ARCHAEOMETRIC ANALYSIS ON THE SELECTED SAMPLES OF GLASS ARTIFACTS RECOVERED IN THE EXCAVATIONS AT ALANYA CASTLE

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ABSTRACT

ARCHAEOMETRIC ANALYSIS ON THE SELECTED SAMPLES OF GLASS ARTIFACTS RECOVERED IN THE EXCAVATIONS AT ALANYA CASTLE

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The archaeological and technical questions about ancient glass have lead to various research activities such as identification and sourcing raw materials used in the glass production, investigation of the ways in which colors can be modified according to furnace atmosphere and times of firing.

Considering research areas and publications it can be suggested that compositional studies of well-dated samples of ancient glass have disclosed useful information concerning raw materials characteristics and production technology. Within this context, aim of this study was to determine the composition and technology of some 13th century Seljuk period window glasses from Alanya Castle archaeological site. During the excavations at the area called Vaulted Galleria in Alanya Castle many glass pieces in different sizes and colors had been found. In this study 10 samples were examined.

Elemental analysis of the samples have been made using two different methods; X-Ray Fluorescence Spectroscopy (XRF) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) to determine major, minor and some trace elements. The XRF and ICP-OES data reflect the typical composition of a soda-lime-silica glass with the average values of; 12.9% (Na_2O): 7.7% (CaO): and 65.5% (SiO_2). Samples were grouped by color as green, blue and purple. Color producing elements are Fe, Mn, Cu and Co.

Most of the samples had shown casting character as production technique.

Keywords: Furnace, Window Glass, Seljuk Period, Alanya Castle, Vaulted Galleria.

ÖZ

ALANYA KALESİ KAZI ÇALIŞMALARINDA ORTAYA ÇIKARTILMIŞ BAZI CAM ÖRNEKLERİ ÜZERİNE ARKEOMETRİK ANALİZLER

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Tarihi camlar hakkındaki arkeolojik ve teknik sorular çeşitli araştırma faaliyetlerine yol açmaktadır. Bunlar cam yapımında kullanılan hammaddelerin tanımlanması, kaynaklarının bulunması, renk oluşumuyla ilgili incelemeler, rengin, fırın atmosferi ve fırınlama zamanına göre değişiminin belirlenmesi gibi alanlardır.

Tarihlendirilmiş cam örneklerinin bileşimlerinin belirlenmesinin, hammadde özellikleri ve yapım teknolojisi ile ilgili yararlı bilgileri ortaya çıkaracağı ifade edilebilir. Bu çalışmanın amacı Alanya Kalesi arkeolojik alanından elde edilen 13. yüzyıl Selçuklu dönemine ait bazı pencere camlarının bileşimlerinin ve teknolojilerinin belirlenmesidir. Alanya Kalesi'nde Tonozlu Galeri denilen bölgede yapılan kazılarda farklı büyüklük ve renkte

cam parçaları elde edilmiştir. Bu çalışmada, bunlardan on adet örnek incelenmiştir. Örneklerin temel, az ve iz element içerikleri X Işınları Floresans Spektrometrisi (XRF) ve Plazma Emisyon Spektrometrisi (ICP-OES) yöntemleri kullanılarak belirlenmeye çalışılmıştır.

Analiz sonuçları camların, tipik soda-kireç-silis camı yapısında olduğunu ve ağırlıkça %12.9 (Na_2O): %7.7 (CaO): ve %65.5 (SiO_2) oranında bulunduğunu göstermiştir. Renklerine göre yeşil, mavi ve mor olmak üzere üç gruba ayrılan örneklerde, renk oluşturan elementlerin Fe, Mn, Cu ve Co olduğu anlaşılmıştır.

Örneklerin çoğunun dökme yoluyla yapıldığı düşünülmektedir.

Anahtar Kelimeler : Fırın, Pencere Camı, Selçuklu Dönemi, Alanya Kalesi, Tonozlu Galeri.

To Mom

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INTRODUCTION

In this chapter general aspects of glass, history of glass and glass technology, aim of the study and archaeological area related with window glass samples studied have been explained.

1.1. Glass: General Aspects

"Glass" in the sense of physics, means a special class of solid matter, which is produced by quenching a melt so fast that no far-reaching crystalline order can be established.

In glass we find the same short range order between nearest neighbor atoms and ions as encountered in all condensed matter, i.e., everything not gaseous or plasma. But in the long range glass resembles a liquid. Sometimes glass is termed a "frozen liquid" though no similarity exists to frozen liquid such as water.

Glass is a homogeneous material with a random, non-crystalline molecular structure.

It is generally obtained by melting a mixture of sand (SiO_2), sodium carbonate (Na_2CO_3) and calcium carbonate ($CaCO_3$) raw materials (batch) at a high temperature, followed by a rapid cooling and so becomes rigid without crystallizing.

The tentative reaction during glass formation can be written as follow;

$nSiO_2 + Na_2CO_3 \rightarrow Na_2O.\ nSiO_2 + CO_2(g)$

Glass combines the rigidity of crystals with the random molecular structure of liquids. It is often described as a vitreous or glassy state.

Glass contains formers, fluxes and stabilizers. Formers make up the largest percentage of the mixture to be melted. In typical soda-lime-silica glass the former is silica (SiO_2) in the form of sand. Melting sand by itself requires the high temperatures of about 1850℃ (Figure 1). But if other elements modifiers are introduced melting point falls to less than 1000℃. Monovalent oxides (R_2O) such as Na_2O (soda) or K_2O (potash) modifiers behave as fluxes by interrupting some of the Si - O bonds and thus breaking the continuous network of SiO_2 (Figure 2). The unattached oxygen atoms become negatively charged and loosely hold monovalent cations in the spaces of network (Cronyn, 1990). This bonding is weak and the cations can migrate out of the network in the presence of water, making these glasses water soluble. To overcome this, a second type of modifier, stabilizer, divalent oxides (RO) such as lime (CaO) or magnesia (MgO) must also be added. Being doubly charged they are more tightly held than the monovalent ions and so hold the fluxes within the network (Cronyn, 1990).

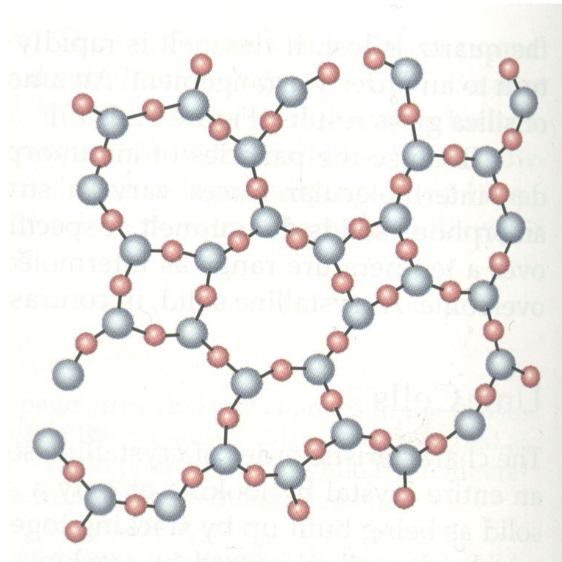


Figure 1: Amorphous quartz glass. Blue dots represent silicon atoms

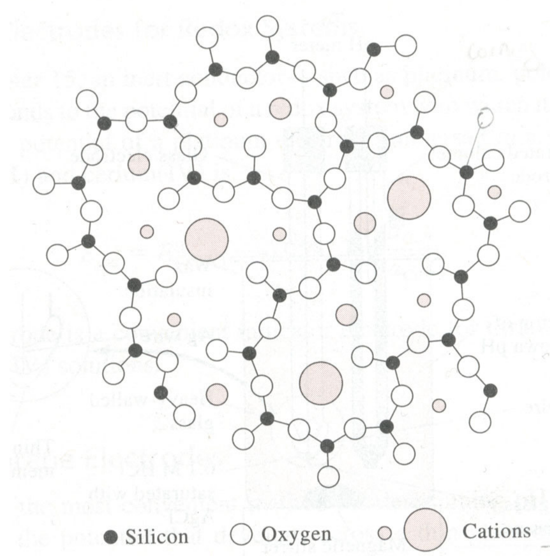


Figure 2: Cross-sectional view of a silicate glass structure

The content and balance of Silica: flux: stabilizer (SiO_2: R_2O:RO) in a glass is critical in determining its melting point and its character. An average soda-lime glass of 73% SiO_2: 22% R_2O:5% RO has a melting point of about 725℃ whilst a similar potash glass will harden at a higher temperature and more quickly (Cronyn, 1990). Types of materials used in glass can be summarized as below;

For silica, sand or quartz pebbles are used.

