermal analyzer. TGA/DTA analysis of two representative powdered samples was done in atmospheric condition. The range of temperature was between 50°C- 900°C. Heating rates in the region was 10°C/min. Analyses were performed in the METU Central Laboratory.

The trace and the results of the TGA/DTA analyses of two representative samples were given in Chapter 3.2.6.

CHAPTER 3

RESULTS AND DISCUSSION

In this chapter the experimental results that were obtained by the examination of plasters of four houses around Ankara Citadel were discussed in terms of material composition and characteristics of binder, aggregates and pigments.

3.1 Characteristics of Binder and Aggregate Parts

Binder and aggregate parts of plaster samples were determined by volumetric method after acid treatment of the samples. The qualitative analyses of soluble salts have been carried out by anion analysis using spot tests. The salt content of the samples was determined by conductivity measurement. In addition, the examination of pozzolanic activity of aggregate parts of the samples was done.

3.1.1 Proportions of Binder and Aggregate Parts Obtained by Acid Treatment

The proportion of lime in binder was determined by the complex formation titration using EDTA standard solution. EDTA makes a complex with Ca^{2+} ions in the solution. The amount of Ca^{2+} ion can be used to

calculate the amount of CaCO₃ in the plasters. The results have shown that the amount of binder CaCO₃ was in the range of 14.3%-82.4%, with an average of 33.4%. (Table 3.1) The amount of CaCO₃ was lower than expected value for historical lime plasters. This may be due to the presence of gypsum as binder. For the dissolution of the binder part 2% acetic acid solution was used. 2% acetic acid solution might not be sufficient in dissolving gypsum to form Ca²⁺ ions. Thus the Ca²⁺ ion titrated would be less than expected. The presence of gypsum can also be proved by the results of element analyses with respect to Ca²⁺ and Sulphur (Table 3.4 and 3.5) and XRD results (Fig. 3.16-3.30).

Table 3.1 The presence of CaCO₃ in plaster samples (%)

Sample	Weight (g)	%CaCO ₃
E-7.1	0.0989	24.5
E-7.2	0.1147	53.7
E-7.3	0.1002	34.3
S-26.1	0.0964	18.2
S-26.2	0.0962	14.3
S-26.3	0.0975	26.5
S-26.4	0.0941	27.7
S-26.5	0.0941	40.2
S-26.6	0.0731	35.7
Y-3.1	0.1052	35.4
Y-3.2	0.1049	19.5
Y-3.3	0.1030	28.6
Y-3.4	0.1012	82.4
Y-3.5	0.1017	38.6
O-13.1	0.0914	22.0

3.1.2 Soluble Salt Content

The soluble salt contents of the plasters obtained by conductivity measurement were in the range of 3.04%-9.22% with Y-3.2 and S-26.2 samples having relatively high salt content (Table 3.2). Actually the amount of soluble salt in all samples is higher than those found in previous studies (Caner, 2003).

Soluble salt content of the samples was also determined by weight difference obtained before and after dissolution of the samples in water. The results are given in Table 3.2. The values obtained were in the range 9.8% and 21.1%. These results were higher than obtained by conductivity measurement. The reason is not known, this may be due to colloidal dispersion of aggregate parts.

Table 3.2 Soluble Salt Content (%) and Results of Spot Test Analysis

Sample	%Salt by weight difference	%Salt by conductivity	PO ₄ ⁻³	SO ₄ ⁻²	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	CO ₃ ²⁻
Y-3.1	12.3	8.21	+	-	+	-	-	-
Y-3.2	11.2	9.22	-	+	+	-	-	-
Y-3.3	10.9	5.58	-	+	-	-	-	-
Y-3.4	11.3	5.32	+	-	+	-	-	-
S-26.1	10.2	6.23	-	+	+	-	-	-
S-26.2	9.8	9.13	-	+	+	-	-	-
E-7.1	21.1	6.20	-	+	+	-	-	-
E-7.2	16.4	3.04	-	-	+	+	+	-

* "+" means presence, "-" means absence

3.1.3 Spot Test Analysis of the Soluble Salts in the Plasters

The results of the spot test analysis of soluble salts in the plasters are given in the Table 3.2.

All plaster samples except one possess soluble salts having chloride ion as the anion. Sulphate is another common anion identified in the plaster samples and it may be due to presence of gypsum. Sulphate ion may also come from air pollution. Two samples, Y-3.1 and Y-3.4, contain phosphate ion. The source of the phosphate ion may be microorganisms. Only one sample, E-7.2, is found to contain nitrate and nitrite ions. Nitrite and nitrate ions cannot be detected in other samples because they may be containing less nitrate and/or nitrite ions than their detection limits. The limits of identification of these ions are 0.05 microgram as nitric acid and 0.04 microgram as nitrous acid, respectively. Nitrate ion may come from the soil, due to decomposition of nitrogenous organic matters and atmospheric pollutants.

3.1.4 Examination of Pozzolanic Activity of Fine Aggregates

Pozzolanic activities of the aggregates are given in the Table 3.3. It is seen that, the plaster samples do not have pozzolanic properties. Hence, the EDTA solution used for the titration of free Ca^{2+} of the blank solution and the samples are the same except one sample, Y-3.2 (Table 3.3). Pozzolanic activity of this sample is also not significant. In addition, the electrical conductivity of the blank sample and the plaster samples were almost identical.

Table 3.3 Results of the Test for the Pozzolanic Activity of Some Aggregates

Sample	EDTA solution used (mL)	EC
blank	20.5	0.114
Y-3.1	20.5	0.113
Y-3.2	20.0	0.114
O-13.1	20.5	0.112
E-7.2	20.5	0.114
S-26.1	20.5	0.115
S-26.6	20.5	0.114

3.2 Mineralogical Properties of Plasters

Plaster samples were examined by optical microscopic analysis of cross sections and thin sections and also by XRD, FTIR and TGA/DTA analyses to determine the mineral phases and texture of the samples.

3.2.1 Cross Sections Analyses

Cross sections, obtained from plasters of four different houses, were observed by optical microscope. The images of the samples are given in Fig. 3.1-3.3.

Cross Section View of Eylül Lane Sample

Three layers can be clearly seen from exterior to interior. Thicknesses of the layers are not the same; it varies from 61 μ to 173 μ (Fig 3.1)

The outmost layer is blue, the middle layer is white and the inner layer is reddish brown.

Particular character of mortar can be clearly differentiated from the homogeneous character of plaster layers. This result shows that size distribution of plaster is much smaller than the size distribution of mortar. (Fig. 3.1)

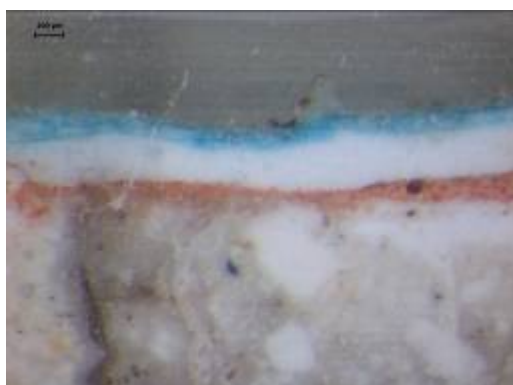


Figure 3.1 Cross section view of the sample E-7

Cross Section View of Yeniıldırımlar Lane Sample

Seven layers can be clearly seen from exterior to interior. Thicknesses of the layers are not the same; it varies from 32μ to 351μ . (Fig. 3.2)

The colours of the layers are brown, blue, yellow, green, white, grey and green from exterior layer to interior layer.



Figure 3.2 Cross section view of the sample Y-3

Cross Section View of Sarıca Lane Sample

Eleven layers can be clearly seen from exterior to interior. Thicknesses of the layers are not the same; and vary from 55μ to 569μ . (Fig. 3.3)

The colours of the layers are yellow, white, blue, white, beige, blue, white, grey, white, grey and green from exterior layer to interior layer.

In this sample the fifth layer has thickness much greater than those of the others. In addition, the particular character of this layer can be clearly distinguished. This difference may be explained by use of different additives and different techniques to increase the strength of the plaster.

Between the first and second layers a black boundary were observed in this sample. This boundary may be an isolation material such as asphalt.

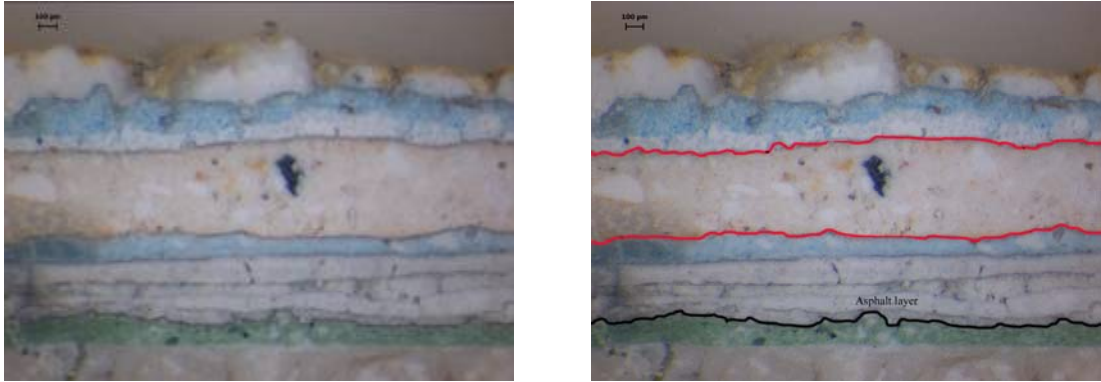


Figure 3.3 Cross section view of the sample S-26, the particular character of the fifth layer is seen clearly

Cross Section View of Öksüzler Lane Sample

Two layers are clearly visible in this sample. Thicknesses of these two layers are not the same, the outer layer is about 70μ and the inner one is about 50μ (Fig. 3.4).

The colour of the outer layer is seen red and inner one is white.

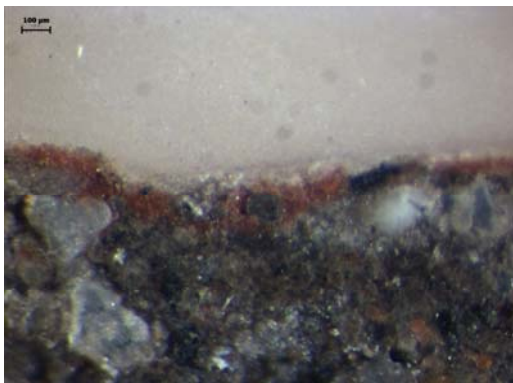


Figure 3.4 Cross section view of the sample O-13

3.2.2 Thin Sections and Optical Microscopy

Observation of thin sections with optical microscope showed that the number of layers distinguished is greater than those found by optical

microscopy of cross sections. In sample Y-3, cross section revealed seven layers but thin section observation revealed twelve layers. (Fig. 3.2 and 3.5) Regarding to this sample, in the outmost layer beside calcite, hematite and trace amount of quartz were identified. The colour of this layer is seen as brown.

In the second layer no other mineral, except calcite, was identified however colouring agent was seen as distributed along the cracks of calcite mineral in this sample. (Fig. 3.6) Here the colour might be ultramarine blue due to its colour.

The third layer is seen white; here the calcite particles are rather large relative to that of the previous layers.

The fourth layer has hematite micro particles and unidentified sub microscopic particles. In this layer the colouring agent is light green, which is distributed in rather coarse calcite particles. In the fifth layer beside calcite; hematite mineral, unidentified sub microscopic particles and small amount of clay particles were seen.

The colour of the fifth layer was observed as brown.

Thickness of the sixth layer is not homogeneous throughout. Here trace amount of biotite, large amount of unidentified sub microscopic particles and small amount of quartz and small amount of clay particles mixed with calcite are characteristics of this layer. Colour of this layer is light green.

In the seventh layer beside calcite, clay and unidentified sub microscopic particles and trace amount of small sized opaque mineral were observed. The colour of the layer is dark green, colouring agent is distributed intensely throughout the layer. (Fig. 3.7)

In layer eight two different sub layers were observed. The upper one was white and consists of micritic calcite particles with some amount of unidentified sub microscopic particles and clay particles. (Fig. 3.8) In the bottom white layer, particles of micritic calcite seemed to be collected as a lime lump.

In layer nine, opaque minerals were observed.

In layer ten, beside calcite, trace amount of quartz, unidentified sub microscopic particles, some amount of opaque minerals and hematite particles were observed. The colour of layer ten is white.

In layer eleven beside calcite, unidentified sub microscopic particles, and trace amount of biotite were observed. The colour of the layer is again white.

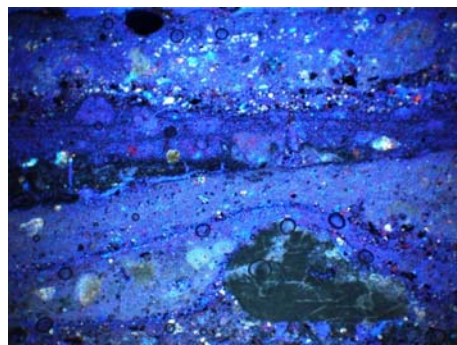
Layer twelve is green and beside calcite, turquoise coloured sub microscopic particles, muscovite mineral particles, trace amount of biotite and quartz, opaque minerals were observed. (Fig. 3.9)

In sample E-7, cross section revealed three layers but thin section observation revealed four layers. (Fig. 3.1 and 3.10) In this sample main mineral was detected as calcite. Beside calcite, trace amount of quartz was also identified. The colours of the layers are orderly green, turquoise, white and red from outer layer to inner layer. In green layer beside calcite, unidentified sub microscopic particles and intensely distributed colouring agent were observed. (Fig. 3.11)

In sample S-26, in addition to eleven layers seen in cross section, two distinct boundaries can be detected in thin section. (Fig. 3.3 and 3.12) The main mineral was found as calcite. (Fig. 3.13)

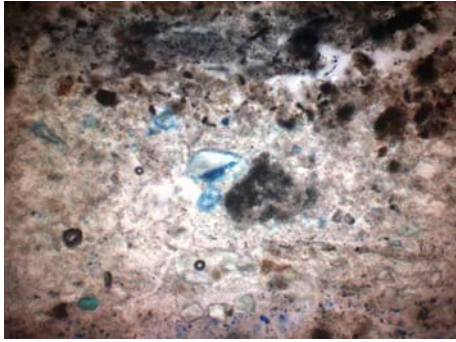


(a) (10x) PPL

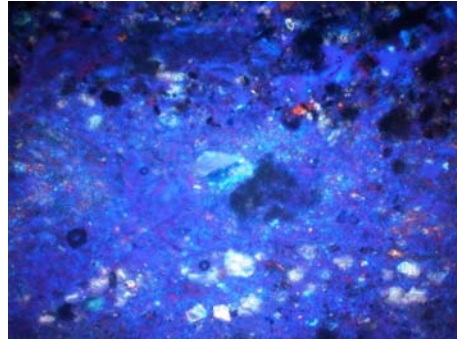


(b) (10x cross nicols)

Figure 3.5 The layers differentiated in thin section of Y-3 plaster, PPL is plane polarized light

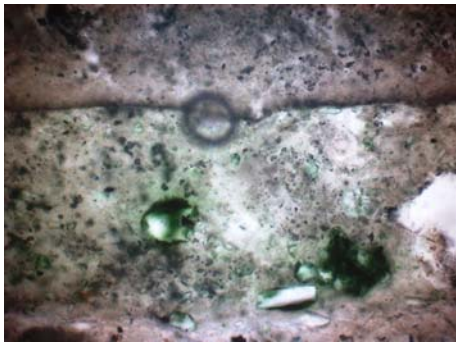


(a) (40x) PPL

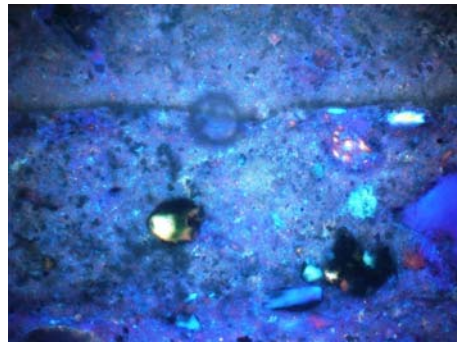


(b) (40x cross nicols)

Figure 3.6 Colouring agent distributed in cracks (Y-3 plaster)

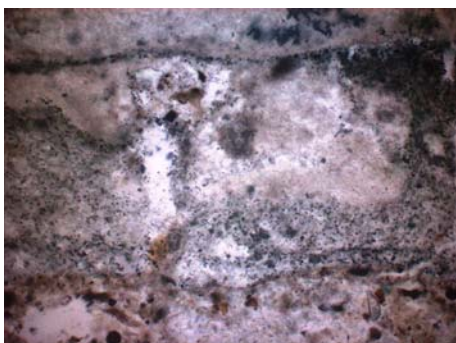


(a) (40x) PPL

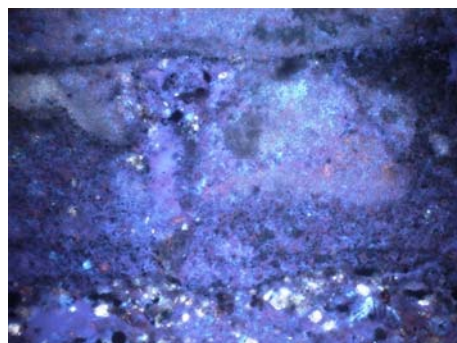


(b) (40x cross nicols)

Figure 3.7 Colouring agent intensely distributed throughout the matrix (Y-3)