As fluxing agent various compounds are used. Some of them are given below;

Soda ash;

Sodium carbonate; Na_2CO_3: It is introduced to the glass batch as anhydrous white powder. During the melting it decomposes and CO_2 is released. Na_2O can also be prepared by using Glauber's salt, Na_2SO_4. In its anhydrous form it is mixed with coal and added to the batch. The sulfurous acid, H_2SO_3 is freed and Na_2O becomes part of the glass, as in the case of soda ash. Another soda source is natron. Natron consists of Na_2CO_3, $NaHCO_3$ and sodium sulphate and chloride. Egyptian natron was the predominant source of alkali for glass makers from Roman times through the early medieval period (Uboldi and Verita, 2003). Another mineral having similar structure, Trona can also be used as soda source.

Potash;

Potassium carbonate; K_2CO_3. It is a grainy, white powder that decomposes into K_2O which becomes part of the glass, and CO_2 which escapes into the atmosphere. Potash (K_2O) is formerly obtained by filtering wood ashes, today it is commercially produced from K_2SO_4.

Various oxides can be used as stabilizer. These substances give the glass physical and chemical properties that are important for its usability. Some of them can reinforce the structural network to improve chemical resistance and mechanical properties. Most commonly used stabilizers are given below;

Lime;

Calcium carbonate, $CaCO_3$ also known as lime. It is found naturally as limestone, marble, or chalk. At a temperature of about 950℃ CO_2 escapes from the lime, leaving CaO within the glass batch.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2\,(g)$$

Alumina;

Aluminum oxide, Al_2O_3 is added to the glass batch to improve chemical resistance and increase viscosity in lower temperature ranges. It is usually added in the form of alkali containing feldspars (for example albite, $NaAlSi_3O_8$). It is also present as impurity in quarts sand or pebbles.

Lead oxides;

Oxides such as yellow lead, PbO, and red lead, Pb_3O_4, are used to introduce lead into the glass. Moderate additions of PbO (13-15% by weight) into glass increase resistance. High lead content lowers the melting temperature, and decreases hardness. But, it increases refractive index of the glass, making it more brilliant.

Barium Oxide;

Barium oxide, BaO, derived from $BaCO_3$, is used mainly for optical glass instead of lime or red lead. Glass containing barium is not quite as heavy as lead crystal (glass having PbO of about 18%) but achieves similar brilliance due to its high refractive index.

Boron Compounds;

Boron trioxide, B_2O_3, and the anhydride of boric acid, H_3BO_3, are very important compounds in special glasses. They produce high melting borosilicate glass that is known with the trade name Pyrex. Borosilicate glass is particularly useful for cooking utensils and laboratory glassware because it expands very little when heated and thus unlikely to crack.

1.1.1. Coloring agents

Only pure chemicals are used as glass coloring agents. Different colors can be obtained by adding oxides of the so-called transition elements (copper, chromium, manganese, iron, cobalt, nickel, vanadium and titanium) or of the rare earths (mainly neodymium and praseodymium) to suitable base glass melts.

Intensive red, orange, and yellow colors are produced by the precipitation of precious metal colloids, as well as those of selenium, cadmium sulfide, and cadmium selenide during the cooling of the melt. Secondary heat treatments are also used to obtain these colors. (Figure 3)

Brown and gray colors are obtained by combining oxides of manganese, iron, nickel, and cobalt, which in high concentrations can also yield black. A list of some compounds and their producing colors is given in Table 1.

Table 1: Some compounds and their producing colors in glass

www.blm.gov.historicbottles/colors.htm

Compound	**Color**
iron oxides	greens, browns
manganese oxides	deep amber, amethyst, decolorize
cobalt oxide	deep blue
gold chloride	ruby red
selenium compounds	reds
mix of manganese, cobalt, iron	black
antimony oxides	white
uranium oxides	yellow green (glows!)
sulfur compounds	amber/brown
copper compounds	light blue, red
tin compounds	white
lead with antimony	yellow

Figure 3: Results of different coloring oxides

http://www.blm.gov/historic_bottles/colors.htm

1.1.2. Opacifiers

When fluorine-containing materials, such as fluorspar (CaF_2) or phosphates are added, small crystalline particles form in the glass, rendering the glass cloudy and opaque. Such glass is used in opal tableware, in opaque or milk glass for architecture, and in flashed opal glass globes for the lighting industry.

1.1.3. Cullet

Glass cullet is not technically a raw material, but it must be added to the melt. Cullet acts as a fluxing agent and accelerates the melting of the sand, conserving both energy and raw materials. For this reason, all glass plants save their cullet, in the form of pieces cut from flat glass or rejects or breakage from hollow glass.

The manufacture of glass is one of a number of high temperature industries that include pottery, metal glaze, and faience productions. Although, strictly speaking, glass is classified as a ceramic and the pyro technology and raw material processing in glass and the other high temperature industries had features in common, the physical and chemical properties of glass are specific and set the material, to some extent, apart from the rest. It is the physical properties of glass that determined the range of functions, which it performed in post societies. Glass was famed into jewelry, inlays in metal surfaces, perfume and water containers and windows. Unlike the natural glass, obsidian, which owes its chemical characterization to the specific geochemical environment in which it is formed, production of man-made glass is more complex. (Henderson 1989)

The processing of raw materials imposes specific physical and chemical characteristics to the glass. The investigation of raw materials, partially fused raw materials and fully fused glass can provide answers to a range of important archaeological and technical questions. These relate to technical composition and structure; the sources for the raw materials; location of manufacture; the archaeological context of the finds; the relationship between chemical characteristics and status of the sites involved. Distinctions between groupings of glass compositions are based upon compositional variation which can be attributed to both natural factors and those imposed by man.

Each glass production site had its own complex and specific ways of manufacturing glass, though sometimes glass production occurs within a broad technical tradition. Natural occurrence and selection of raw materials, the purification of the raw materials, the addition of scrap glass (cullet) to the melt and, to the lesser extent, the use of specific equipment such as furnaces, crucibles and tongs which could introduce trace impurities, all contribute to variation in glass composition. (Sayre 1961, Henderson 1989)

1.2. History of Glass and Glass Technology

The invention of glass more than 3500 years ago is remained in uncertainity. The Roman historian Pliny attribute it to Phoenician (the region between Mediterranian and Lebanon) sailors. He recounted how they landed on the beach, propped a cooking pot on some blocks of natron (Mineral of Na_2CO_3) thay were carriying a cargo, and made a fire over which to cook their meal. To their surprise, the sand beneath the fire melted and ran in liquid stream that then cooled and hardened into glass (Zerwick 1990). Today, scholars believe that the glass evolved from the manifacture of faience , an older material with a white interior and a colorful, shiny surface . Faience which can be made at a lower temperture than glass, is composed of crushed quartz and alkali. These same ingredients, mixed in slightly different proportions, form a true glass if subjected to a higher temperature.

The oldest records of glass are from 1700 BC in Mesopotamia, but Egyptian glassmakers began making pieces of jewelry as early as 3000 BC, as proven by the relics of a glass furnace dated back to about 1350 BC. The glass objects that have been found in Egypt and Mesopotamia share some similarities, but we don't know exactly when or where man began to make glass (Zerwick 1990).

Core molding was the earliest method of glass production. The core was modeled in clay, fixed to a metal rod, given the shape of the desired vessel and then dipped into molten glass. When cool, the clay core was picked out leaving a small hollow glass object. Simple casting and pressing methods such as pouring molten glass into molds were also used. These techniques were good for the production of flat and deep bowls only, and mass production was still impossible. Glass beads believed to be from the same period were also found in China. They are most likely the product of technological interchange between China with Mesopotamia and Egypt. Later in Egypt, the glassmakers painted colorful feather or zigzag patterns on the surface of glass vessels. The real origins of modern glass lay in Alexandria during the Ptolemaic Dynasty (330 BC – 323 BC). The glassmakers in Alexandria developed a new technique called Mosaic glass. Glass canes of different colors were cut crossways to make decorative patterns. Millefiori glass, with colorful flower patterns, is a type of mosaic glass. It is during Egypt's 18th Dynasty (1550 BC ~ 1292 BC) that real glassmaking began, with goblets and bottles as the main glass products. The goblet of Thutmose III (1479 –1425 BC) during this period is confirmed to be the oldest goblet ever found. (The Corning Museum of Glass 1998)

The earliest glass-making differed in its chief purpose from glass-making today. Glass appears to have been used first as a gem . As late as Ptolemaic times (330 BC – 325 BC) glass gems were among the most prized possessions; and even today glass is used extensively for ornamental jewelry.The glass used for this purpose by the Egyptians was usually colored. Glass was used later for hollow vessels, especially unguent jars and small vases, which were not blown but molded. The process was laborious and of limited scope. A core of sand was built up on a wooden or metal rod , then covered with glass by building up hit by hit with the viscous glass not much above its softening temperature.

Later , probably about 1200 BC another technique was developed, that of pressing glass into open molds. By this means shapes such as bowls, dishes and cups , which could not be made by the sand- core process, were added to the repertory of the types which were at the disposal of the glass makers.

Transparent glass was rare, the quality of transparency not being important for the uses for which glass was intended. White opaque glass was made in the 18th Dynasty (1550 – 1292 BC) by the use of the tinoxide . Blue glass was used extensively ; and its color usually was due to copper, which gave a turquoise blue, very different in hue from the dark cobalt blue glass common today. Copper was also the coloring agent in red glass. Green glass was colored with copper and iron.

The invension of glass blowing caused an industrial revolution, which changed a luxury into a necessity . Glass had been used only for small and precious articles , but the process of the blowing the glass with the aid of a blowpipe made possible the production in the quantity of a better and cheaper articles. (Figure 4)

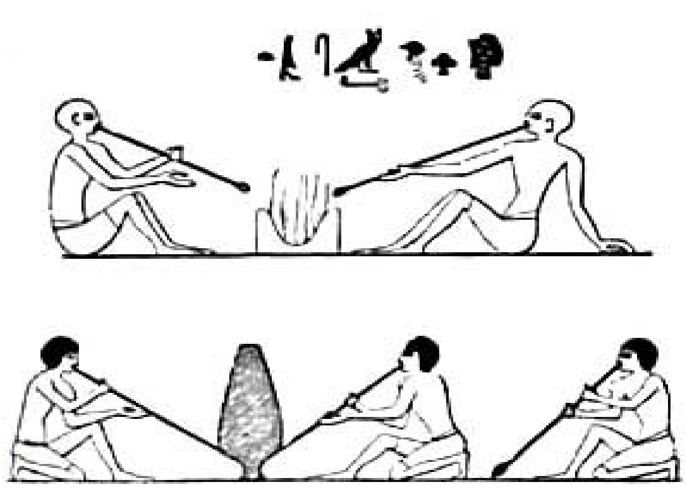


Figure 4: Glass workers in ancient Egypt.
www.crystalinks.com/egyglass.jpg

The time and place of the first glass blowing are not certain. It formerly was thought to have been in the 20 th Dynasty (1186 – 1069 BC). Around 200 BC, Syrian craftsmen in the area between Sidon and Babylon made a breakthrough with the discovery of the glassblowing pipe. The glassblowing pipe is made from a hollow metal pipe with a mouthpiece at one end. The glassmaker places a gob of molten glass on the other end and blows through the mouthpiece to inflate it into a hollow body. The blown glass, with its large surface contact with the air, cools quickly. Small objects harden in 2-3 minutes and larger ones in about 10 minutes, making glass vessels easy to produce in mass quantities. The blowing of glass with a pipe enabled thin-walled, fine glasses in a large variety of shapes to be made. In addition, using a mold with this technique allowed the standardization and duplication of objects. The Romans perfected cameo glass, in which cutting away a layer of glass to leave the design in relief produces the design (The Corning Museum of Glass 1998).

The glass objects of that period are generally named Roman Glass, and they are characterized by filigree, mosaic, and engraved decors. In Roman architecture translucent sheets of alabaster or mica were commonly used as the window material, but it is also during this time that glass was first used to enclose wall openings. Case in point: Two small 230mm x 540mm flat panes of glass were used in the ceiling window of the bathhouse in the plaza of Pompeii. It is believed that the expertise and technology of glass manufacture of Roman Empire was spread throughout Europe, and as Far East as China. Glass in ancient times was mostly colored, but with the development of glass making technology, production of thin and clear glass became possible (Corning Museum of Glass 1998).

With the breakdown of the Roman Empire, glassmakers moved to the East and to the other regions, and not only preserved the glassmaking techniques, but also developed new patterns and styles. Frank glass, Sassan glass, Islamic glass and Byzantine glass are the representative types of the period. The production of enameled and colored glass flourished as well. Stained glass, developed in the Byzantine Empire, was especially popular in muslim countries, and became the basis for the glass arts of the West.

During the 13th and 14th centuries, glassmaking was revived in Venice. Glassmakers of the island of Murano developed soda lime, and Venetians termed this clear and thin glass crystalloid. After the fall of the Roman Empire glassmaking traditions appear to have continued around the Mediterranean and the Near East. Venetian glassmakers gained a reputation for technical skill and artistic ability, which is still in evidence today. By the 15th century, Venice developed a thriving glass export business, but its monopoly did not last forever. Despite their attempts to protect their technological secrets, the knowledge soon spread throughout Europe.

Window glass was used by the Romans as early as the 1st century AD, and is a common find on Roman sites in Britain. Roman glassmakers employed two differing processes for producing windowpanes. The earlier method is known as "cast glass", and produces panes of uneven thickness that are fire polished, or "glossy" on one side, and pitted, with a matt finish on the other.

The later technique is known as "cylinder glass" and produces panes of even thickness, which are glossy on both sides. This method is well known, being first documented by Theophilus in the 12th century AD, and still being employed on an industrial scale in the 19th century in glassmaking centers such as Charleroi in Belgium. A cylinder of glass is blown, both ends are opened; it is split longitudinally, reheated and opened out flat. However, the precise technique of making cast glass has been lost since the Romans ceased to use it in the 3rd century AD (Figure 5). It has often been suggested that molten glass was poured into a mould in much the same way as metals are cast. Some of the arguments against such a method are that it would not reproduce both the forms of the edges and corners and the tool marks seen on original Roman glass.

Figure 5: Glass furnace
(Screen shot taken from Discovery Channel, *Meet the Ancestors*)

Using this method successfully depends upon various factors. The pane has to be heated in a way that allows one area to heat up whilst the opposite area stays relatively cool. This allows the cooler area to be gripped and pulled using a pair of pincers whilst pinning the hotter area down near its edge using a metal rod. This produces a corner, and subsequent heating and stretching will turn the disc into a rectangle. This rectangle can be stretched by heating one half and leaving the other half cooler, pinning the hot side down with a long metal rod and gripping and pulling the cooler side with a pair of pincers. By varying the areas to be heated and stretched, the pane can be enlarged until it is the required size (the size of the initial gather will have a bearing on this - the larger the gather, the larger the pane) (Figure 6). Small adjustments to the straightness of the sides can be made using a metal hook to gently pull the glass where the side is curving inwards.

Figure 6: Window glass made by using ancient Roman casting techniques (Discovery Channel, *Meet the Ancestors)*

Between the seventh and ninth centuries the Middle East produced refined and elegant new styles of glass making.The muslims adopted something from every culture with which they came in contact. From the Chinese who had reached such an advanced stage that their capital , Ch'ang An, was the largest city in the world , the Arabs learned papermaking . They translated Euclid's *Elements of Geometry* from the Greek. From İndia, they adopted the numerical system which we used today. Glass that imitated rock crystals was treasured by Islamic princes. Some of this glass was thought to be as valuable as gold and silver, substances prohibited by religion. The relie-cutting on vessels was a difficult and costly process.It was achieved by outlining the design on the surface and then carefully cutting away the blackground to leave the design in relief, or raised. The rarest of all Islamic relief-cut glass was made with the cameo technique, having colored ornament against a colorless back ground

From the fifth centuries onwards, in the period following the break up of the Roman Empire, the art of glass rapidly declined in accomplishment. In Europe for nearly a thousand years, apart from a very few interesting new types, the glass vessels commonly made were not worthy of comparison with those in use under the Empire.

Europian glass hardly recovered before the fifteenth century, when the Renaissance not only gave a new impetus to the luxury arts of form but brought a reviwed awareness of the Roman achievement. On the other hand, in Egypt and the Near East , from the 8 th or 9th centuries onwards if not earlier, the glassmakers took up the Roman tradition with renewed vitality, and under the rule of the Tulunid Caliph of the Egypt, the Abbasaids of Bagdad, and above all under the Fatimids, Ayyubids and Mamelukes of Cairo, they craeted a new art of decorated glass (Zerwick 1990).