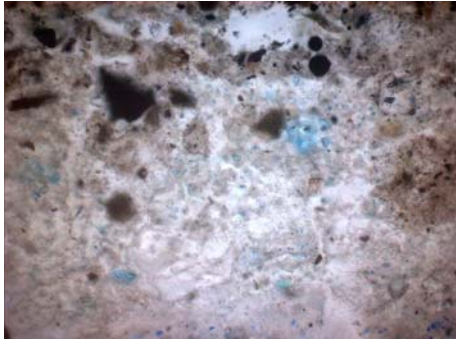


(a) (40x) PPL

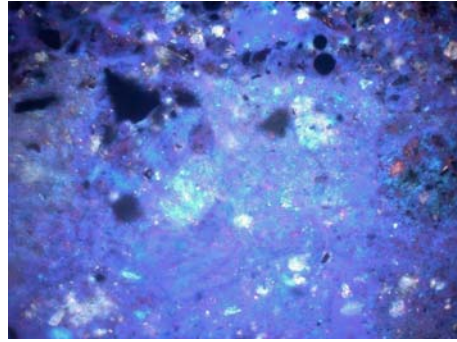


(b) (40x cross nicols)

Figure 3. 8 General view of layer eight in Y-3 plaster



(a) (40x) PPL

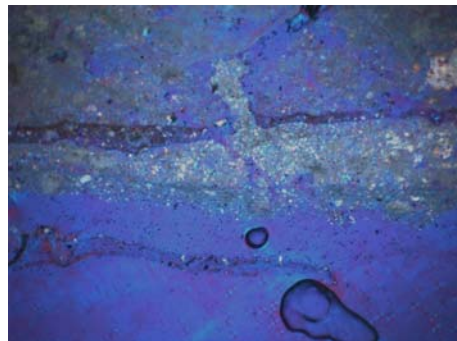


(b) (40x cross nicols)

Figure 3.9 Turquoise coloured sub microscopic particles (Y-3)

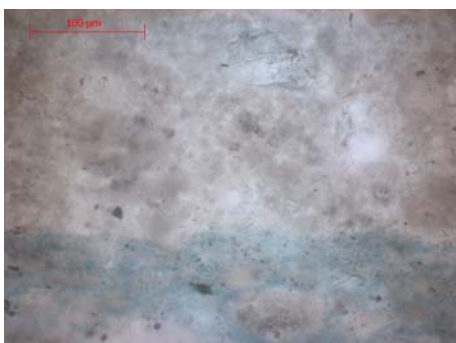


(a) (10x) PPL

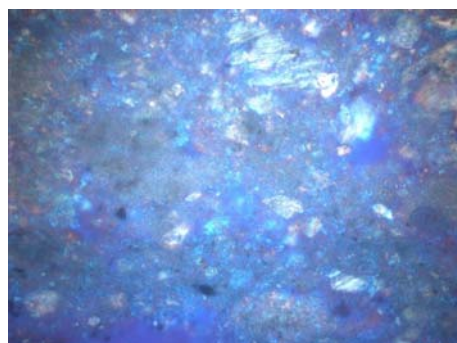


(b) (10x cross nicols)

Figure 3.10 The layers differentiated in thin section of E-7 plaster



(a) (40x) PPL

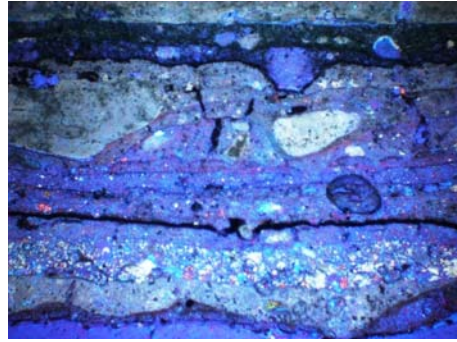


(b) (40x cross nicols)

Figure 3.11 Colouring agent intensely distributed throughout the matrix (E-7)

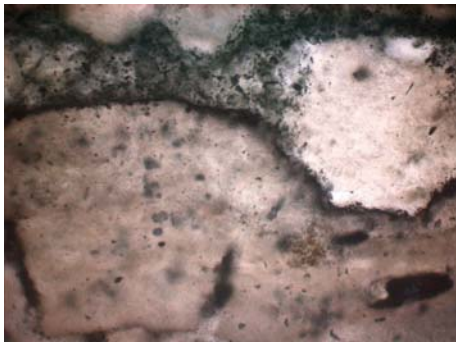


(a) (10x) PPL

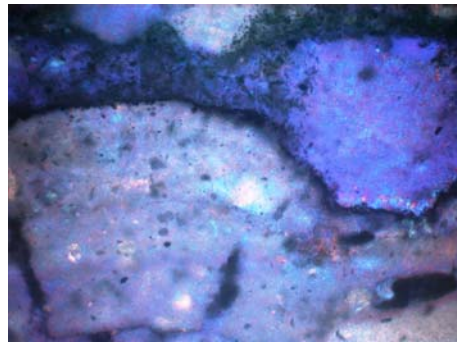


(b) (10x cross nicols)

Figure 3.12 The layers differentiated in thin section of S-26 plaster

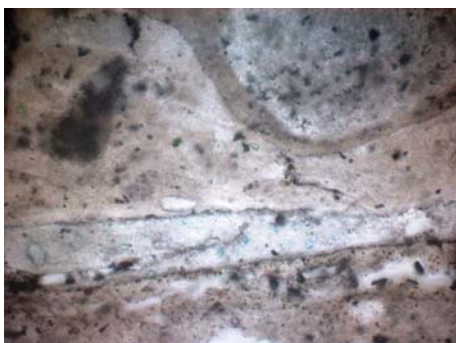


(a) (40x) PPL

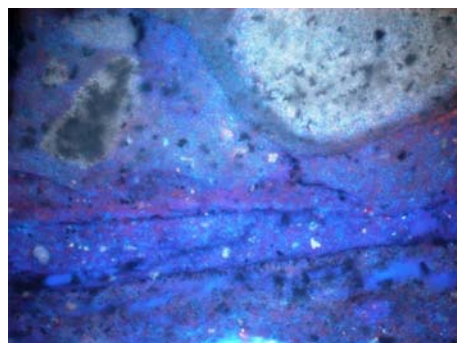


(b) (40x cross nicols)

Figure 3.13 General view of thin section of S-26 plaster layers

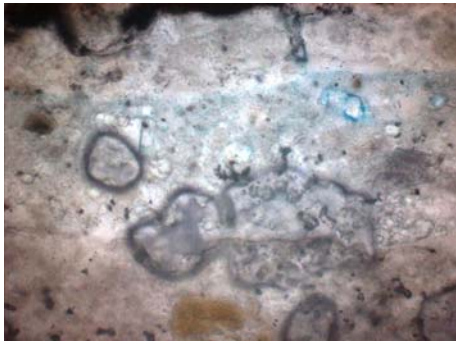


(a) (40x) PPL

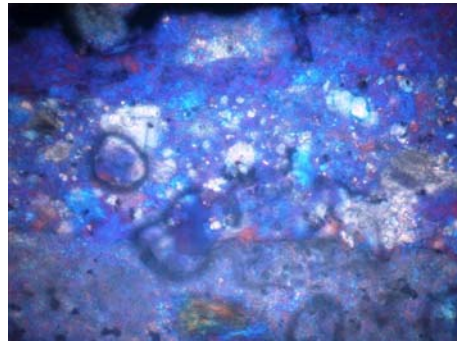


(b) (40x cross nicols)

Figure 3.14 General views of thin section of S-26 plaster layers



(a) (40x) PPL



(b) (40x cross nicols)

Figure 3.15 General views of thin section of S-26 plaster layers

Scale is given in Figure 3.10 (a) and 3.11 (a) for 10x and 40x magnification.

3.2.3 X-Ray Diffraction (XRD) Analyses

X-Ray powder diffraction analyses were carried out on all samples for binder and aggregate parts and acid insoluble aggregate parts. XRD traces of the samples are given in Fig 3.16- 3.30.

XRD trace of all samples indicated that the main minerals of plaster layers are calcite and gypsum. (Fig 3.16- 3.30) Besides calcite and gypsum, most of samples had minor amount of quartz, feldspars, Opal-A and micas.

All plaster layers of house E-7 have calcite and gypsum as the main mineral (Fig. 3.16- 3.18). E-7.2 plaster sample has relatively less gypsum mineral (Fig. 3.17). After treatment with 2% acetic acid, presence of quartz peak became more intensified.

All plaster layers of house S-26 have calcite and gypsum as the main mineral (Fig. 3.19- 3.24). Besides these main minerals, minor amount of quartz, feldspars and Opal-A were also detected. After treatment with 2% acetic acid, presence of minor amounts of Opal-A became more evident in sample S-26.5 and S-26.6 (Fig. 3.23- 3.24).

All plaster layers of house Y-3 have calcite and gypsum as the main mineral (Fig. 3.25- 3.29). Besides these main minerals, minor amount of quartz, feldspars and Opal-A were also detected. After treatment with 2%

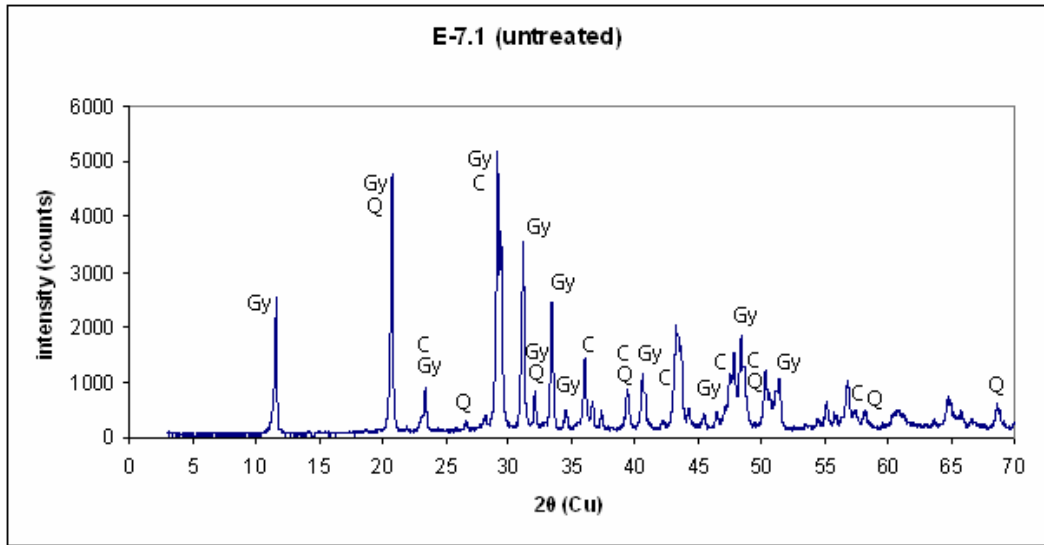
acetic acid, presence of minor amounts of Opal-A became more evident in sample Y-3.1, Y-3.4 and Y-3.5 (Fig. 3.27- 3.29).

The plaster layer of house O-13 has calcite and gypsum as the main mineral (Fig. 3.30). After treatment with 2% acetic acid, presence of quartz and feldspar can be seen more clearly (Fig. 3.30).

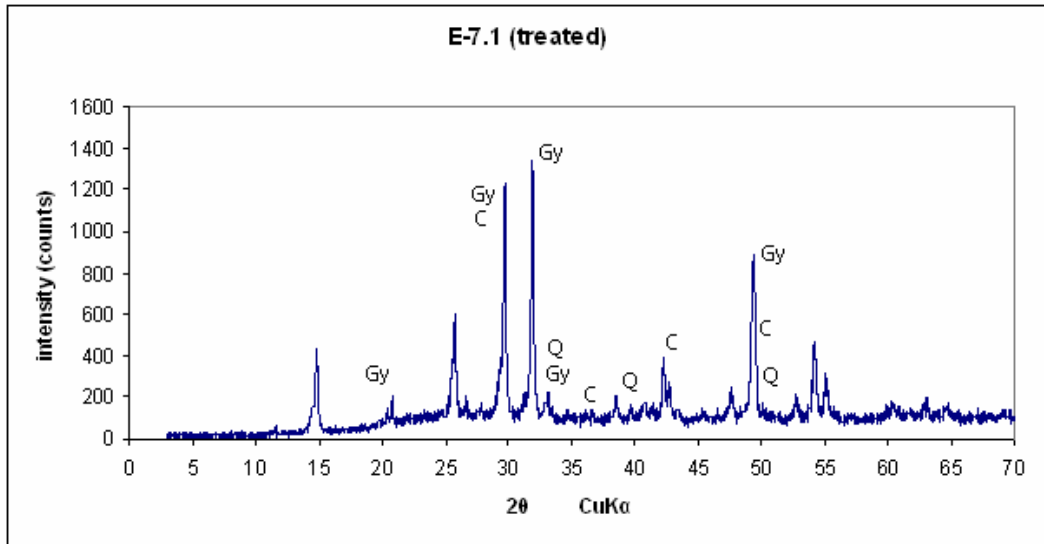
Plaster layer of E-7.1 has more gypsum mineral compared to other house's plaster layers (Fig.3.16).

All plaster layers were also evaluated with respect to pigment composition. In the plaster samples E-7.3 and O-13.1 hematite peaks were seen in the XRD traces of treated samples (Fig. 3.18 and Fig 3.30). The red colour of these layers may come from hematite mineral.

The mineral gypsum is known to be highly soluble in water comparing with CaCO_3 . Solubility product constant, K_{sp} , of CaSO_4 is equal to $2.4 \cdot 10^{-5}$ while that of CaCO_3 is equal to $4.5 \cdot 10^{-9}$ at 25°C . However, it has been found that the solubility of gypsum is very low in the historic gypsum mortars and plasters. This might be provided by the addition of some organic additives (Middendorf and Knöfel, 1997). The wide use of gypsum in plasters was likely to be due to their advantages over lime in terms of lower energy requirements for their calcinations, higher mechanical properties, especially of compressive strength and for their rapid solidification (Middendorf and Knöfel, 1997; Tunçoku, 2001).



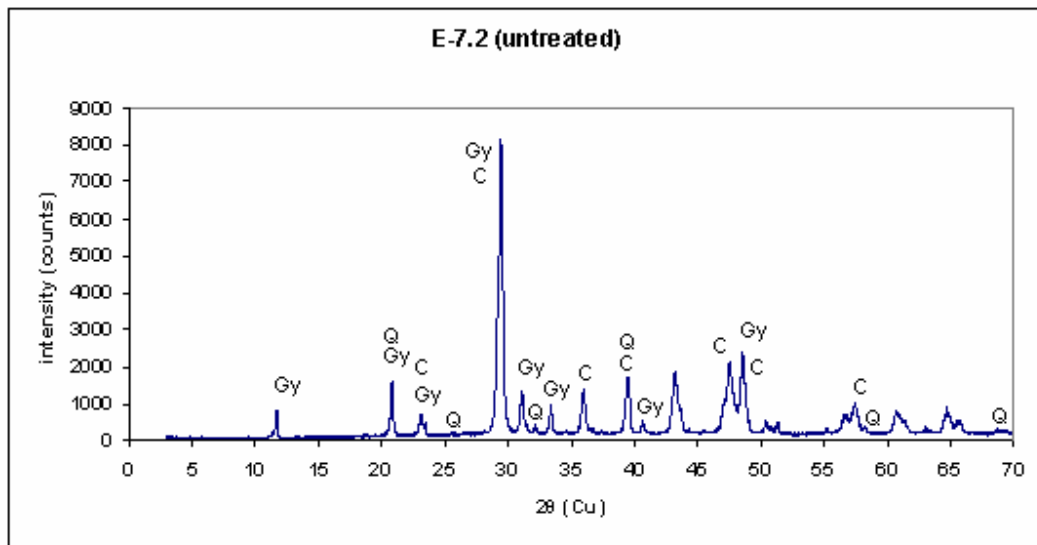
(a)



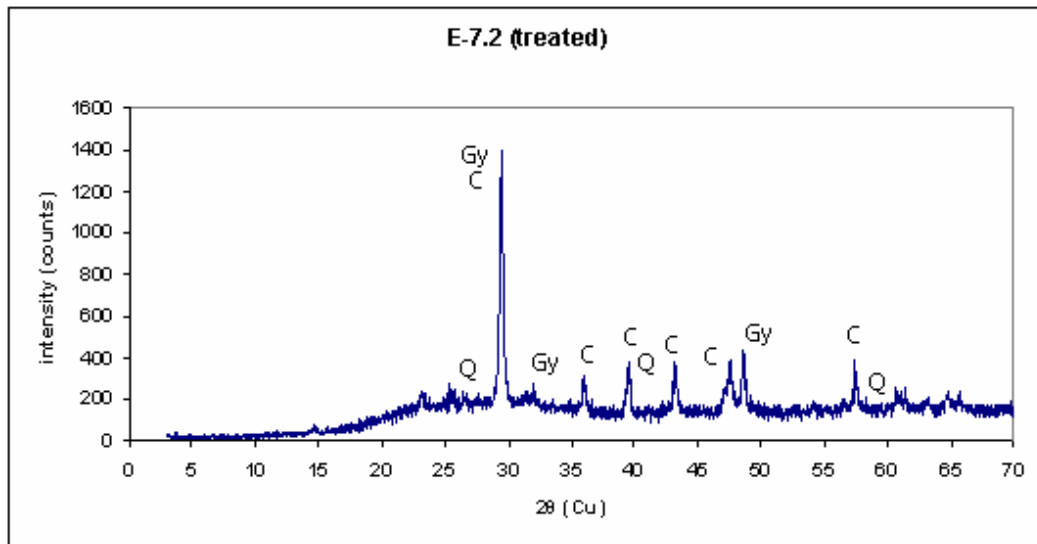
(b)

Figure 3.16 (a) XRD trace of E-7.1 rough plaster layers (b) XRD trace of E-7.1 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz



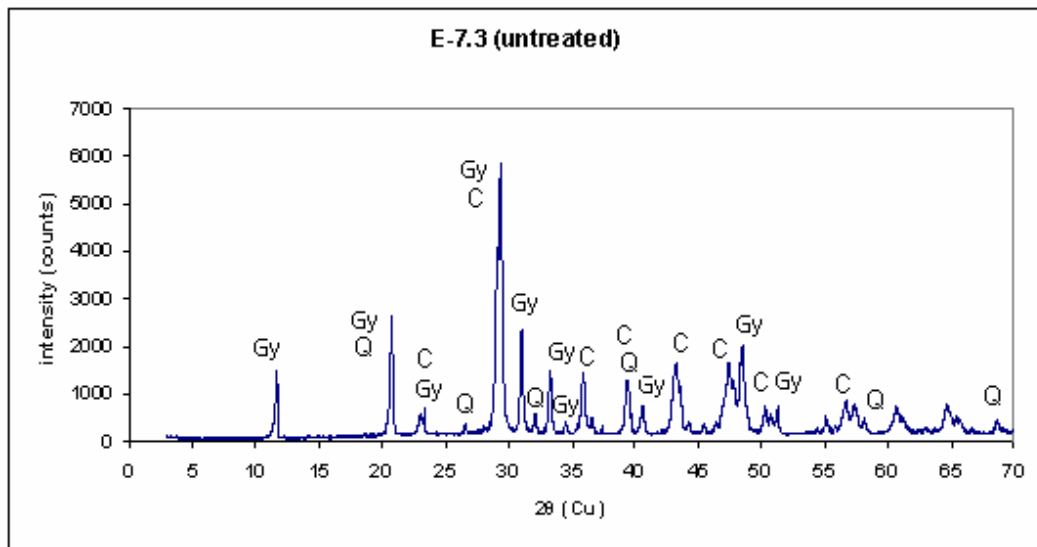
(a)



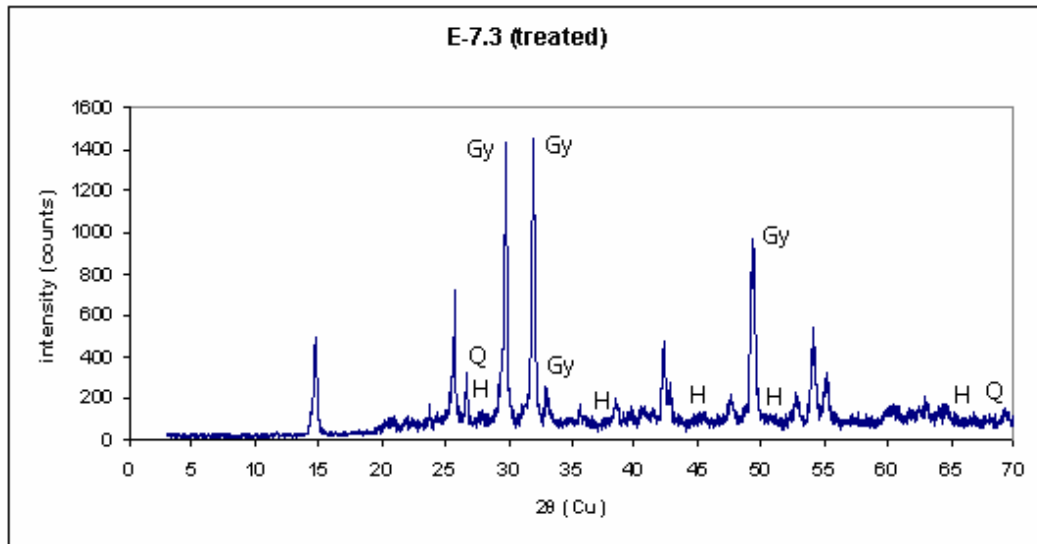
(b)

Figure 3.17 (a) XRD trace of E-7.2 rough plaster layers (b) XRD trace of E-7.2 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz



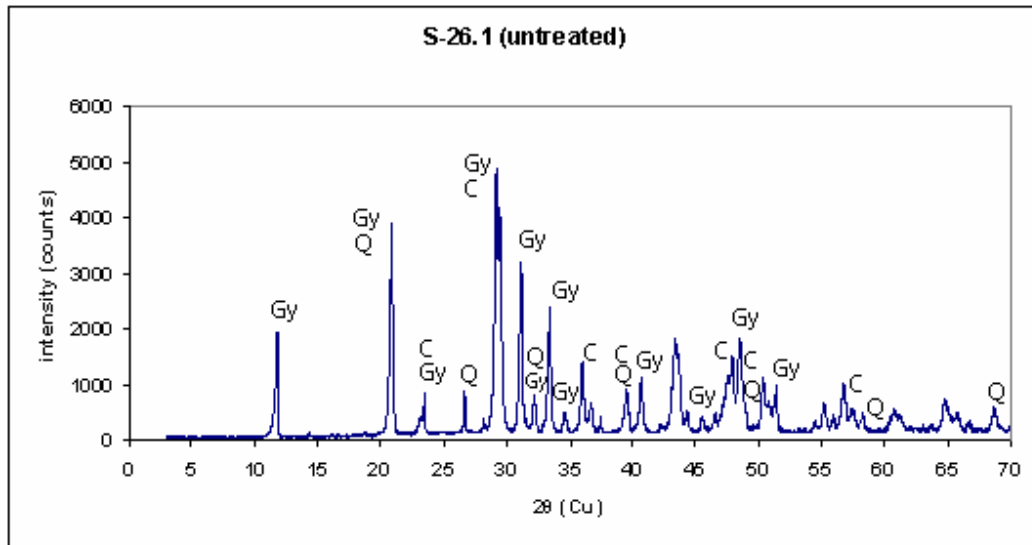
(a)



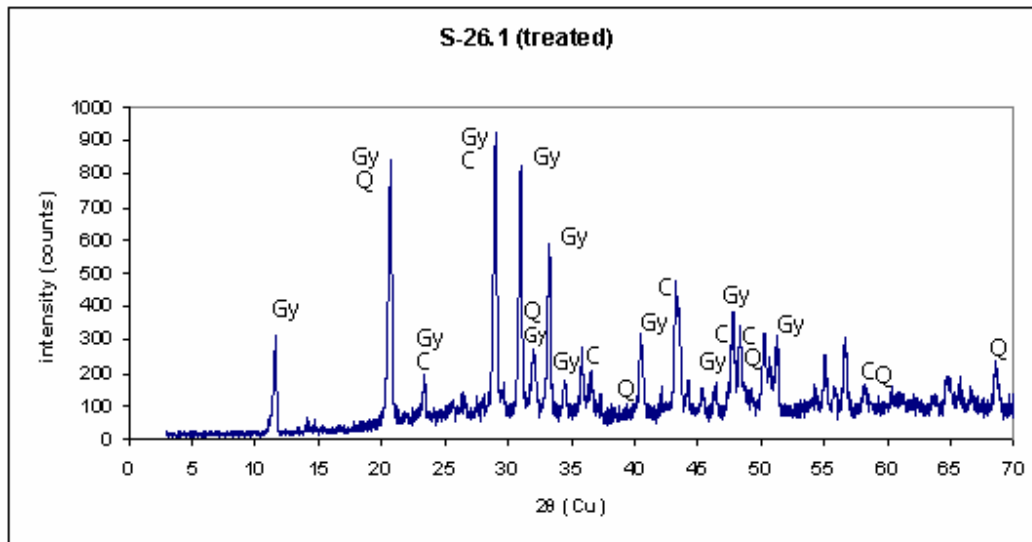
(b)

Figure 3.18 (a) XRD trace of E-7.3 rough plaster layers (b) XRD trace of E-7.3 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz, H; Hematite



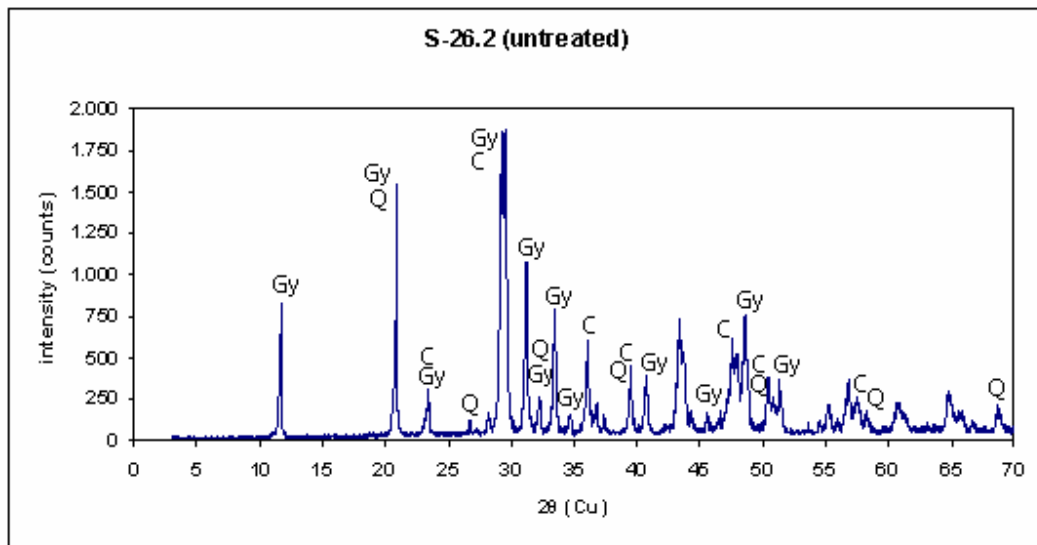
(a)



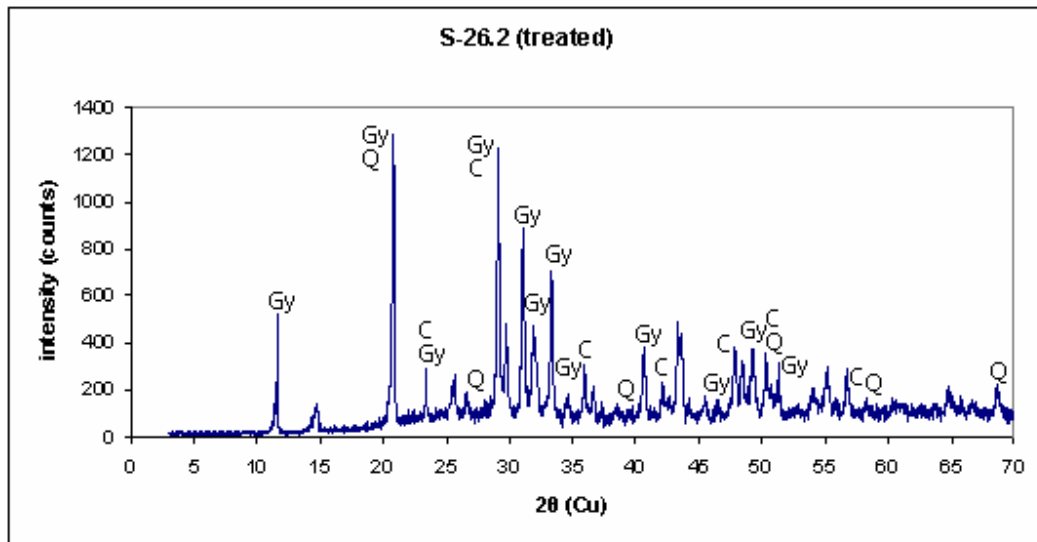
(b)

Figure 3.19 (a) XRD trace of S-26.1 rough plaster layers (b) XRD trace of S-26.1 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz



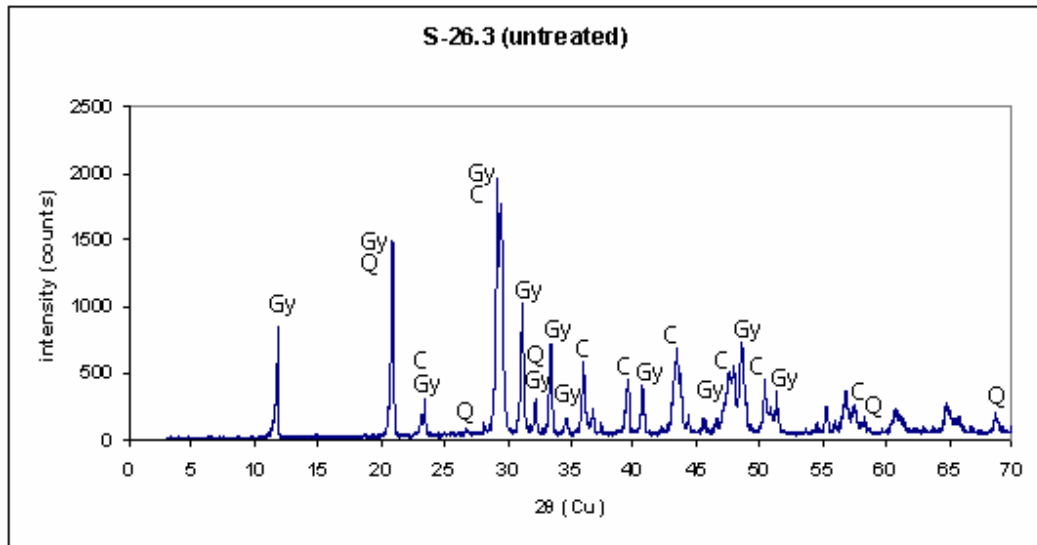
(a)



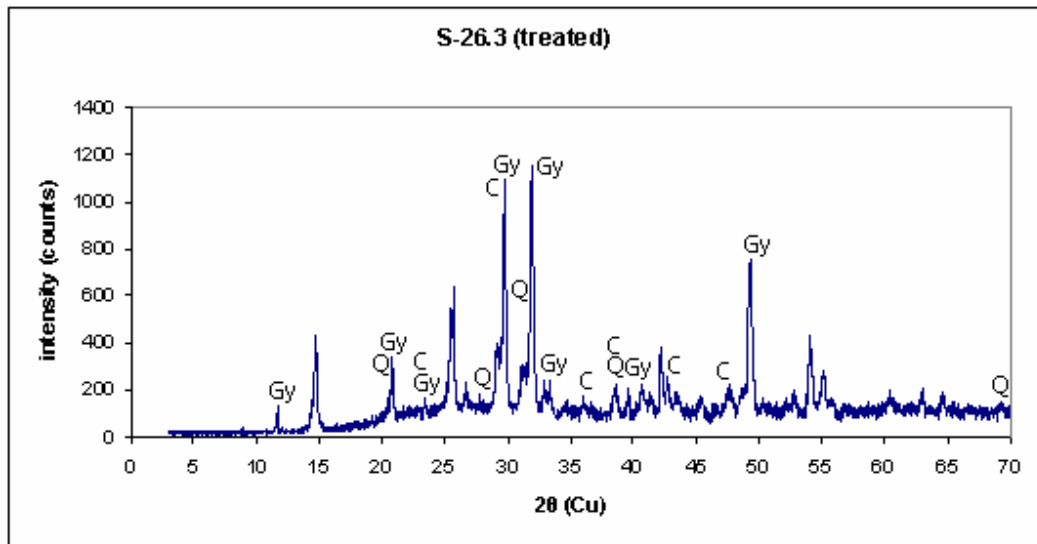
(b)

Figure 3.20 (a) XRD trace of S-26.2 rough plaster layers (b) XRD trace of S-26.2 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz



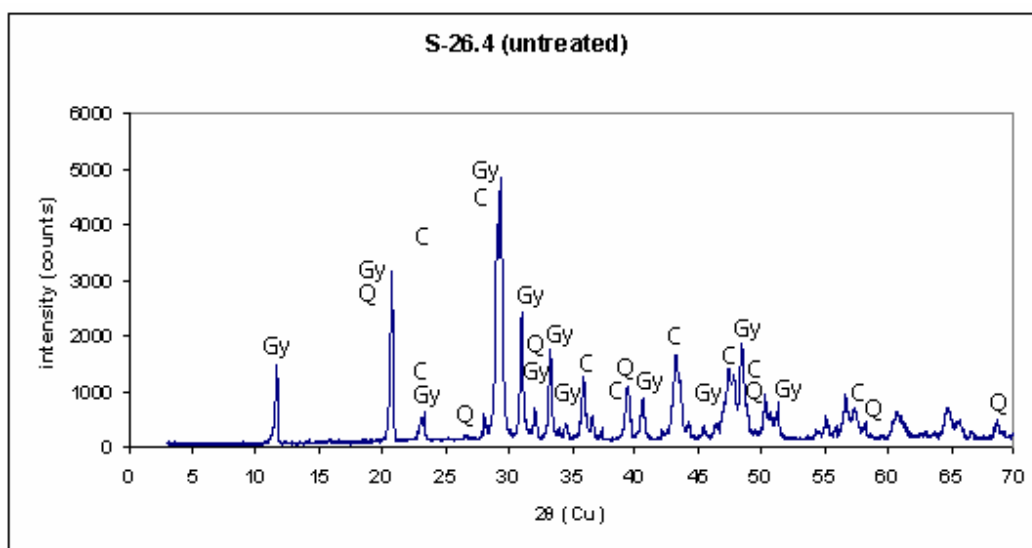
(a)



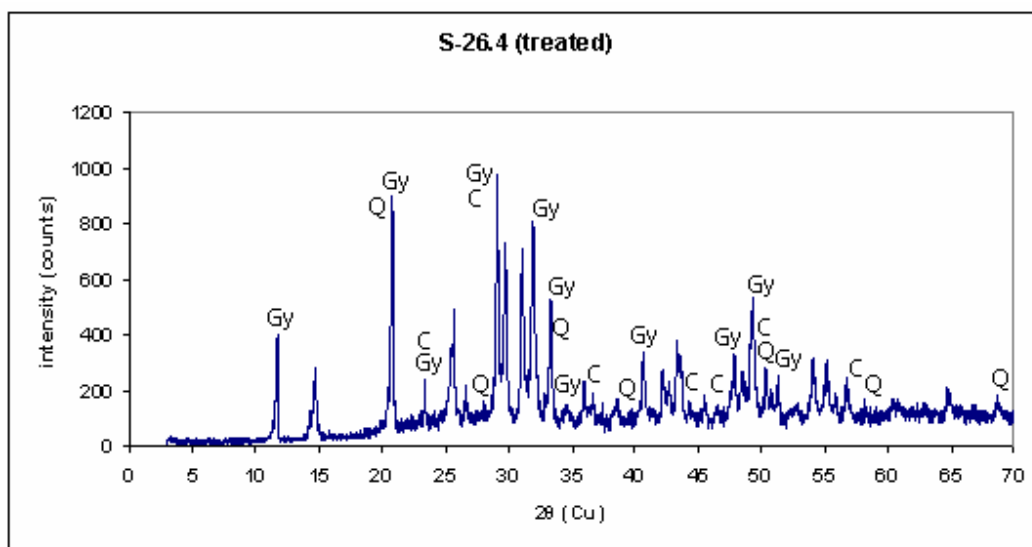
(b)