Between the fifth and eight centuries (the so-called Merovingian or Frankish period) a few new types were heated in Western Europe in a glass which had degenerated into a greenish imperfect material, usually full of striations and bubbles, but which occasionally obtained to a natural beauty of color in deep greens, greenish blues and brownish ambers.

The glass made in the East in early Islamic times can seldom be dated with any great precision. The Islamic world was at the time virtually a single cultural unit, and the court of the Abbasid Caliphs at Bagdad, for instance, not only drew finished wares made in the countries as far distant as China, but attracted artisians from Egypth, Persia and the other parts of the Abbasid realm. The Abbasid court moved from Bagdad to Samaria the 9th centuries, later the city was occupied only between the years 836 and 883. Excavations on the site of Samarria, were therefore of the graetest value in establishing the date of certain types of glass and pottery (Zerwick 1990).

Medieval window glass is typically of the potash-lime-silica type, due to the incorporation of alkali in the form of wood or plant ash. Conversely, earlier glass, e.g. Roman, is of the soda-lima-silica.

Variety on account of mined sodium salts being incorporated; glass of the latter composition has generally proved to be more durable. Later European glass tends to be of the mixed alkali type (Morey 1960).

Plaster stained glass windows flourished in the Islamic lands in 13th Century AD. initially in mosques and public structures and later in residences (Freestone and Collen 1998). Overtime this ornate architectural element, which is still manufactured today, underwent stylistic changing based on local tastes and influences, the quality of craft and the availability and diminishing cost of glass. The plaster tracery delineator stylized floral / vegetal motifs or repeats geometric patterns with inlaid hits of colored glass in varying degrees of complexity.Various terms refer to these plaster window types, they are called Serveni-Menkuş by the Ottomans, Gamariya or Shemsiya by the Egyptians and Takhrim by the Yemeni (Doganis etal 2004).

Windows of colored glass are known to have existed in the sixth century AD and are of Eastern region.

Two different methods existed for the manufacture of window glass. Both were used during the same periods, but independently of each other (Gallien, 1970).

The crown glass technique was dependent upon the dexterity and strength of the glassmaker. By this method a bubble of glass was blown and cut open. It was then transferred to the pontil, freely rotated and spun in front of the furnace opening and frequently reheated. By applying centrifugal force, a large, circular pane glass was obtained in this way and a very high polish achieved due to repeated reheating, the so-called fire-polish. The finished glass pane was fairly thin and showed the wavy lines caused by the spinning. In the center of the crown remained the typical bull eye, the slightly thickened part of the glass to which the part, of iron red, was attached. This part could not be used and was cut out.

The wastage caused by cutting straight pieces of glass from circular panels, and by removal of the bull's eye, is avoided in the manufacture of window glass by the broadsheet technique. Broadsheet is manufactured by blowing and swinging the paraison in such a way as to form long cylinder, which is opened and cut off straight at both ends. The resultant cylinder is placed on to a wooden stand and cut open lengthwise by passing a hot iron straight down the inside. The opened cylinder is then placed into a "flattened oven" where it is re-heated and flattened by passing a wooden plane over the glass and finally using the polisseir, a wooden tool which makes the sheet a perfect plane.

In addition, as a third method, casting method was also used for small panes or mirrors, but the need for subsequent polishing made this an expensive alternative (Ewen, 2003). Today, of course, the manufacture of sheet glass is entirely mechanized and runs as a continuous process.

1.3. Aim of the Study

The archaeological and technical questions about ancient glass have lead to three main areas of research. The first one is the identification and sourcing the raw materials used in the glass production through its chemical analysis (Sayre and Smith 1961; Henderson, 1989).

The second one is the investigation of the ways in which colors can be modified according to furnace atmosphere and times of firing. The third area of research is the chemical characterization of the glass products. The use of a specific combination of raw materials provides a chemical “finger print” of the glass which is often specific to the time and sometimes the place of manufacture.

Considering research areas and the publications it is possible to suggest that compositional studies of well-dated samples of ancient glass have disclosed useful information concerning glass technology, sources of raw materials and production center and trade.

Chemical analysis of the major elements in the glass has not been significantly beneficial in this regard, but that of minor and trace elements may yield meaningful data (Uboldi and Verita, 2003)

Within this context, aim of this study was to determine the composition and technology of 13th Century Seljuk window glasses from Alanya archaeological site. This will be the introductory study to determine sources of raw materials of the window glasses that were produced in Alanya and the relevant technology.

It should be useful to give information about Alanya and Alanya Castle.

1.4. Alanya and Alanya Castle

Figure 7: Alanya Castle

Alanya castle is located approximately 250 meters above the sea level on a very streep hill with a peninsula area. At ancient ages, Carcesium, which the city Alanya had been called was mentioned by Strabon, as fortress build on a streep rocky hill (Figure 7). Caracesium was well protected from the attacks, with the defence advantages of its locational benefits, The Hellenistic fort walls in the middle citadel, which were built without using mortar are of Tryphon period (140 BC - 8 BC). It was destroyed by Roman Army under the command of Pompeious in 65 BC for being used as a shelter for pirates, Later on, it started to be named as Katonoras by Byzantinians. The church, known as “Arap evliyası “ in the middle citadel is a very good example of the Byzantinian era (Figure 9). From XIII th century the castle was under the rule of Kir Fard, a Greek or Armenian king, until the invasion of Anatolian Seljuk emperor Alaeddin Keykubat. From then the city was named as Alaiyye to honor the congueror, Alaeddin. After strenghtening the castle walls he built an harbor, a dockyard and for their protection a tower called as Red tower. Finally at the inner castle a palace was built for himself as a winter hold in 1221. In the building the developments of the Seljukian art and architecture can be clearly seen. (Arık 1987). As the fail of the Anatolian Seljuk empire the city was set under the control of Karaman Oğulları in 1293. After about 200 years, in 1427, it was sold to Memlukians at a price of 5000 gold piece and finally a few years later, city was felt by the Ottoman invasion.

Figure 8: Castle Entrance

As it is said that Alanya castle is located 250 meters above the sea level. A 6 km town wall with 140 watch towers winds around the castle. It made it almost impossible for attackers to go undiscovered. On the way up the winding and sometimes very steep road you will find small cafes and cosy restaurants today. Near the “Sultan’s Palace” a church/mosque which is a very important relic of the Christian and Islamic heritage of the town is present . A small legent about the castle is the sacrifice of the prisoners. When the dungeons became overcrowded, the prisoners who had been there the longest were packed together on a lifter platform at the edge of the castle. One by one the prisoners pushed each other over the edge until only one was left. He then got three shots at throwing a stone over the edge and into the sea. If he failed he too was pushed over the edge with certain death as a result!

After this introduction chapter, description of the glass samples studied and the methods used for their analysis were explained in chapter 2. In chapter 3, the results obtained from the investigation of 13th century Seljukian glass samples were presented and discussued. In the final chapter (Chapter 4) the conclusions of the study was given.

Figure 9: Byzantine Chapel (Arap Evliyası)

CHAPTER 2

MATERIALS AND METHODS

The archaeological excavations at Alanya castle have begun in 1985 with surface research by Prof. Dr. M. Oluş Arık within the following year excavation on the south-eastern part of the inner castle the Seljukian palace was completely appeared.

During the excavations at the area called Tonozlu Galeri (Figure 10) among the south-western part of the inner castle bordered by the south fortes, many glass pieces in different size and colors had been found.

In this study, some of these window glass pieces have been examined, with archaeometrical point of view.

The 10 samples we studied had been excavated in section VIII, located at south-eastern part of the inner castle (Figure11). There were two windows placed on the south-eastern and north-eastern walls and two doors on the north-western and south-western walls (Arık 1989).

Section VIII, just before the excavations had started was full of rubble starting at a height of 1.85 m. at the south-western wall and lowering through 1.00 m. at the north-eastern wall. Within this rubble many mosaic, china ceramic and glass pieces had been excavated including the samples we studied.

Figure 10: Vaulted (Tonozlu) Galleria

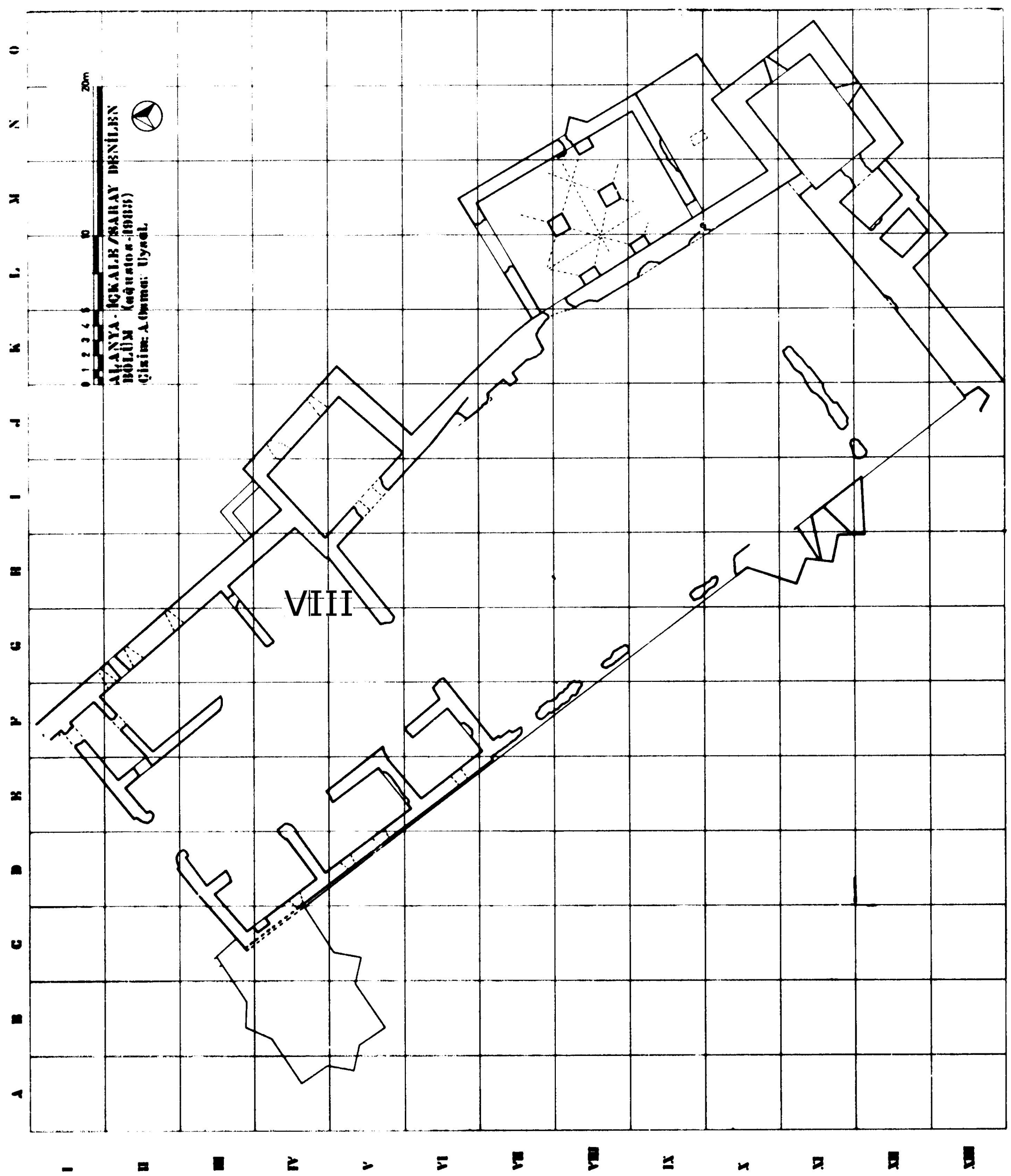


Figure 11: İnner Castle (Palace) Plan (by A. Osman Uysal)

The radius of the window glasses differ between 14cm to 24 cm. Flat edges differs as thick and thin at the cross section. Most of them horizontally flat and gives small arc at the middle part. There has been an increase in thickness through the mid parts which had given clues about the production techniques. Some of the glasses were remarkably thick but some were showing more proportional but wavy character. Investigations of the samples have been done in the following ways:

a) Visiual examinations, taking their photographs
b) Technical drawings.
c) Color determination.
d) Elemental analysis.

The photographs of the samples are given in Figure 12 - 21. Technical drawings are given in figure 22 - 31. Color of the samples has been determined by using Munsell color catalogue. The results are given in Table 2.

Table 2: Munsell Color Table of the samples (AL represents Alanya glass sample)

Sample no	Visual color	Munsell color code
AL1	Purplish blue	5 PB 3/8 – 3/10
AL2	Yellow	2,5 Y 8/4 – 8,5/2
AL3	Yellow	5 Y 7/6 – 8/4
AL4	Greenish yellow	10 GY 4/6 – 4/8
AL5	Yellow	10 Y 8/4 – 8,5/4
AL6	Yellow	10 Y 8/2 – 8,5/2
AL7	Greenish yellow	5 GY 9/4 – 8/6
AL8	Red	2,5 R 5/6 – 6/6
AL9	Blue	10 B 4/10 – 5/10
AL10	Blue	5 B 5/8 – MAX.

Elemental analysis of the samples has been done by using XRF and ICP-OES methods. XRF analysis have been done in General Directorate of Mineral Research and Exploration laboratories and matrix and minor elements, content of the samples have been determined. Trace element content of the samples has been determined in METU Center Research laboratories. Results are given together in Table 3.

The major elements in window glass are Si, Na, K, Ca and Mg, Minor elements are mainly Fe, Ti, Al, Pb. Trace elements are generally color causing elements such as Cu, Mn, Co, Ni, and Sb. Iron is also the element that affects coloring of the glass.

Results of the element analysis given in Table 3 are the average of many analytical results. The error in the analysis is less than 3%.

Table 3:

Percentages of the elements by weight in the glass samples of Alanya Castle

Sample %	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
SiO_2	63.0	66.8	68.7	64.5	66.3	64.3	64.5	64.3	63.5	64.0
Na_2O	13.2	13.1	10.4	10.3	10.0	10.5	8.5	10.6	10.7	9.8
K_2O	2.0	4.4	2.2	1.7	2.1	4.1	6,.7	1.5	1.4	1.8
CaO	8.2	5.6	6.2	8.5	7.4	8.5	8.5	8.5	8.7	8.8
MgO	0.2	0.1	0.2	0.2	0.3	0.3	3.0	0.2	0.4	0.6
Fe_2O_3	2.9	1.3	2.6	2.6	2.6	1.7	0.7	0.2	1.5	1.1
Al_2O_3	5.8	3.0	3.3	3.5	1.9	3.5	3.5	3.5	N.D.	N.D.
MnO	0.6	3.2	1.0	1.4	1.1	1.4	0.04	1.5	1.5	0.8
CoO	0.09	Neg	Neg	0.04	Neg	Neg	Neg	Neg	0.04	0.01
TiO_2	0.5	0.1	0.1	0.2	0.1	0.1	0.2	0.2	N.D.	N.D.
Cr_2O_3	0.05	Neg	0.004	Neg	0.005	0.003	Neg	0.003	Neg	0.003
NiO	Neg	Neg	Neg	Neg	0.003	0.003	0.003	0.004	0.005	0.005
ZnO	Neg	0.004	Neg	Neg	0.002	0.002	0.005	0.003	Neg	Neg
P_2O_5	0.1	0.1	0.1	0.1	0.4	0.1	0.1	0.1	N.D.	N.D.
CuO	0.04	0.07	0.04	2.61	0.04	0.013	0.01	2.71	N.D.	N.D.

Neg: Negligible

N.D.: Not Detected

CHAPTER 3

RESULTS AND DISCUSSION

Visual and microscopic observations of the samples showed that window glasses studied had two different styles at the edges; with ribbons and flat (Figure13). The cross section of flat edges in some samples is thick in some others thin.

Most of the samples are horizontally flat and give small arc at the middle part. There has been an increase in thickness through the midpoint (Figure 14).

Two of the samples seemed as bottle or cup pieces (Figure 14 and 16)

All these showed that production technology probably is casting. Some of the glasses are remarkably thick, but some others are of more proportional and wavy character. (Figure 12, 15 and 19).

Window glasses studied were grouped in colors as yellow, green, blue and purple (Table 2).

The XRF and ICP-OES data reflect the typical composition of a soda-lime-silica glass (Table 3). The glass forming component, silicon dioxide, varies between 63.0% and 68.7%, with the average of 65.3% by weight.