Figure 3.21 (a) XRD trace of S-26.3 rough plaster layers (b) XRD trace of S-26.3 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz



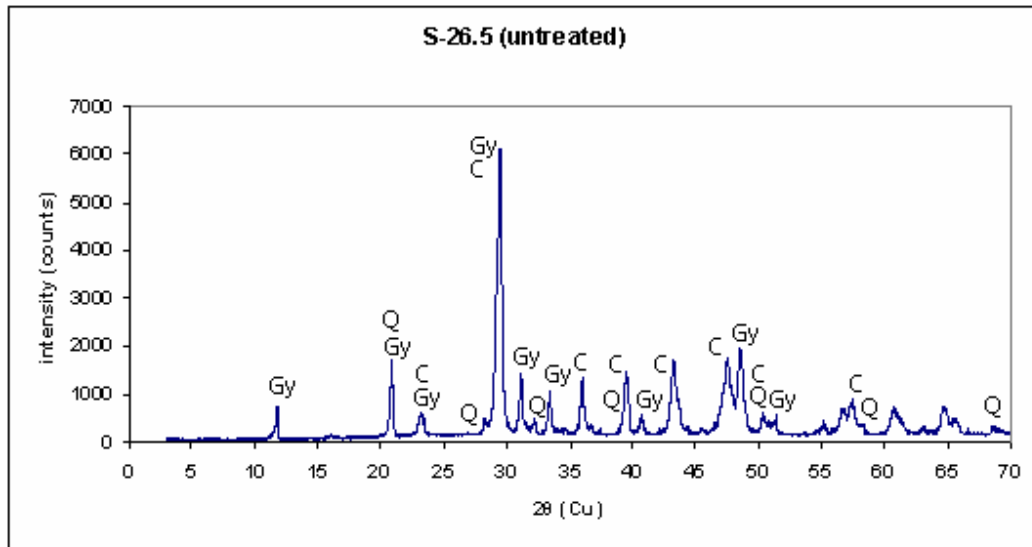
(a)



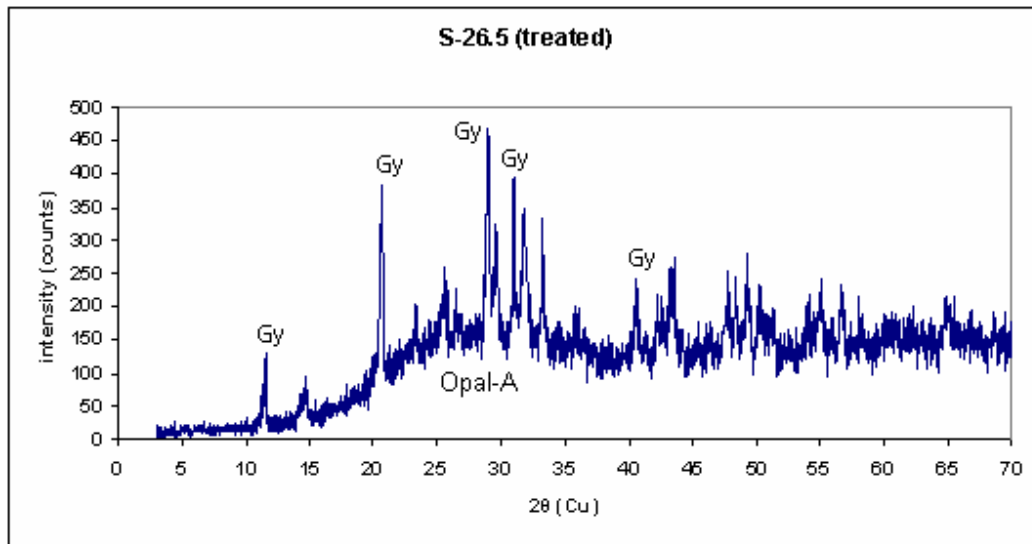
(b)

Figure 3.22 (a) XRD trace of S-26.4 rough plaster layers (b) XRD trace of S-26.4 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz



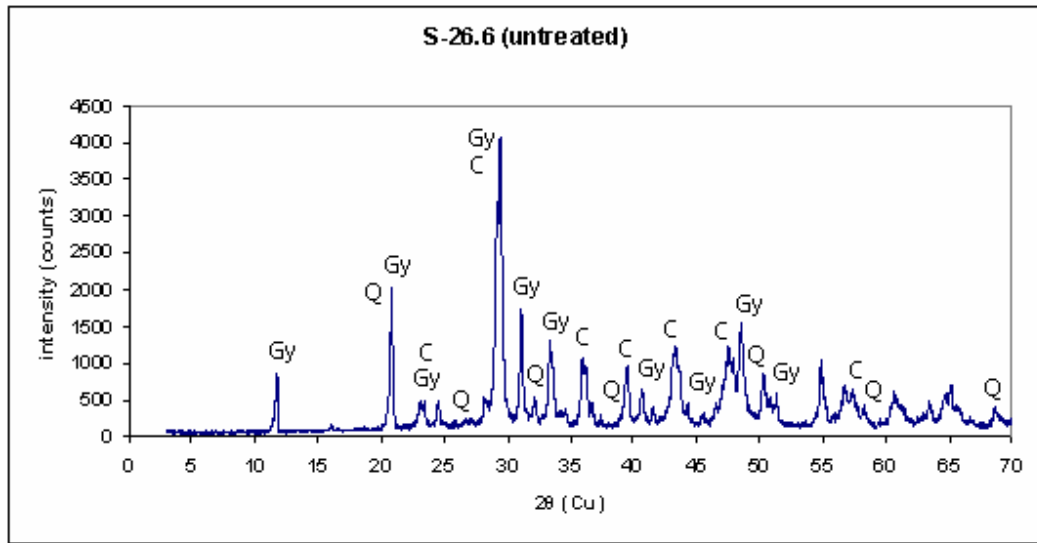
(a)



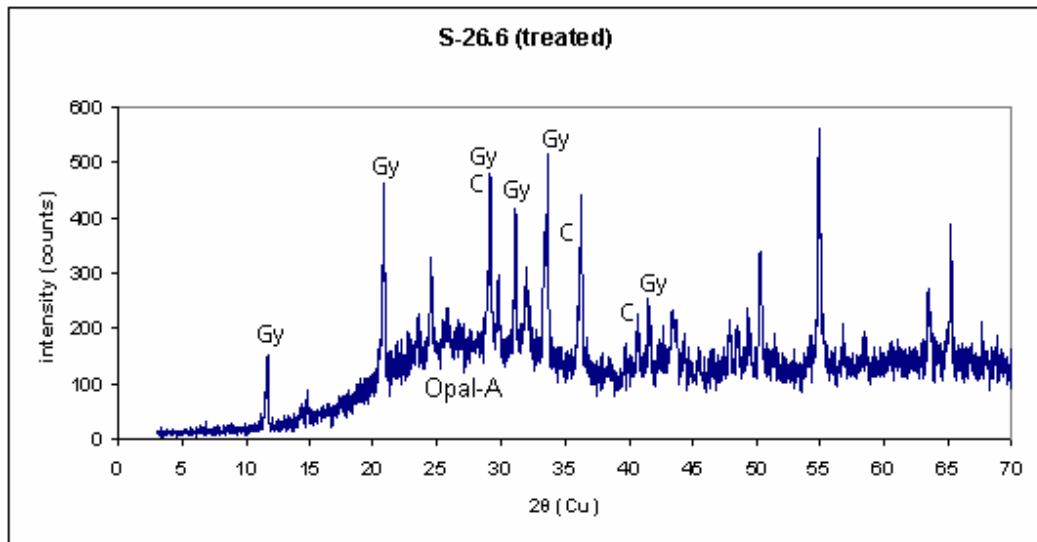
(b)

Figure 3.23 (a) XRD trace of S-26.5 rough plaster layers (b) XRD trace of S-26.5 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz



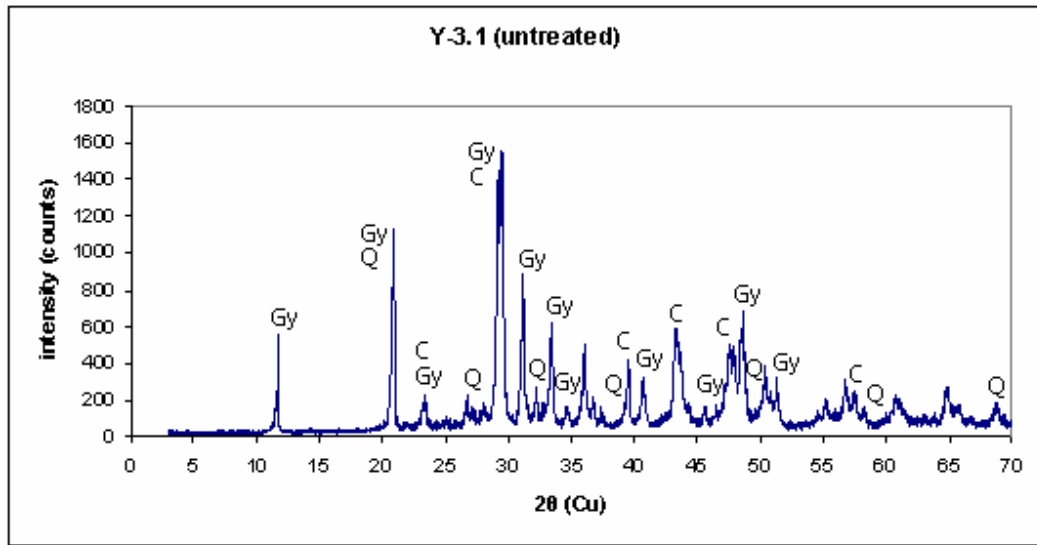
(a)



(b)

Figure 3.24 (a) XRD trace of S-26.6 rough plaster layers (b) XRD trace of S-26.6 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz



(a)

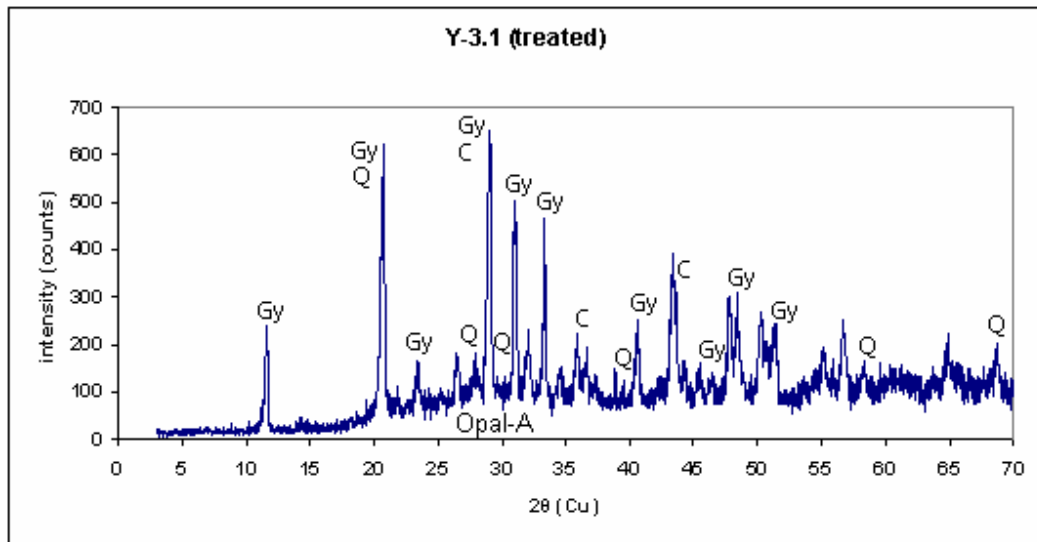
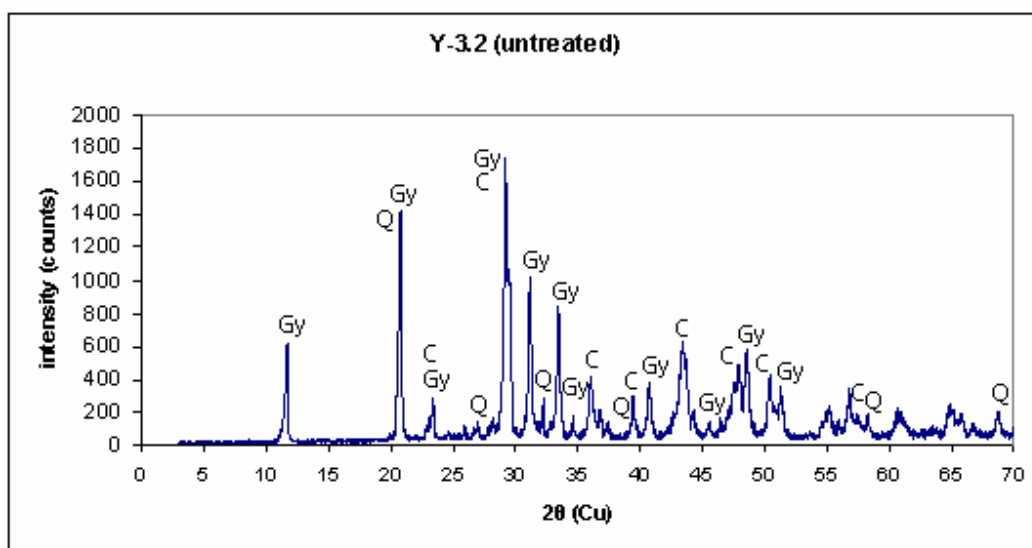
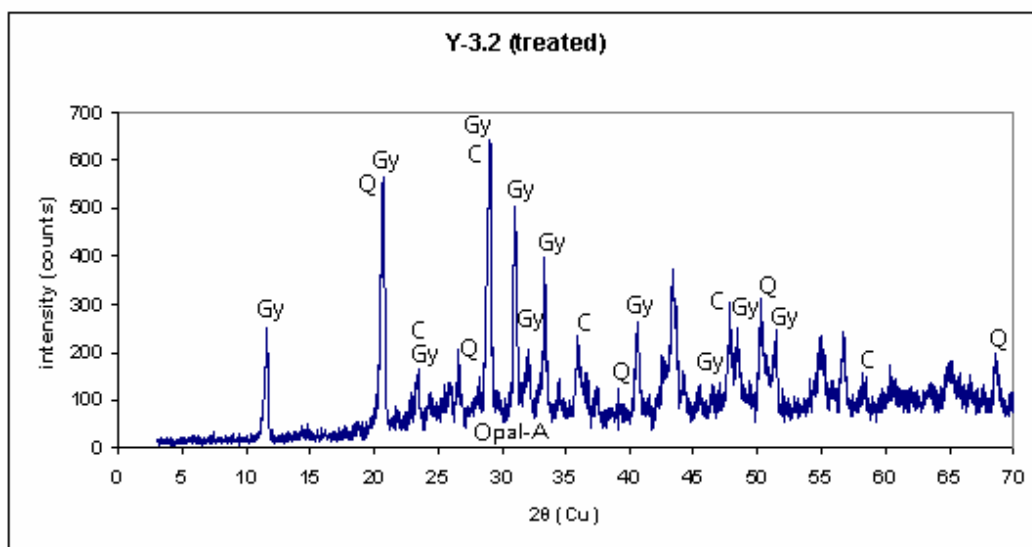


Figure 3.25 (a) XRD trace of Y-3.1 rough plaster layers (b) XRD trace of Y-3.1 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz

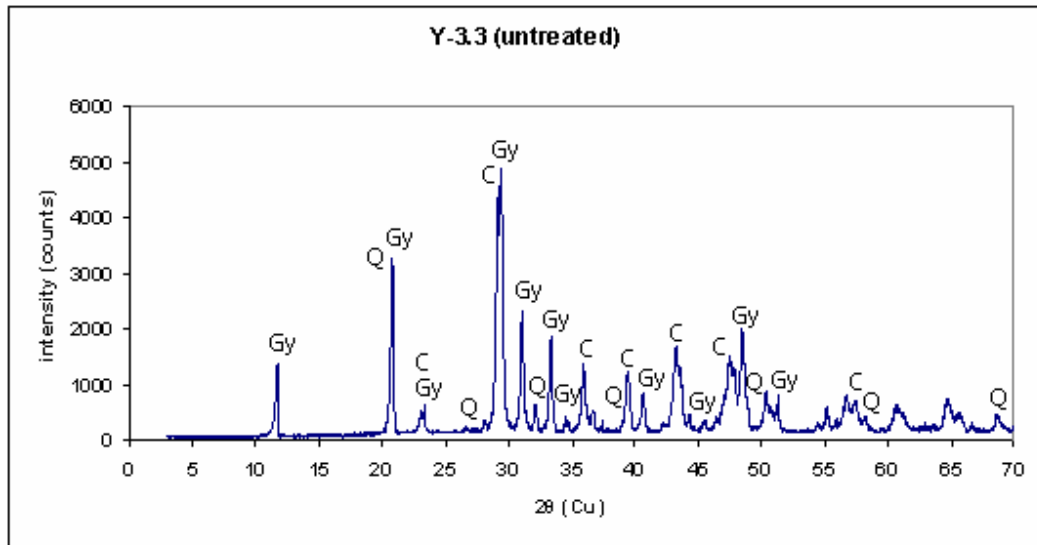


(a)