One of the modifier component (fluxing agent), Na_2O varies between 8.5% and 13.2%, the average being 10.7% by weight. The other fluxing agent, K_2O varies between 1.3% and 2.2%, with the average of 1.7%. by weight.

Third modifier component (stabilizer) CaO varies between 5.6% and 8.8%, the average being 7.7% by weight.

Potassium oxide and magnesium oxide (magnesia) contents are rather low Magnesium oxide (MgO) varies between 0.1% and 3.0%,with the average of 0.9% by weight.

Presence of K_2O (~ 2%) and magnesia (~ 1%) shows that some amount of plant ash was used in window glass production (Freestone, 2002).

Aluminum oxide (alumina) content of the samples varies between 1.9% and 5.8 %, with the average of 3.5%.

Alumina content of a glass is usually derived from the raw material used as a source of silica. Six samples have almost the same amount of alumina (3.4 %), two samples (Sample 1 and 5) have quite different Al_2O_3 (5.8 and 1.9 %). Presence of same amount of Al_2O_3 in six samples showed that one type of quartz sand was used for their production. The two samples AL1 and AL5 may be imported to the site or they may be produced in different workshops.

Another impurity element TiO_2 varies between 0.1% and 0.5%, with the average of 0.2%. Amount of TiO_2 is also almost same in all samples which supports the assumption that one type of quartz sand was used which come from the same source.

P_2O_5 is present at a few tenths of one percent in all samples, which may indicate the use of plant ash as a source of alkali (Freestone, 2002). For most of the samples, there is more or less inverse relationship between soda and lime (Table 2). This result is consistent with the results of previous studies (Freestone, 2002).

As color effective elements (Chromopheres), Fe, Mn, Cu, Co, Ni and Cr have been determined.

Amount of Fe_2O_3 varies between 0.2% and 2.9%, with the average of 1.7%.

Amount of MnO varies between 0.6% and 3.2%, with the average of 1.0%.

Amount of CuO varies between 0.01% and 2.71%. There are two groups regarding CuO content. One group has low amount of CuO (samples 1,.3 , 5 and 7) within the range of (0.01-0.04%). The second group (samples 4 and 8) has rather high amount of CuO within the range of (2.61-2.71%).

Amount of CoO in all samples excluding sample 10 was found to be less than 0.01% and sample 1 has 0.09% CoO.

Amount of Ni varies between 0.003% and 0.005%, with the average of 0.004%.

Amount of Cr_2O_3 varies between 0.003% and 0.0050% (average of 0.004%). But three samples (samples 2, 4 and 7) have negligible amount of Cr_2O_3

Blue color of sample 1 may come from the effect of Fe, Mn, Cu, Cr, Co and Ni in decreasing order.

Yellow color of sample 2 may come from the effect Mn, Fe, Cu, Co and Ni in decreasing order.

Similarly, (yellow) color of sample 3, may come from the effect of Mn, Fe, Cu and Cr.

One function of nickel oxide in glass or glaze is that of a colorant. The color imparted depends up on the kind and amount of other oxide. It can be used to produce blues, grays, greens, browns and yellows.

The sole use of chromium in glass or glaze is as coloring agent. When present as Cr_2O_3 it makes the well-known crome green. In the presence of ZnO brown colors result due to formation of zinc chromate. High lead glazes form yellow lead cromate (Cullen 1973).

From structural point of view, it is important to note that the higher the silica content, the better the glass matrix cohesion and glass properties such as mechanical resistance and chemical stability. In contrast, as the silica content increases, the softening point and the temperature of vitreous transition (the so-called Tg) also rises. This is the reason why some network-modifying oxides such as Na_2O and CaO were used as melting or fluxing agents. In this regard composition of window glass samples studied are in good conditions.

Sodium oxide could be obtained from Natron (or another similar mineral called Trona) naturally occurring mineral containing high percentages of Na_2CO_3. The use of this mineral is also indicated by the presence of minor amounts of MgO and K_2O for all samples except sample 6 (Table 3). Thus, the use of plant ashes has less possibility for their production. In addition, Turkey has plenty amounts of Trona mineral in various locations such as Beypazarı in Ankara. In the production of sample 6 which has K_2O and CaO as 4.1 and 8.5 % respectively, using the plant ash is more probable.

On the other hand, the calcium oxide could have been provided from some calcium-rich materials such as limestone or calcite, while the rest of the components (e.g. MgO, TiO_2 or Fe_2O_3) could be considered as impurities accompanying the sands used as raw material.

The majority of the main components of glass are colorless. Therefore, to produce a colored glass some coloring agents are needed.

Ancient glasses were commonly colored by ionic coloring agents (Chromophores) using transition metal ions (Pollard and Heron 1996).

The sole function of cobalt in glass or glaze is as coloring agent. Cobalt oxide is a base, and is a member of RO group. Being an effective flux, it dissolves in the glaze or glass structure as cobalt ions. Usually the ion is divalent. The trivalent state is also possible and the color imported depends upon the valence and coordination of the dissolved ions. The color, however, is the characteristic cobalt blue.

The blue color results from the low occurrence of CoO since Co^{2+} ions have a very high coloring capacity, even at very low concentrations, giving a powerful deep-blue color to the glass.

The Co^{2+} ions commonly adapt a tetrahedral coordination which gives to two triple absorption bands. One of them is in the visible region of the spectrum at around 540, 590 and 640 nm, respectively, and the other one is in the near IR region at around 1400, 1600 and 1800 nm, respectively.

Blue color was obtained from the addition of the Co^{2+} chromophore to the glass matrix using some kind of cobalt-rich mineral salts or other cobalt-rich materials such as cobalt-bearing alum.

Cobalt can be added to a glass melt by using a frit rich in cobalt, or by adding scrap glass that is already deeply colored by cobalt (Henderson, 1989).

The presence of Fe^{2+} ions gives a blue color to the glasses because of their absorption bands at around 1100 nm. Such a color moves to green when the ratio of Fe^{2+}/Fe^{3+} diminishes since the Fe^{3+} ions are responsible for yellow color due to their absorption bands at around 380, 420 and 440nm, respectively (Bamford, 1962).

Compounds of iron are present in all natural raw materials running from a trace in rare substances to several percents in others.

Various colors are imported to glass by iron depending upon the components of the glaze, the firing atmosphere, the concentration or proportion, and upon the valence of the iron in the glaze.

Iron compounds import green, yellow, red, brown or black depending on glaze compositions, iron concentrations degree of oxidation of reduction.

Theoretically, ferrous iron in solution in glass or glazes makes a very intense blue color and ferric ions yield a reddish color. Because almost certainly the glaze contains an equilibrium mixture of ferric and ferrous ions, the color of a glaze results from a mixture of ferric and ferrous ions.

Antimony may perform two important functions in silicate fusion such as glass. It can act both as an opacifier and as a coloring agent. When used alone, it does not appear to be capable of yielding colored melts. The yellow ascribed of it is caused either by the presence of the oxides of Pb or Fe. (Cullen 1973)

In a further study antimony would be analyzed in order to explore whether the yellow color is affected by the presence of Sb beside Fe or not.

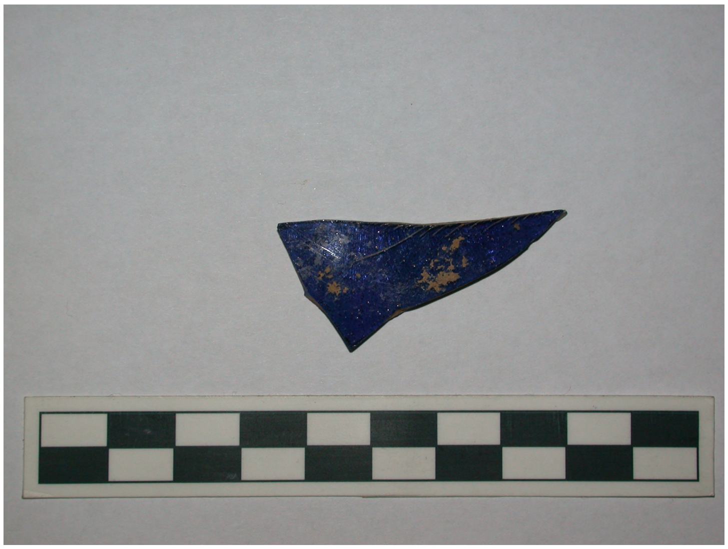
Brown color is resulted from a combination of iron and manganese oxides and purple color is also obtained by the combination of iron and manganese oxide. The manganese oxide levels in the purple glass are higher than non-purple glasses.