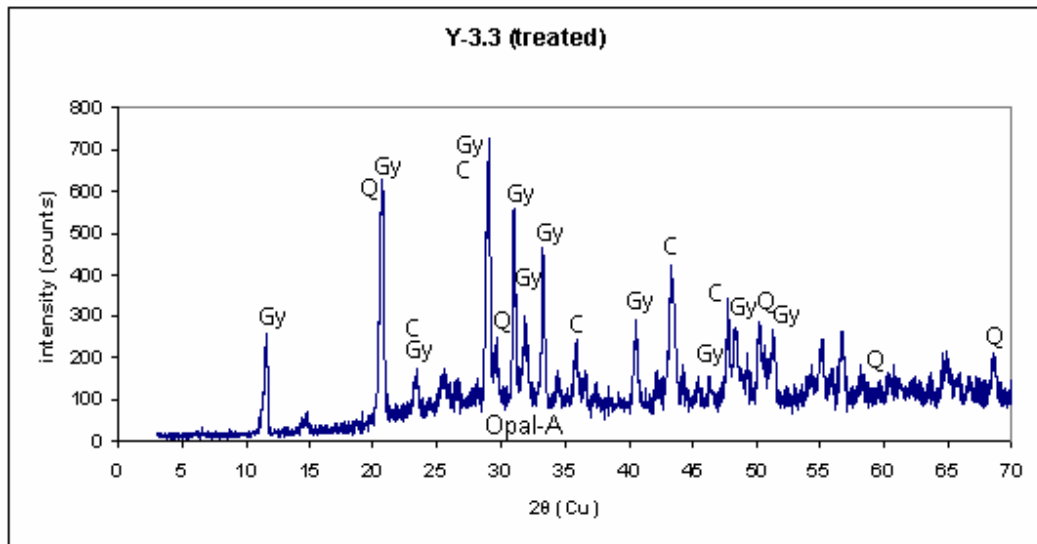


(b)

Figure 3.26 (a) XRD trace of Y-3.2 rough plaster layers (b) XRD trace of Y-3.2 treated plaster layers
 C: Calcite, Gy: Gypsum, Q: Quartz



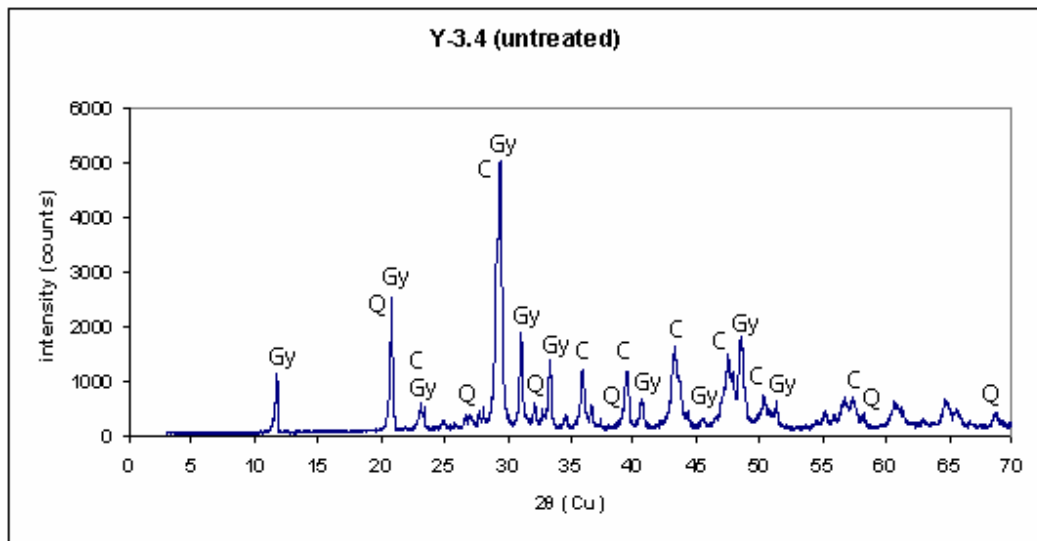
(a)



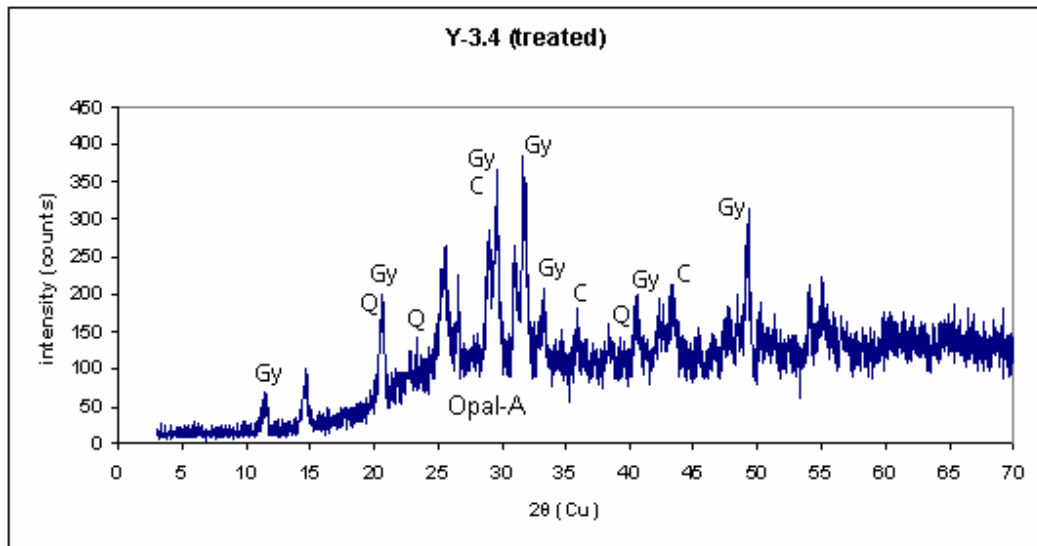
(b)

Figure 3.27 (a) XRD trace of Y-3.3 rough plaster layers (b) XRD trace of Y-3.3 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz



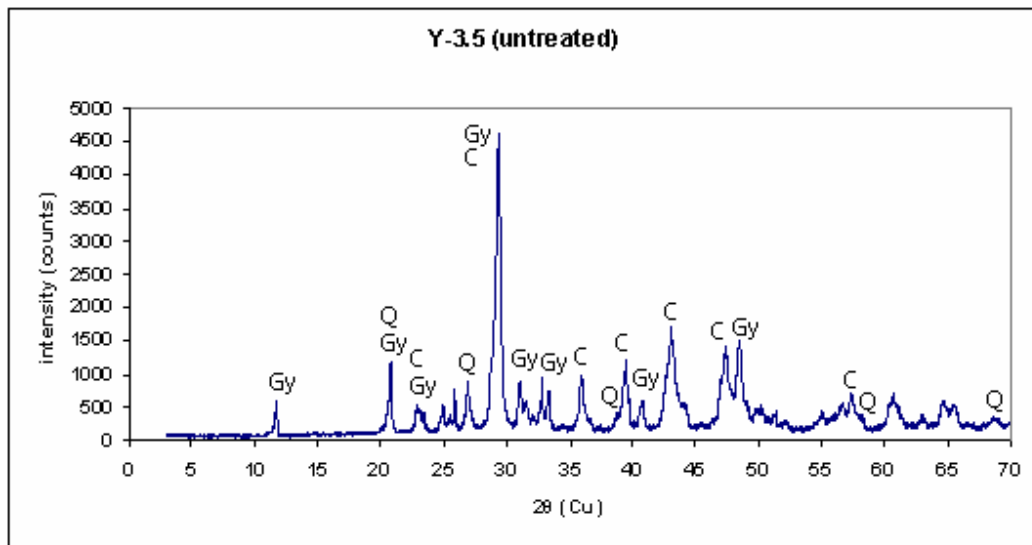
(a)



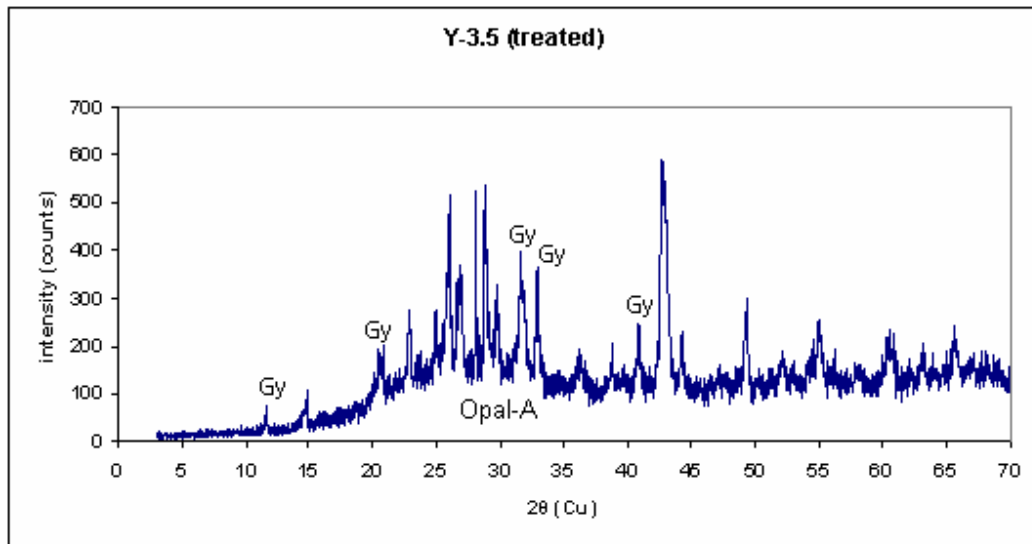
(b)

Figure 3.28 (a) XRD trace of Y-3.4 rough plaster layers (b) XRD trace of Y-3.4 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz



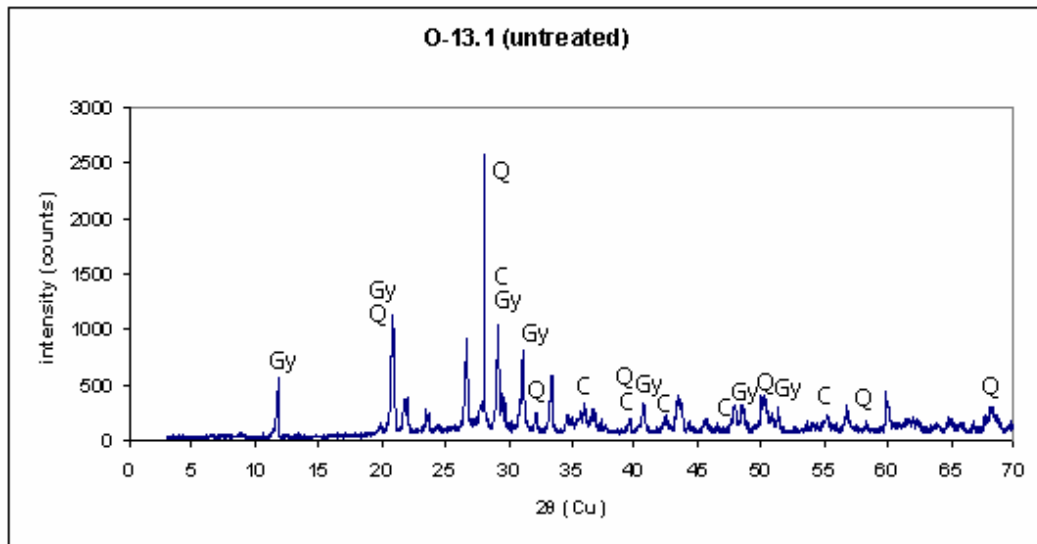
(a)



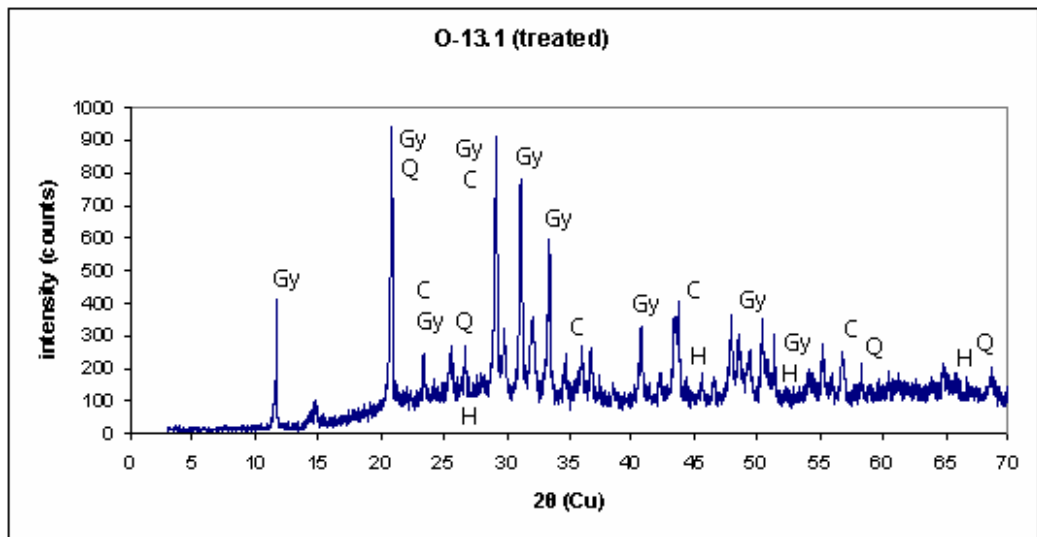
(b)

Figure 3.29 (a) XRD trace of Y-3.5 rough plaster layers (b) XRD trace of Y-3.5 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz



(a)



(b)

Figure 3.30 (a) XRD trace of O-13.1 rough plaster layers (b) XRD trace of O-13.1 treated plaster layers

C: Calcite, Gy: Gypsum, Q: Quartz, H: Hematite

3.2.4 FTIR Analyses

FTIR spectra of some untreated and all acetic acid treated samples of plaster layers were obtained. FTIR trace of both types of samples showed the presence of gypsum and calcite with the stretching mode of carbonate at

around 1450 cm^{-1} (Fig. 3.31- 3.50). The SO_4^{2-} ion possesses four active fundamental peaks in the infrared, at 981 cm^{-1} , at 451 cm^{-1} , at 1104 cm^{-1} , and at 613 cm^{-1} . The spectra of untreated samples seem to be more complicated than treated ones may be due to the effect of soluble salts present in the untreated samples.

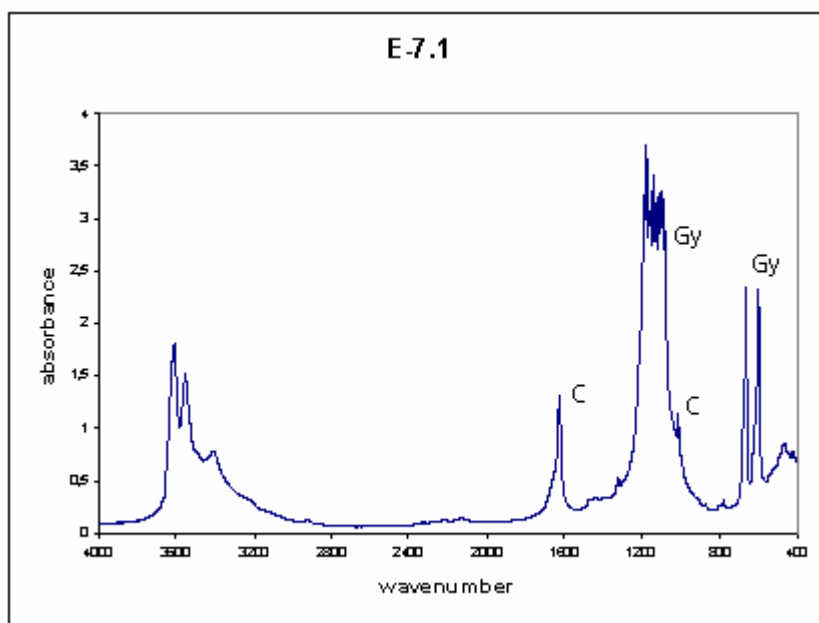


Figure 3.31 FTIR trace of E-7.1 layer at: 2% CH_3COOH treated.

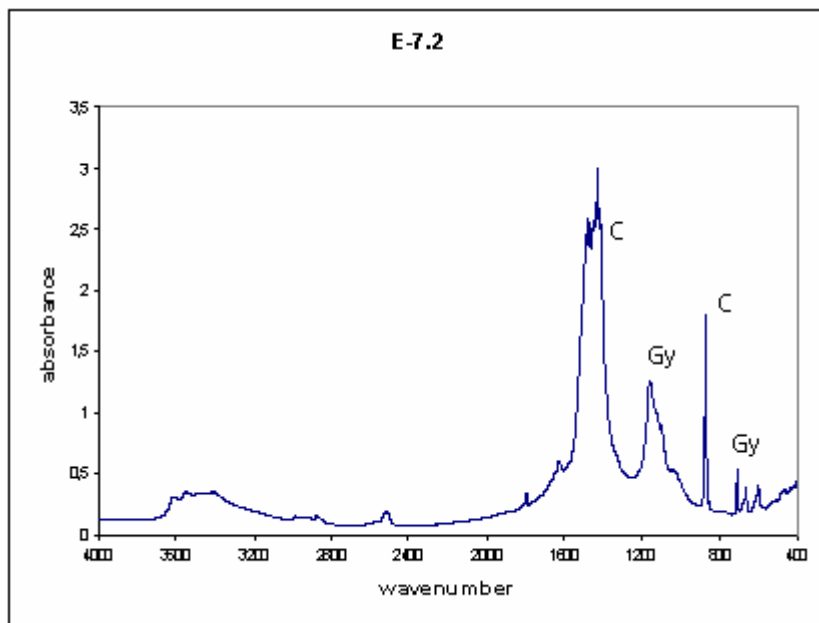


Figure 3.32 FTIR trace of E-7.2 layer at: 2% CH_3COOH treated.