Manganese may be provided by the addition of manganese-rich mineral such as pyrolusite (Henderson, 1989).

Finally it can be said that green, blue and purple colors of the window glass samples studied may come from mainly Fe, Mn, Cu and Co elements. Fe may be present as impurity in the sand used; Mn, Cu and Co may be added on purpose. Their proper combinations result in producing green, blue and purple color in the window glasses studied.

Photographs of the samples

Al 1



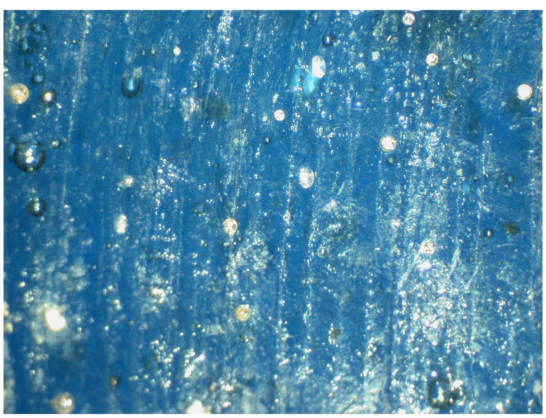


Figure 12

AI2

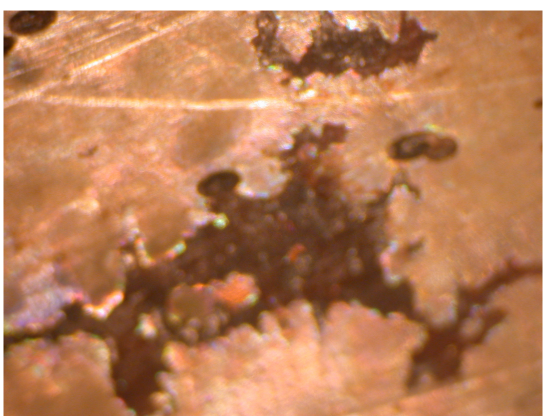
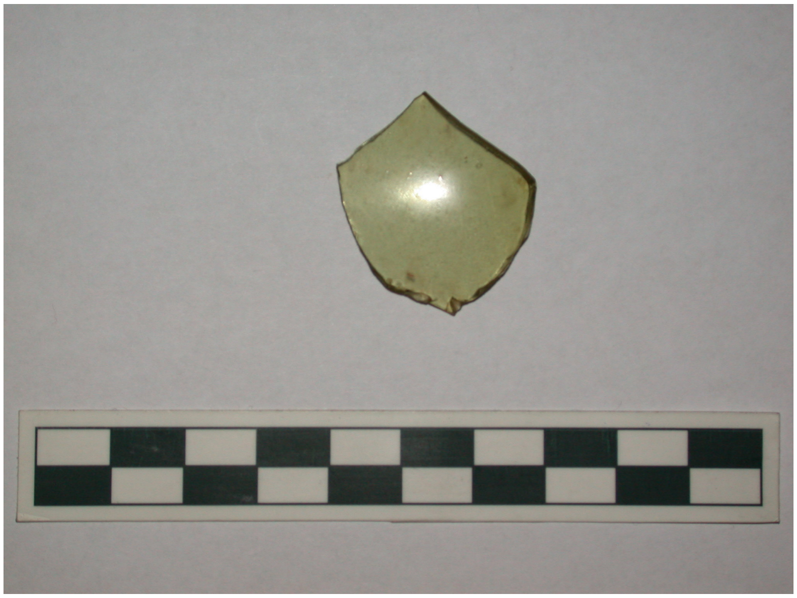