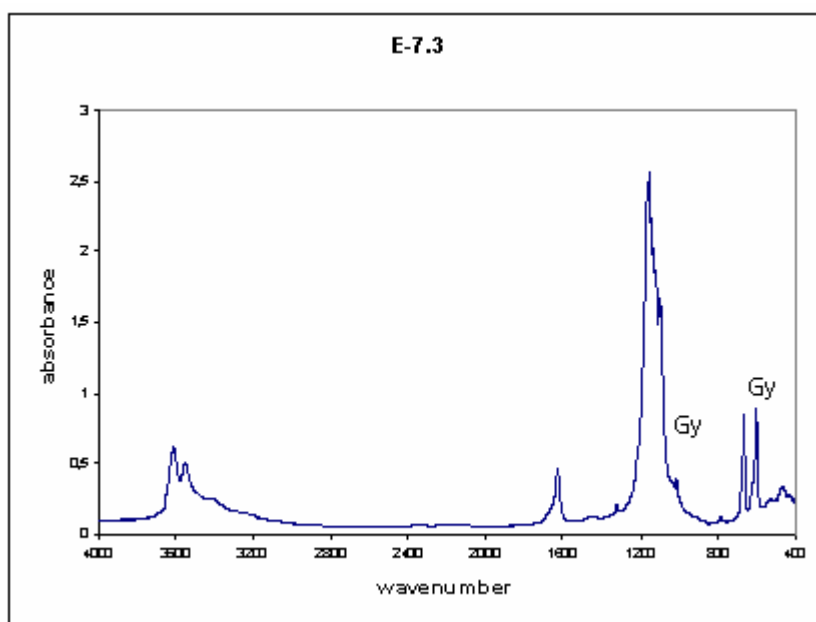


Figure 3.33 FTIR trace of E-7.3 layer at: 2% CH₃COOH treated.

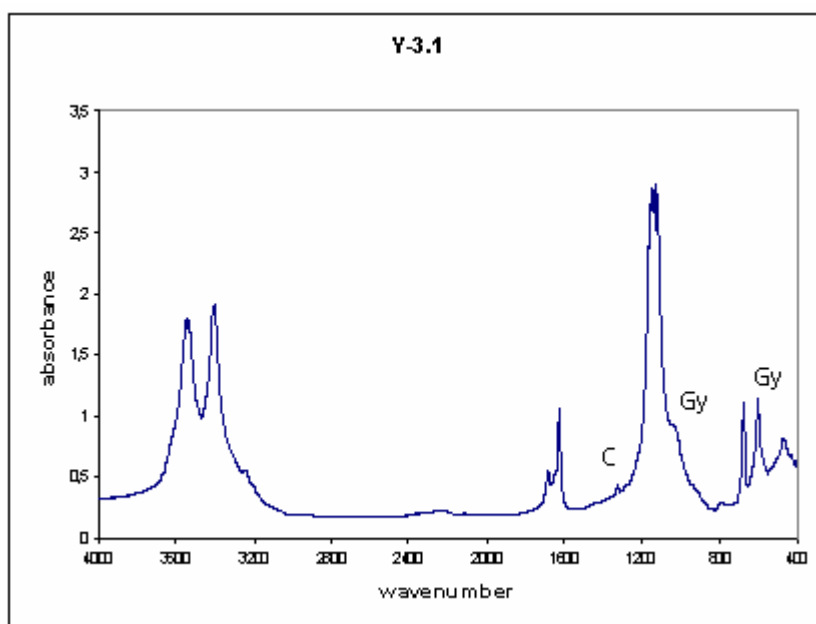


Figure 3.34 FTIR trace of Y-3.1 layer at: 2% CH₃COOH treated.

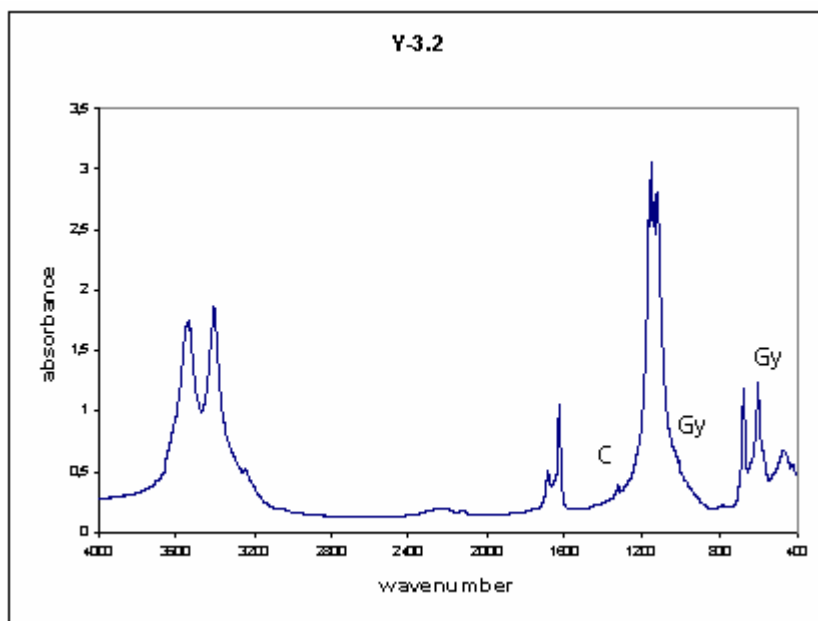


Figure 3.35 FTIR trace of Y-3.2 layer at: 2% CH₃COOH treated.

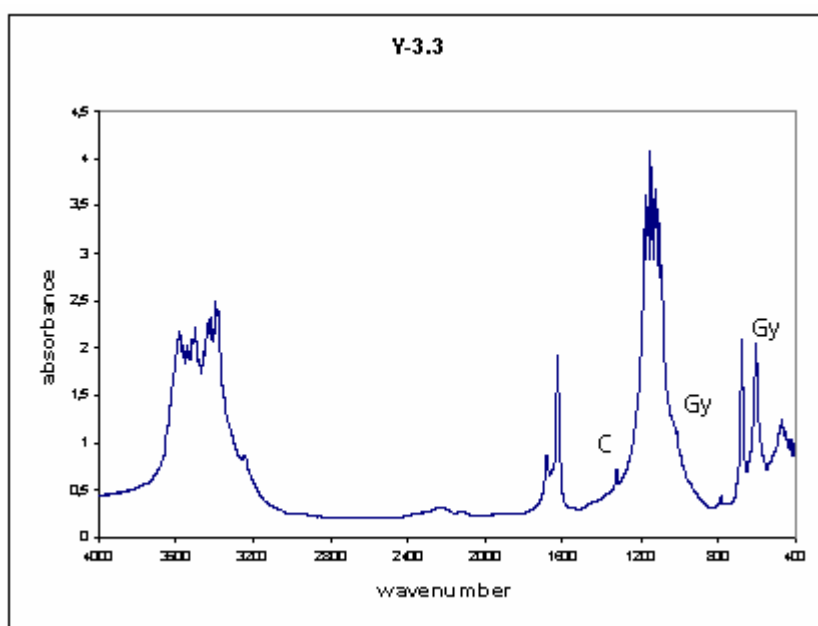


Figure 3.36 FTIR trace of Y-3.3 layer at: 2% CH₃COOH treated.

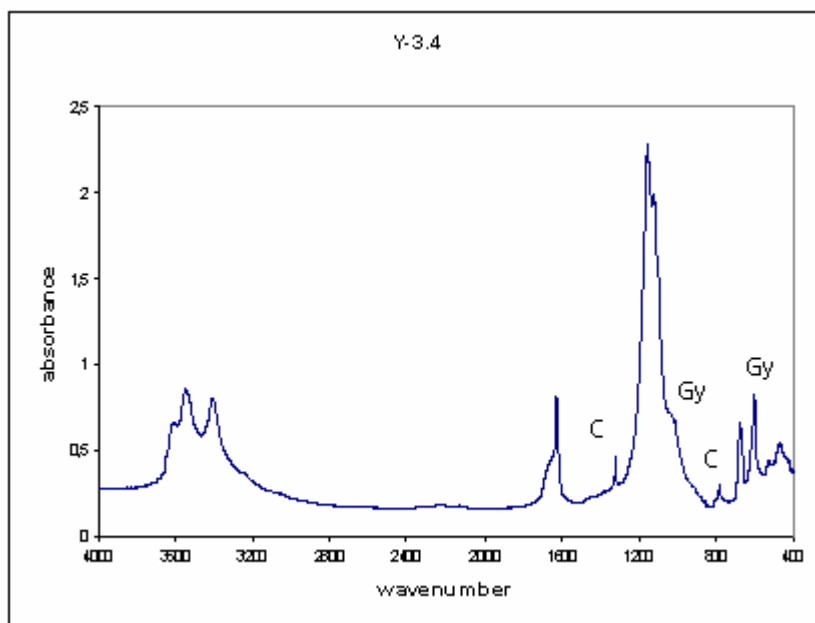


Figure 3.37 FTIR trace of Y-3.4 layer at: 2% CH₃COOH treated.

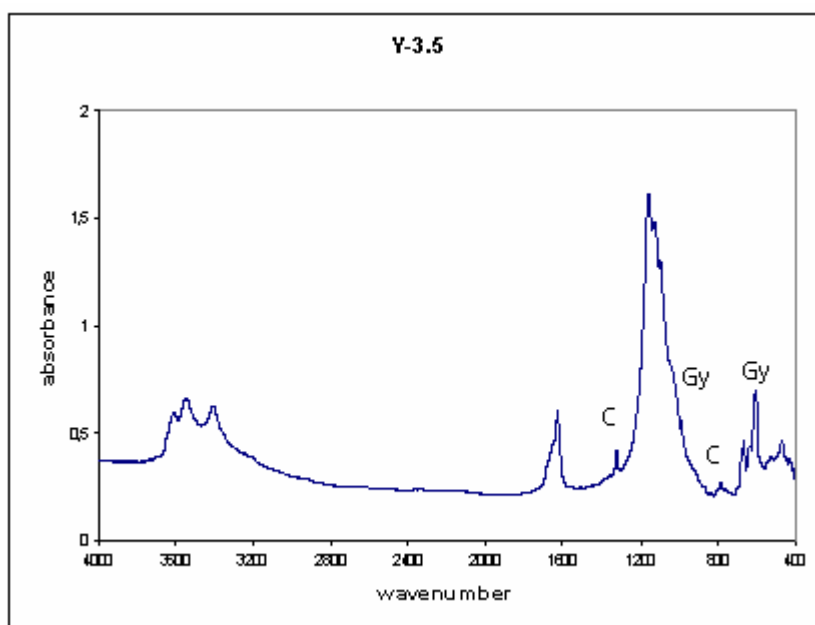


Figure 3.38 FTIR trace of Y-3.5 layer at: 2% CH₃COOH treated.

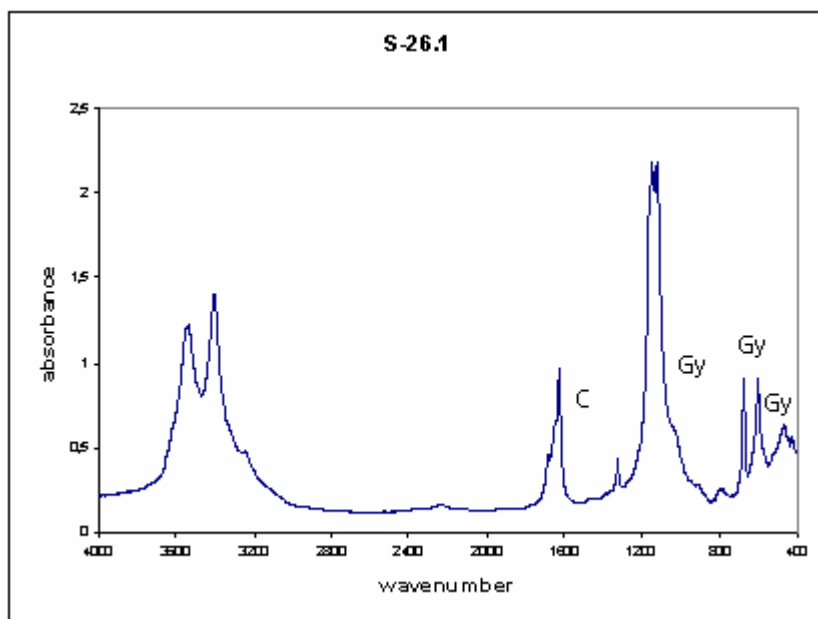


Figure 3.39 FTIR trace of S-26.1 layer at: 2% CH₃COOH treated.

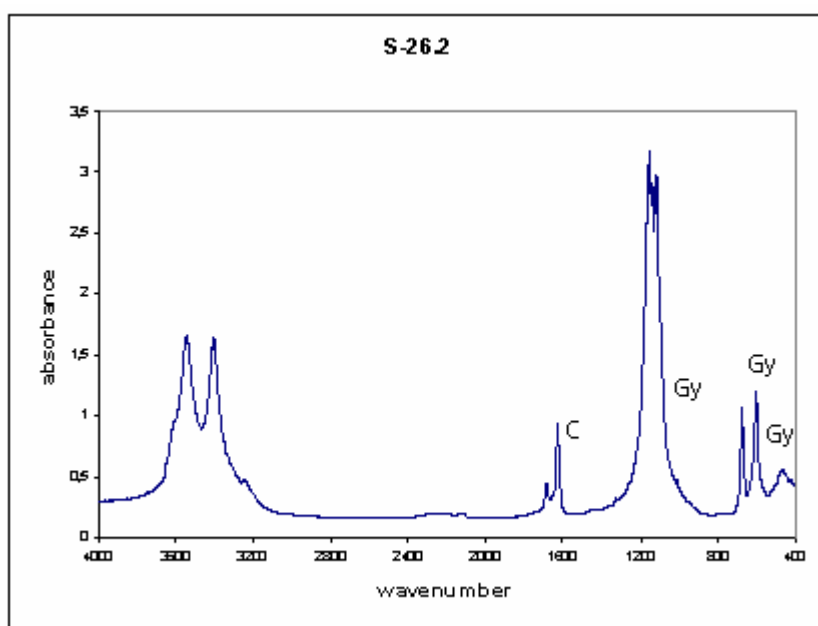


Figure 3.40 FTIR trace of S-26.2 layer at: 2% CH₃COOH treated.

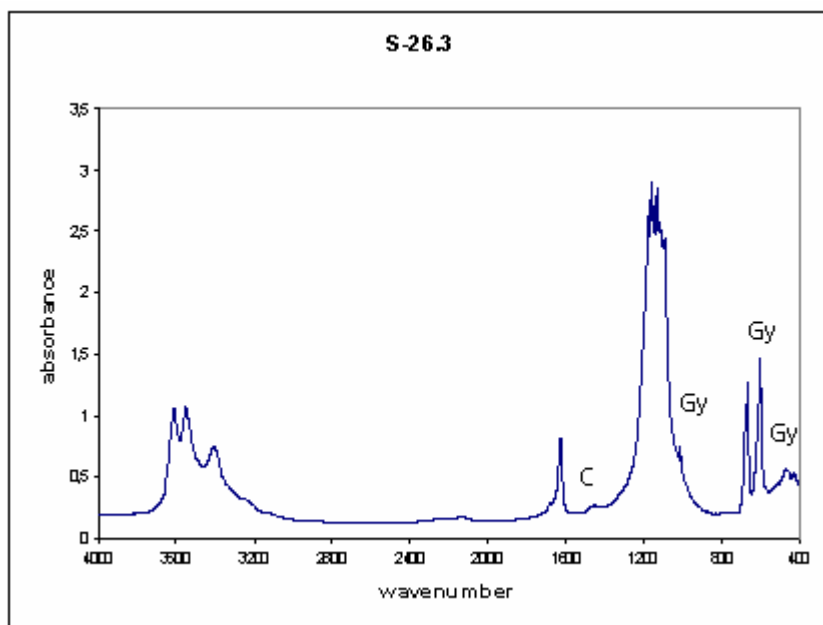


Figure 3.41 FTIR trace of S-26.3 layer at: 2% CH₃COOH treated.

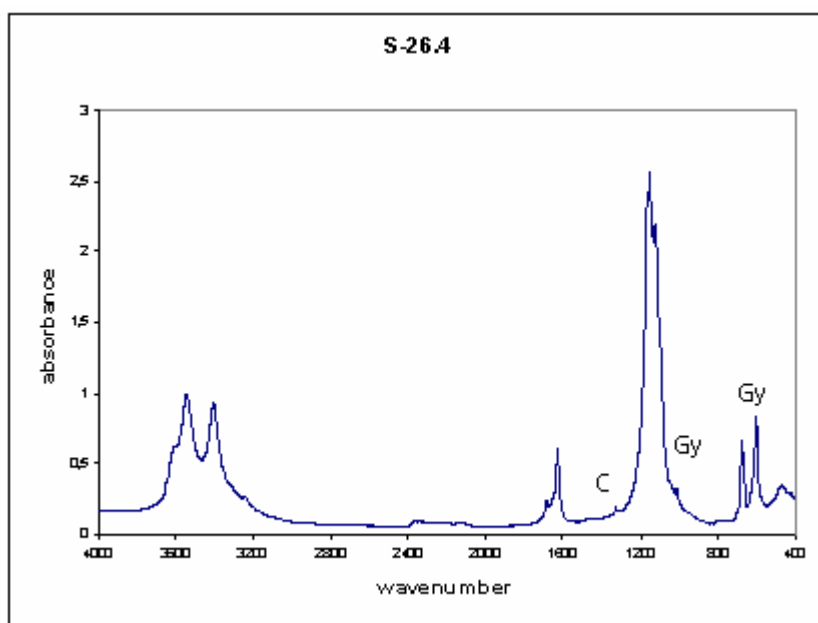


Figure 3.42 FTIR trace of S-26.4 layer at: 2% CH₃COOH treated.

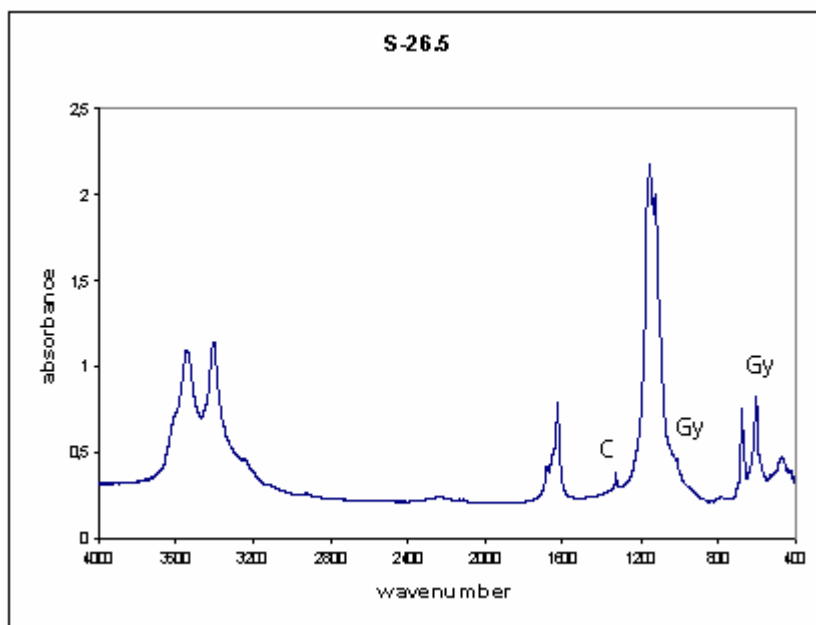


Figure 3.43 FTIR trace of S-26.5 layer at: 2% CH₃COOH treated.

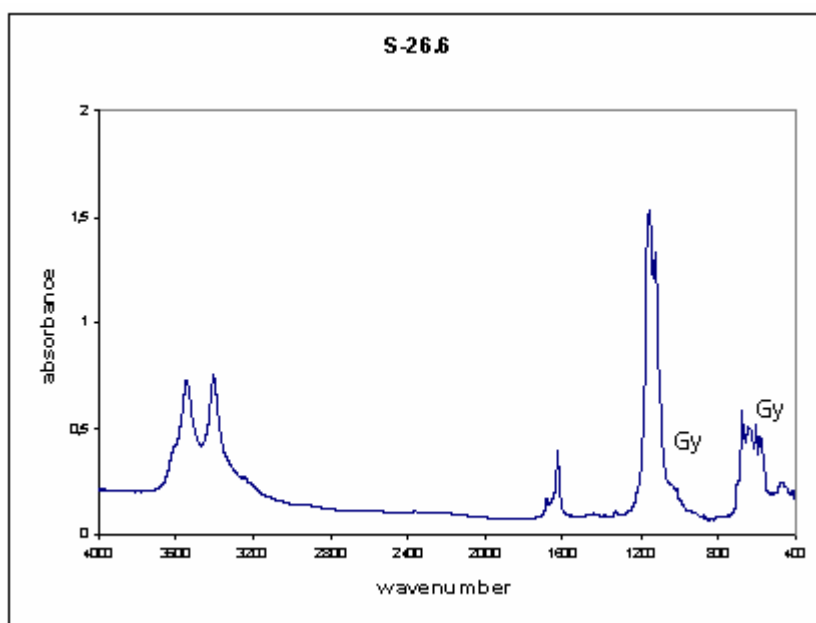


Figure 3.44 FTIR trace of S-26.6 layer at: 2% CH₃COOH treated.

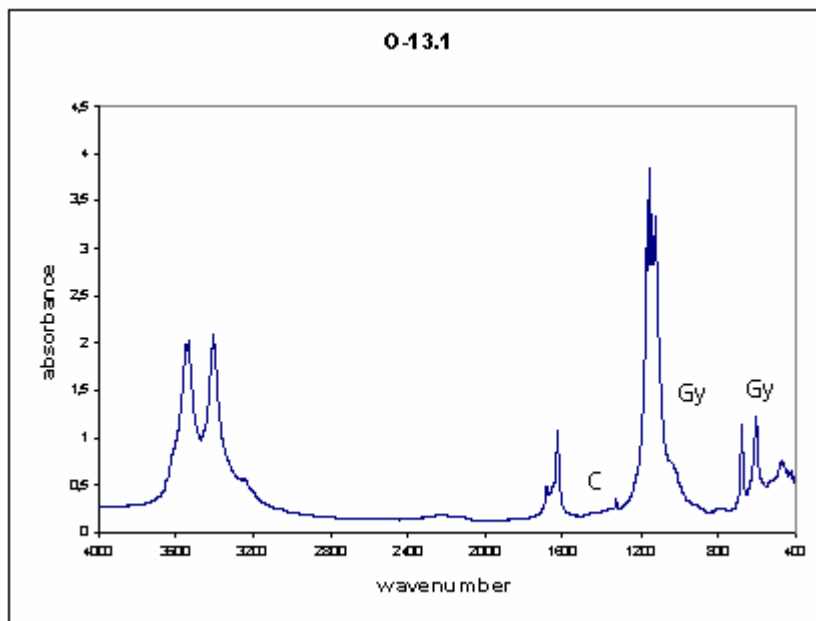


Figure 3.45 FTIR trace of O-13.1 layer at: 2% CH₃COOH treated.

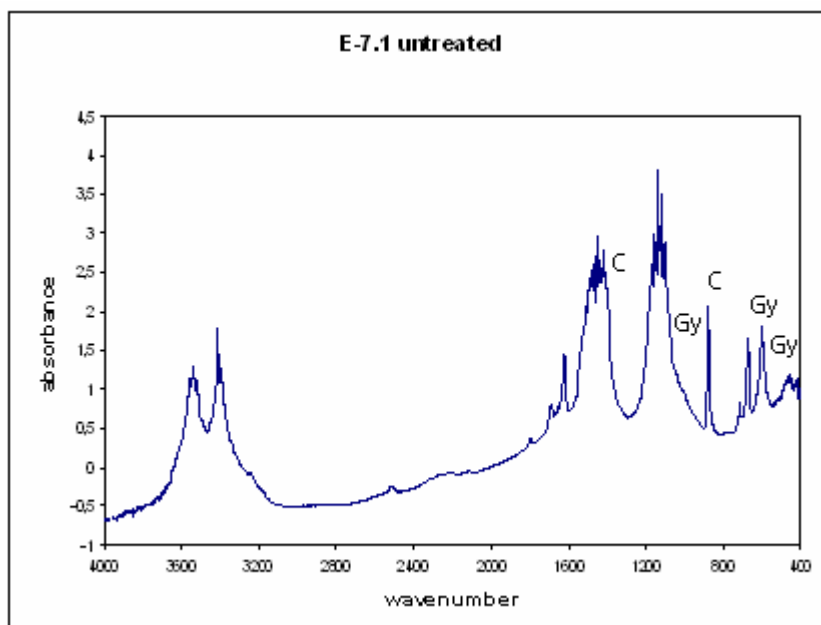


Figure 3.46 FTIR trace of untreated E-7.1 layer

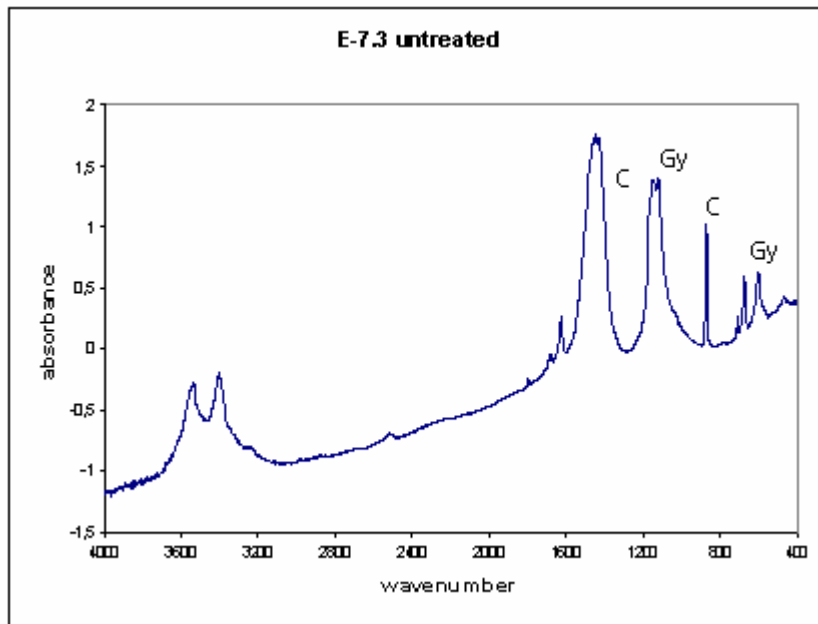


Figure 3.47 FTIR trace of untreated E-7.3 layer

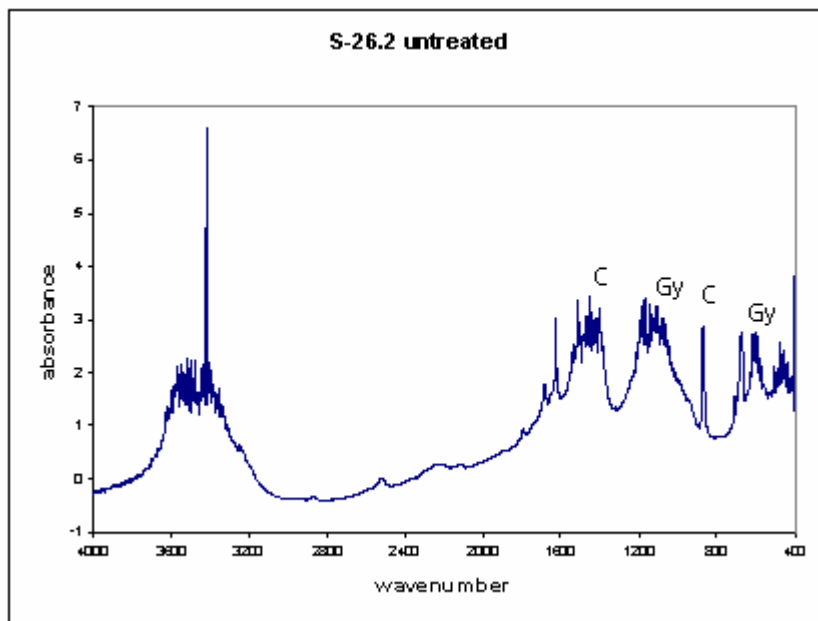


Figure 3.48 FTIR trace of untreated S-26.2 layer

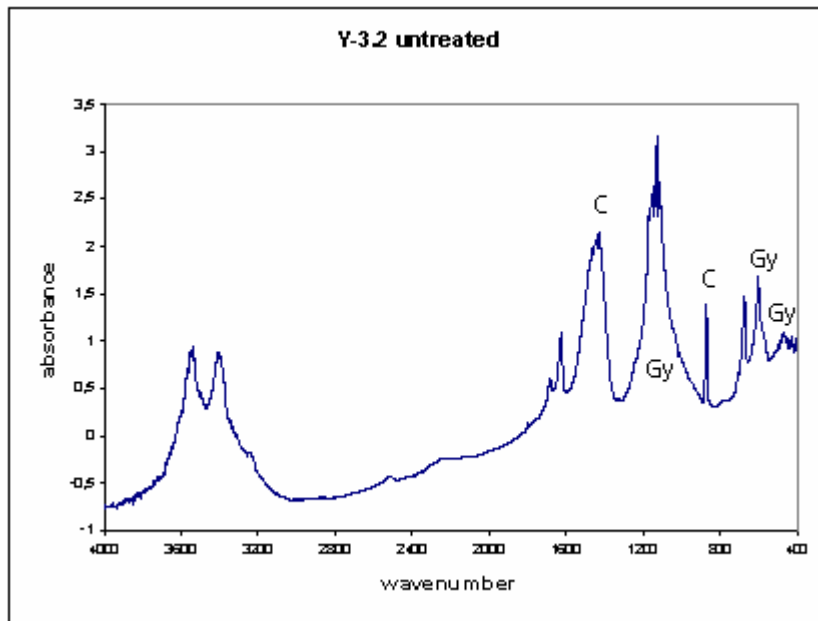


Figure 3.49 FTIR trace of untreated Y-3.2 layer

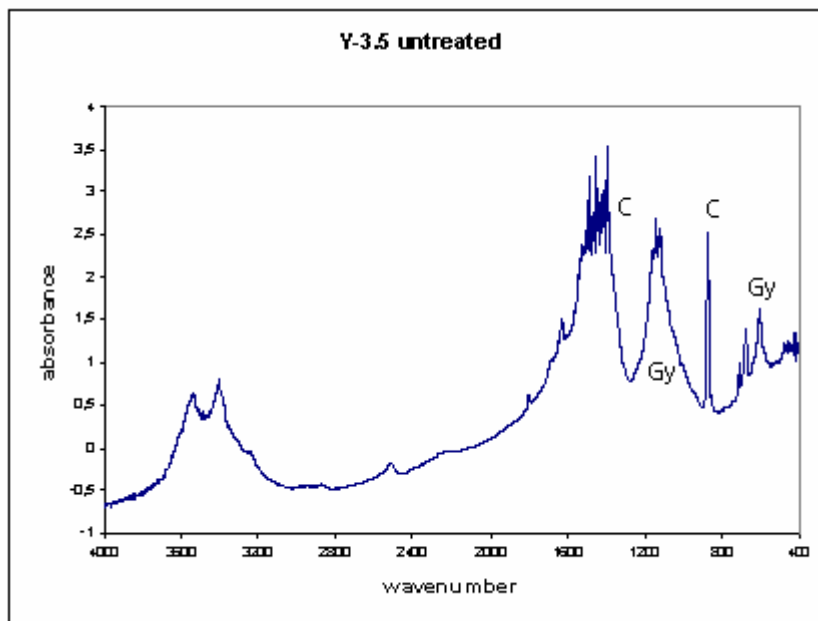


Figure 3.50 FTIR trace of untreated Y-3.5 layer

3.2.5 Element Analyses (ICP-OES)

Colour related elements in samples seemed to be Fe, Sb, Cr, Ni, Mn and Cu. In addition to these elements, Co and Hg are also colour related elements but their amount in the samples may be lower than their identification limits, 3.5 ppm and 6.2 ppm respectively, so that they could not be identified in the plaster samples.

In the Table 3.4 and 3.5 elements were given as their most abundant oxides in the soil.

It is known that Fe is effective in many colours, from violet to yellow.

Amount of Fe_2O_3 varies between 0.79% and 1.06%. In the same house for different coloured layers changing in iron content is as follows. In the white layer (E-7.2) iron content is smallest, which is about 0.16% as Fe_2O_3 . For green coloured layer (E-7.1), iron content is about 0.53% as Fe_2O_3 . In the red coloured layer (E-7.3), it was about 0.79% as Fe_2O_3 . With respect to iron compounds, red colour generally corresponds to higher oxidation state, Fe^{+3} ; green colour corresponds to lower oxidation state, Fe^{+2} .

Yellow (S-26.1) and brown (Y-3.1) coloured layers of other houses also seem to have iron content to be higher and almost similar to that obtained for red coloured layer. On the other hand the blue coloured layer observed in Y-3.5 has again lower iron content as it is seen in white colour E-7.2. It can be concluded that iron is one of the efficient element in the formation of yellow, red and brown colours.

The amount of sulphur was found high and in the range of 11.14% and 26.98%. Sulphur may have come from two sources; first, comes from binder gypsum and second, comes from colouring material ultramarine mineral, which gives blue colour. Presence of ultramarine may be supported by the presence of considerable amount of aluminium. Amount of Al as Al_2O_3 varies in the range 0.19% and 2.55% (Table 3.4 and Table 3.5)

Sample Y-3.1 has brownish blue colour, and this sample have the highest MnO_2 content. The source of the brown colour of this layer may be MnO_2 . The source of blue colour of this sample may be ultramarine mineral

because of the higher amount of sulphur and higher amount of Al_2O_3 compared with the other samples.

E-7.2 sample has the higher percentage of Ca element compared to other samples. The white colour of this layer may be based on the calcite or gypsum minerals.

The green plaster sample of Y-3.5 may be gained this colour from Fe, Cr and Cu oxides.

Table 3.4 Percentage of elements in plaster layers of Eylül Lane House

Oxide	E-7.1 (blue,green) (%)	E-7.2 (white) (%)	E-7.3 (red) (%)
CaO	33.5 (± 0.108)	43.6 (± 0.149)	40.1 (± 0.243)
SiO ₂	5.28 (± 0.003)	2.07 (± 0.003)	6.18 (± 0.005)
Al ₂ O ₃	0.74 (± 0.005)	0.19 (± 0.001)	0.79 (± 0.003)
Fe ₂ O ₃	0.53 (± 0.003)	0.16 (± 0.001)	0.79 (± 0.005)
SO ₂	26.98 (± 0.096)	11.14 (± 0.278)	16.58 (± 0.304)
Sb ₂ O ₃	1.44 (± 0.020)	0.82 (± 0.017)	1.72 (± 0.012)
Cr ₂ O ₃	0.0022	0.0095	0.0018
MnO ₂	0.0081	0.0046	0.0103
Ni ₂ O ₃	0.00137	*	0.00125
CuO	0.0083	0.0063	0.0033

* Elements cannot be detected

Table 3.5 Percentage of elements in different plaster layers of Sarıca Lane House and Yeniöldırımlar Lane House

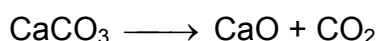
Oxide	S-26.1 (yellow) (%)	Y-3.1 (brown, blue) (%)	Y-3.5 (green) (%)
CaO	35.3 (± 0.064)	34.5 (± 0.104)	40.6 (± 0.233)
SiO ₂	3.36 (± 0.004)	8.57 (± 0.012)	2.93 (± 0.007)
Al ₂ O ₃	0.40 (± 0.003)	1.32 (± 0.010)	2.55 (± 0.018)
Fe ₂ O ₃	1.05 (± 0.003)	0.79 (± 0.008)	0.26 (± 0.001)
SO ₂	25.84 (± 0.073)	21.04 (± 0.082)	13.46 (± 0.267)
Sb ₂ O ₃	1.07 (± 0.005)	2.09 (± 0.013)	1.18 (± 0.010)
Cr ₂ O ₃	0.0023	0.0055	0.0020
MnO ₂	0.0085	0.0182	0.0098
Ni ₂ O ₃	*	0.0031	0.0021
CuO	0.0014	0.0061	0.0021

* Elements cannot be detected

The percentage of error in Cr, Mn, Ni and Cu are not shown in Table 3.4 and 3.5 because they are very low.

3.2.6 Thermogravimetric Analyses

TG/DTA traces of two samples, S-26.6 and Y-3.5, have been obtained. According to TG/DTA results of sample S-26.6 (Fig 3.51) there was two endothermic and four exothermic reactions. Two weight losses were observed in endothermic reactions. At 150°C, physically bonded water was released. The weight loss of about 900°C indicates CO₂ release. The percentage of water was about 8% and the percentage of CO₂ was about 21% in this sample. The result shows that, the calcite, the main mineral in the plasters, was calcined at about 900°C and CO₂ was released because of the following reaction;



From above reaction it can be said that the amount of CaCO₃ is about 47.7 % in the sample.

The peak at around 900°C indicates that the calcite is not pure calcium carbonate it may be dolomitic calcite which contain MgCO₃ together with CaCO₃, because pure calcite should be calcined at higher than 900°C. Dolomitic calcite shows other small peaks around 700 °C but to see these peaks the heating rate should be 5 °C/min. Therefore these peaks cannot be detected. (Mackenzie, 1970)

In the TGA/DTA curve of the second sample (Fig 3.52), Y-3.5, two endothermic reaction peaks were observed similarly with sample S-26.6. Like previous sample, here the first peak around 150°C indicates the physically bonded water release, which is about 6% of the total amount of sample. The second peak around 900°C shows the exhausting of CO₂ gas, which is about 27 % by weight. In this sample the percentage of CO₂ is more than the first sample, so the amount of CaCO₃ is also higher than the first sample. The amount of CaCO₃ was calculated about 61.3 % by weight.

The reasons of exothermic peaks may be explained in other ways. They may come from certain salts which may undergo oxidation during the

course of heating. An example of this is dehydrated gypsum. CaSO_4 (gypsum) may be rearrangement in anhydrous CaSO_4 from the hemihydrate to anhydrate structure. (Mackenzie, 1970) On the other hand exothermic peaks may arise from the presence of organic additives.

The peak at around 573°C may correspond to quartz crystals. (Fig. 3.51 and 3.52)

The two peaks between 350°C and 550°C in the TGA trace of sample S-26.6 may indicate the existence of the organic additives to the aggregate. (Fig. 3.51)

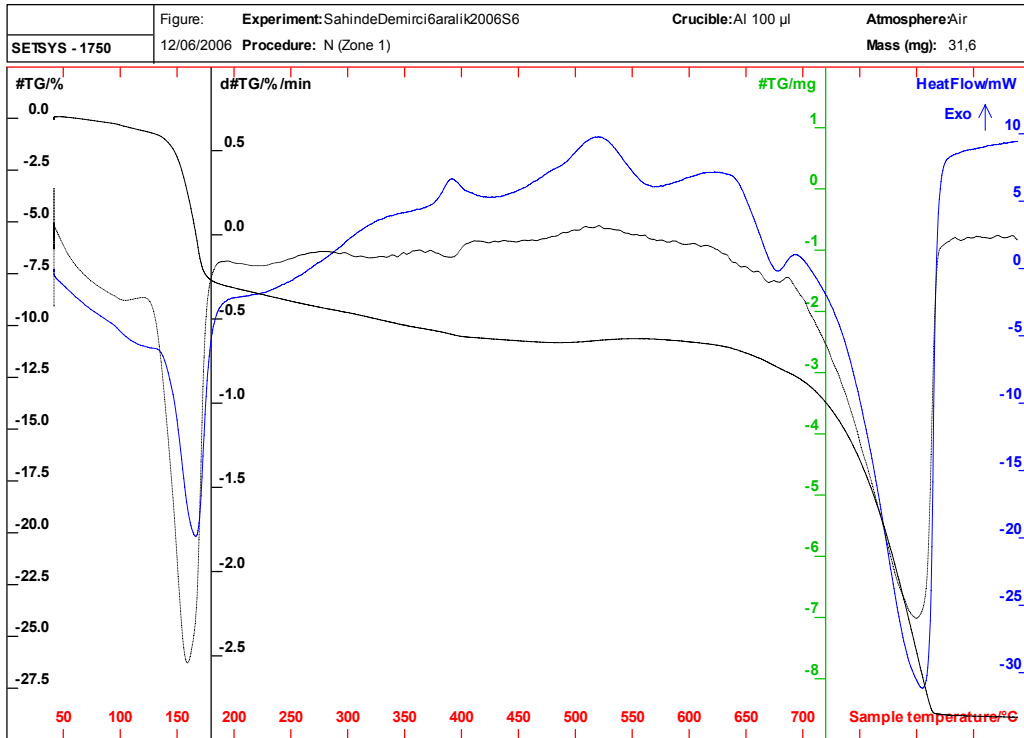


Figure 3.51 TGA trace of a green plaster layer S-26.6

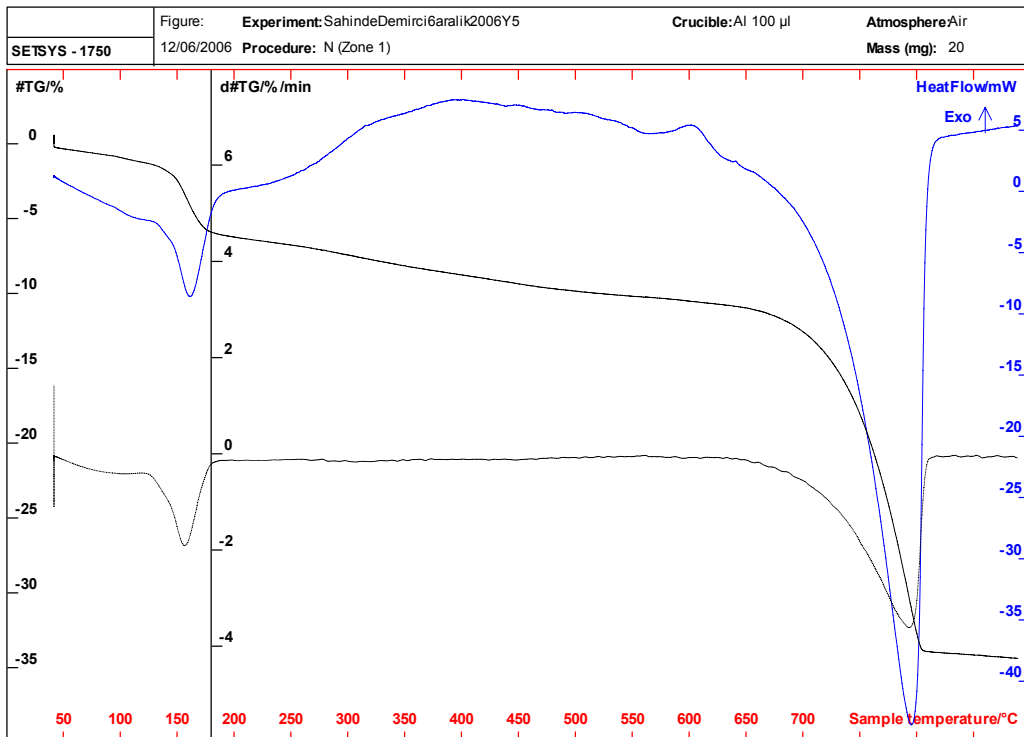


Figure 3.52 TGA trace of a green plaster layer Y-3.5

3.3 Overall Interpretation of Experimental Results

Plaster samples were examined by optical microscopic analysis of cross sections and thin sections and also XRD, FTIR and TGA/DTA analyses to determine the mineral phases and texture of the samples.

The binders of plasters were found to be lime and gypsum with the average percentage of 37.9% as CaO in terms of ICP-OES results. The average percentage of binder as calcium carbonate (CaCO_3) is 67.6% according to elemental analysis. The average percentage of aggregate is found as 32.4 % (Table 3.4 and 3.5) The amount of lime in the plaster layers seemed to be greater than gypsum regarding to XRD trace. (Fig.3.16)

The thicknesses of the plaster layers were in the range of 31μ to 569μ , average being 153μ . It seems that white layers have greater thicknesses with respect to coloured layers. Apart from colouring layers, two black layers were detected indicating the use of asphalt for the purpose of isolation. In cross section view of some of the samples, distinct boundaries can be seen. (Fig. 3.3)

The soluble salt content of the samples was found to be higher than expected. This might be due to the solubility of gypsum, formation of sulphate due to air pollutant SO_2 and chloride salts coming from soil and water. About three decades ago, Ankara was one of the most polluted cities in Turkey. Sulphur dioxide, the major pollutant in the atmosphere, was mainly due to the combustion of sulphur containing coal used for domestic heating. (Tokmak, 2005)

Observation of thin sections with optical microscope showed that number of layers distinguished is greater than those found by optical microscopy of cross sections. For example, in sample Y-3, cross section reveals seven layers but thin section observation reveals twelve layers.

Pozzolanic activity of plaster samples were found to be very low although Opal-A mineral was detected in XRD trace of the treated samples. This may be due to the presence of gypsum in the samples. According to previous studies gypsum has disadvantage due to the interaction of

sulphates present in the aqueous phase with calcium silicate hydrate, C-S-H, gel formed in aggregates. (Palomo *et. al.*, 2001) In fact, gypsum has considerable advantages including quicker solidification and good adhesion of plaster to mortar. (Middendorf and Knöfel, 1998)

Colour forming elements seemed to be Fe, Sb, Cr, Ni, Mn and Cu. In addition, presence of sulphur accompanied with excess aluminium corresponds to ultramarine blue which is approved in the results of ICP-OES for green-blue, E-7.1, and green, Y.3.5, plaster layers. (Tablo 3.4 and 3.5)

In binders the main mineral were found to be micritic calcite and gypsum. In addition, quartz, Opal-A and minor amount of feldspars and micas were detected in XRD trace.

Use of organic additives was detected in two plaster samples by TGA/DTA.

Calcite and gypsum peaks were observed in FTIR trace. Organic additives can not be approved by FTIR trace.

CHAPTER 4

CONCLUSIONS

In this study, fifteen plaster samples obtained from four houses around Ankara Citadel built in the late Ottoman period (17th-18th century) were examined using various analytical techniques.

Number of plaster layers was found to be considerably high as much as twelve layers in some samples. Various different colours including yellow, blue, red, green, white and brown were identified visually and under optical microscope.

The thicknesses of the layers were in the range of 31 μ to 569 μ , having median value of 122 μ . No relationship between the thicknesses and the colours of the layers was found.

In the thin section examination, in two samples, two black boundaries between plaster layers were identified which could be an indication of the use of asphalt for isolation purposes, like dampness proofing or heat insulation.

The binders of plasters were found to be lime and gypsum with the average percentage of 37.9% as total CaO. Although the amount of lime was assumed to be greater than that of gypsum by considering relative peak intensities of gypsum and calcite in XRD traces, it is known that gypsum has considerable advantages including quicker solidification and good adhesion of plaster to mortar. Therefore, gypsum might be added to increase the strength of the plaster. The other main component aggregate in plasters was found to be 62.1% as average. In red plaster samples, hematite was identified, which might be colour forming mineral.

In binders the main mineral were found to be micritic calcite and gypsum. Besides, quartz and Opal-A were found in some of the samples. Opal-A was taken important role in the carbonation process. In addition, minor amount of feldspars and micas were identified in some of the sample layers.

The soluble salt content of the samples was found to be in the range of 3.04%-9.22%, with an average being 6.6%. The main anions found were sulphate and chloride. In one sample nitrite and nitrate were also identified. The soluble salt content of the plaster samples were found higher than expected, due to the results of previous studies on historical plasters. The reason for high amount of sulphate should be the presence of gypsum which is rather soluble in water. The other high concentrated chloride may come from soil and water in contact.

Pozzolanic activity of plaster samples were found to be very low although Opal-A mineral was detected in XRD trace of the treated samples. This may be due to the presence of gypsum in the samples. Gypsum has disadvantage due to the interaction of sulphates in the aqueous phase with calcium silicate hydrate gel, C-S-H, formed in aggregates.

Fe, Sb, Cr, Ni, Mn and Cu were found to be colour giving elements. Optical microscopic investigation of this sections showed that pigment particles were homogeneously distributed in the matrix. This indicates the qualified plastering technology of the Ottoman craftsman.

Investigation of plaster samples using some analytical techniques such as TGA, showed the indication for the presence of organic additives but clear identification was not established.

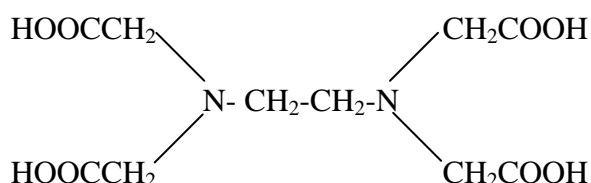
It can be concluded that the survival of these historic plasters depend on quite a number of properties related to their material characteristics and technology. Further analyses will better define some points such as the origin of the pigments and identification of organic additives.

The studies on ancient plaster technologies are essential for their conservation and for the selection and preparation of repair plasters. The

knowledge gained from them would help to improve modern plaster technology.

APPENDIX A

In this titration standard ethylenediaminetetraacetic acid, commonly shortened to EDTA, solution was used. EDTA is a poly acid having four acidic hydrogen and can be shown as H_4Y . It has the open formula given below;



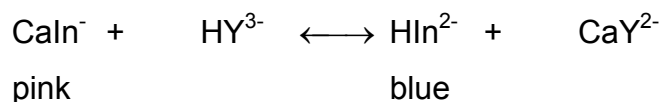
Open formula of EDTA (ethylenediaminetetraacetic acid)

Anionic form of EDTA, Y^{4-} , forms 1:1 stable complex with most of the metal ions like calcium. It is a remarkable reagent not only because it forms chelates with all cations but also because most of these chelates are sufficiently stable to form the basis for a titrimetric method.

In the analysis, 0.01 M standard EDTA solution was used. It was prepared from disodium EDTA salt. For this purpose, exactly 3.7224g of disodium ethylenediaminetetraacetic acid salt was dissolved in distilled water and make the volume 1 L by adding sufficient distilled water in a volumetric flask. EDTA solution was standardized with reference calcium solution which was prepared by dissolving 0.1600 g reagent grade $CaCO_3$ in small amount of concentrated HCl and diluted with distilled water up to 100 mL. Then 10 mL of solution was taken, diluted to about 100mL and pH values of the solutions were adjusted to 10-12 using few drops of 10% NaOH solution. Then about 1 mL calcon indicator was added to the solution and solution was titrated with EDTA solution (Black, 1965).

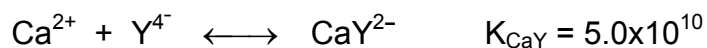
Calcon is Eriochrome blue black R, having formula $C_{20}H_{13}N_2O_5NaS$. Calcon indicator was prepared by dissolving 0.02 g calcon in 100 mL ethyl alcohol. The colour of the indicator solution is violet. When the indicator is added to calcium solution, the colour of the solution becomes pink because calcon forms complex with Ca^{2+} . This colour was continued until equivalence

point was reached, where a little excess EDTA decomposed the complex forming stable calcium EDTA complex. The removed calcon ion turns the solution colour to blue.



where In^{3-} shows calcon anion that forms complex with calcium, HY^{3-} indicates EDTA anion and HIn^{2-} shows free calcon ion. (Skoog *et al.*, 1996; Harvey, 2000)

For the standardization of calcium solution, 42.1mL EDTA as an average was used for the titration of 10mL of the standard calcium solution. Standardization was repeated at least three times. The molarity of EDTA solution was calculated as 0.0096 M. The complex formation reaction with Ca^{+2} can be written as follow;



Where, Y^{4-} shows anion of EDTA that forms complex with calcium ion.

APPENDIX B

Determination of phosphate, PO_4^{3-} , ions: A drop of test solution was placed on a filter paper. A drop of 0.26 M ammonium molybdate $((NH_4)_2MoO_4)$ solution was added. The filter paper was held over hot wire gauze or near a Bunsen burner to accelerate the reaction. Then a drop of 0.003 M benzidine reagent $(NH_2C_6H_4C_6H_4NH_2)$ was added and the paper was held over ammonia. The formation of a blue fleck or ring is due to presence of phosphate ions. Limit of identification of the test is 1.25 microgram as P_2O_5 . (Feigl, 1958)

Determination of sulphate, SO_4^{2-} , ions: A drop of test solution was placed on a test tube. Then 1 or 2 drops of 2M hydrochloric acid and 1 or 2 drops of a 10% solution of $BaCl_2$ (barium chloride) were added. Formation of white precipitate is due to sulphate ions (Teutonico, 1988).

Determination of chloride, Cl^- , ions: A drop of test solution was placed on a test tube and 1 or 2 drops of dilute nitric acid and 1 or 2 drops of silver nitrate solution $(AgNO_3, 0.1M)$ were added. Formation of a white gelatinous precipitate indicates the presence of chloride ions (Teutonico, 1988). Limit of identification of the test is 0.3 microgram as chlorine. (Feigl, 1958)

Determination of nitrite, NO_2^- , ions: A drop of test solution was placed on a spot plate. A drop of sulfanilic acid $(NH_2C_6H_4SO_3H)$ solution, which is prepared by solving 1 g of sulfanilic acid in 30% acetic acid, was added. Then, a few drops of α -naphthylamine $(C_{10}H_7NH_2)$ solved in glacial acetic acid solution was added. Formation of a red-pink colour indicates of nitrite ions (Teutonico, 1988). It is due to the formation of a red azo-dyestuff. Limit of identification of the test is 0.04 microgram as nitrous acid (HNO_2) (Feigl, 1958).

Determination of nitrate, NO_3^- , ions: A drop of test solution was placed on a spot plate. A drop of 2M acetic acid, sulfanilic acid ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$) and α -naphthylamine ($\text{C}_{10}\text{H}_7\text{NH}_2$) and a few mg of zinc dust were added. The formation of a red colour indicates the presence of nitrate ions (Teutonico, 1988). Limit of identification of the test is 0.05 microgram as nitric acid (Feigl, 1958).

Determination of carbonate, CO_3^{2-} , ions: A drop of test solution was placed on a test tube. One or two drops of 4M hydrochloric acid were added. The appearance of bubbles of gas (CO_2) indicates the presence of carbonate ions (Teutonico, 1988).

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