Figure 13

AI3



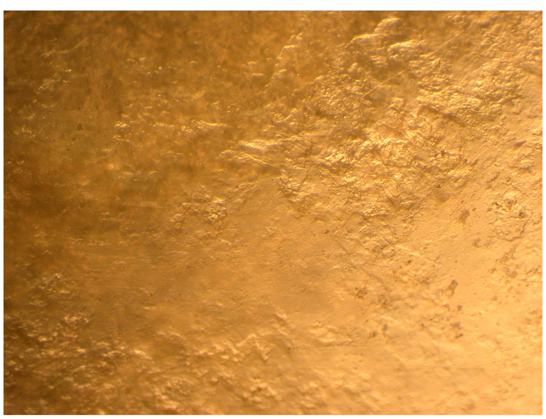


Figure 14

AI4

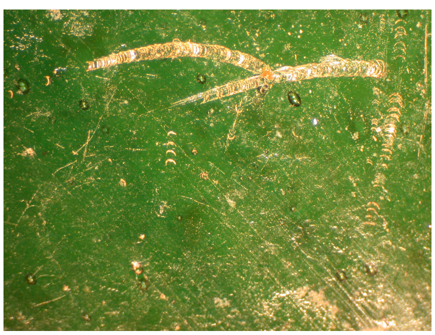


Figure 15

Al 5

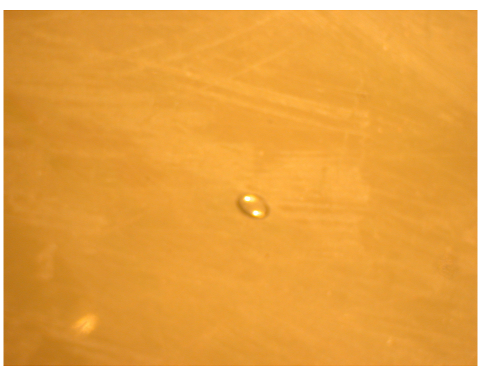


Figure 16

AI6

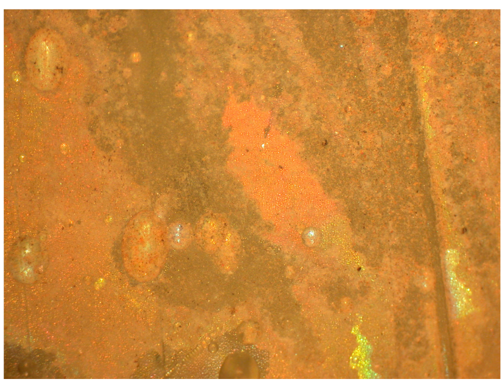


Figure 17

Al 7

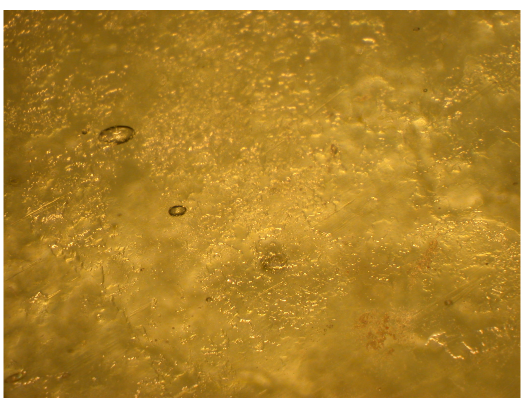


Figure 18

Al 8

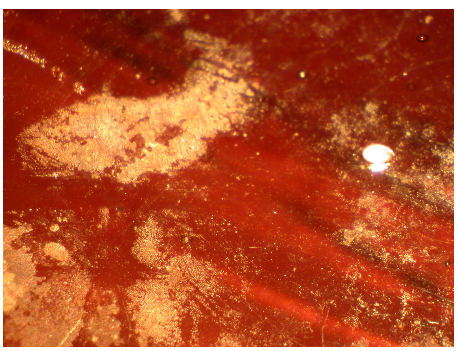


Figure 19

Al 9

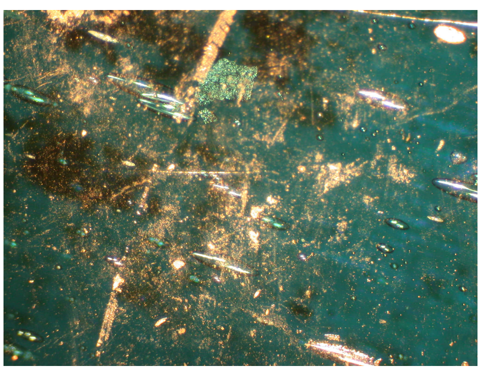
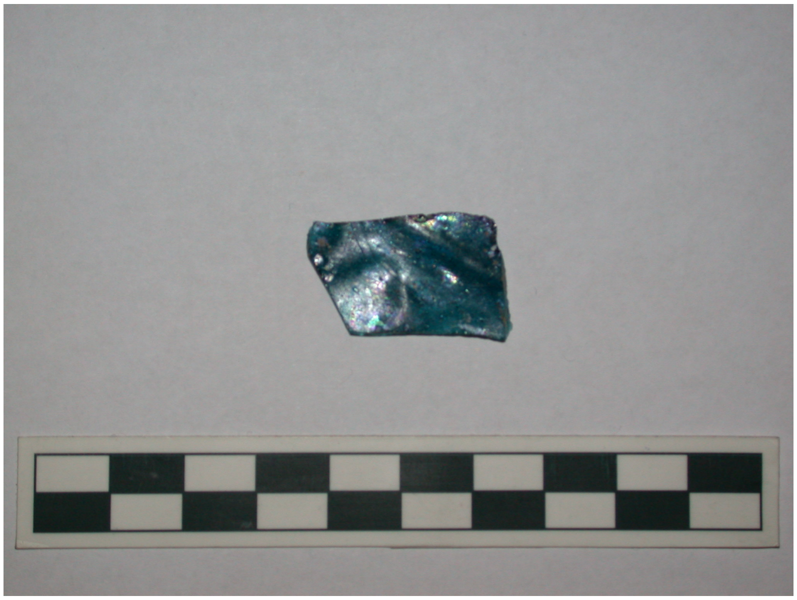


Figure 20

Al 10



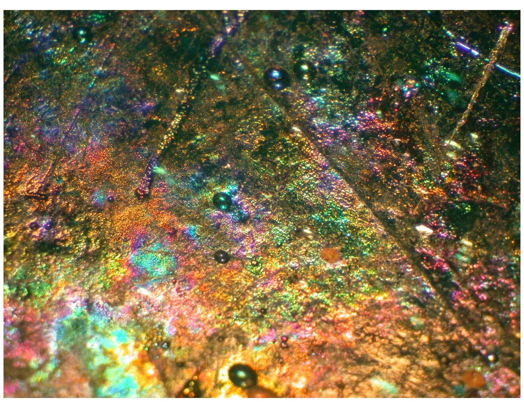


Figure 21

Technical Drawings

Al 1

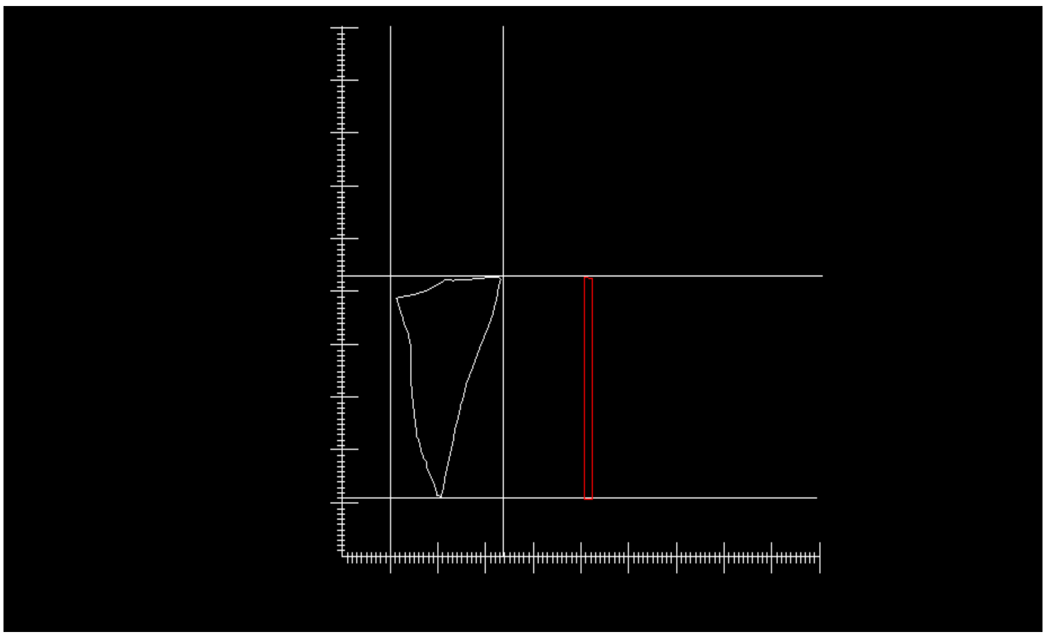


Figure 22: Sample no 1 each dimension 10 cm long

Al 2

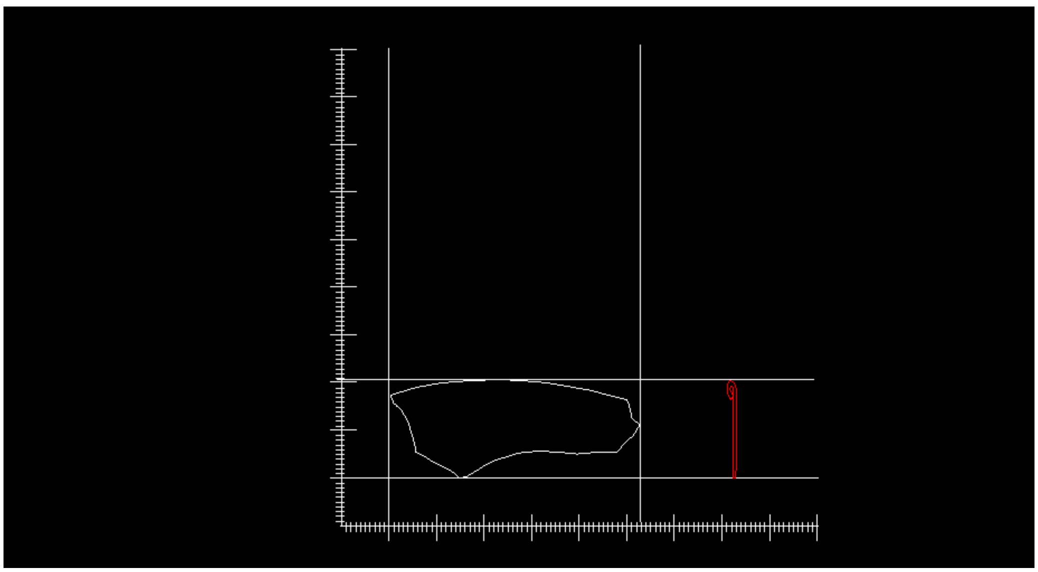


Figure 23 : Sample no 2

Al 3

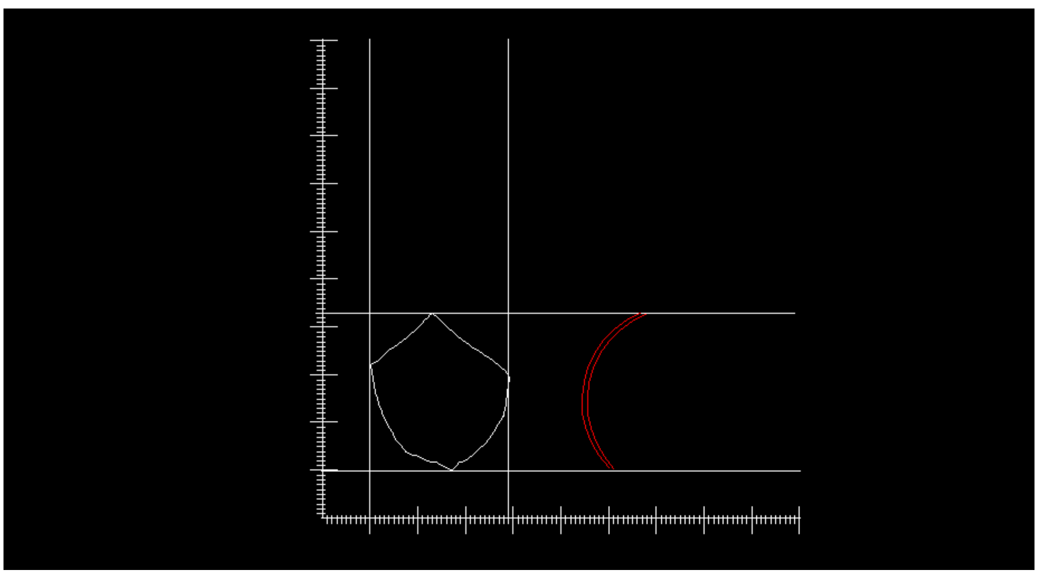


Figure 24: Sample no 3

Al 4

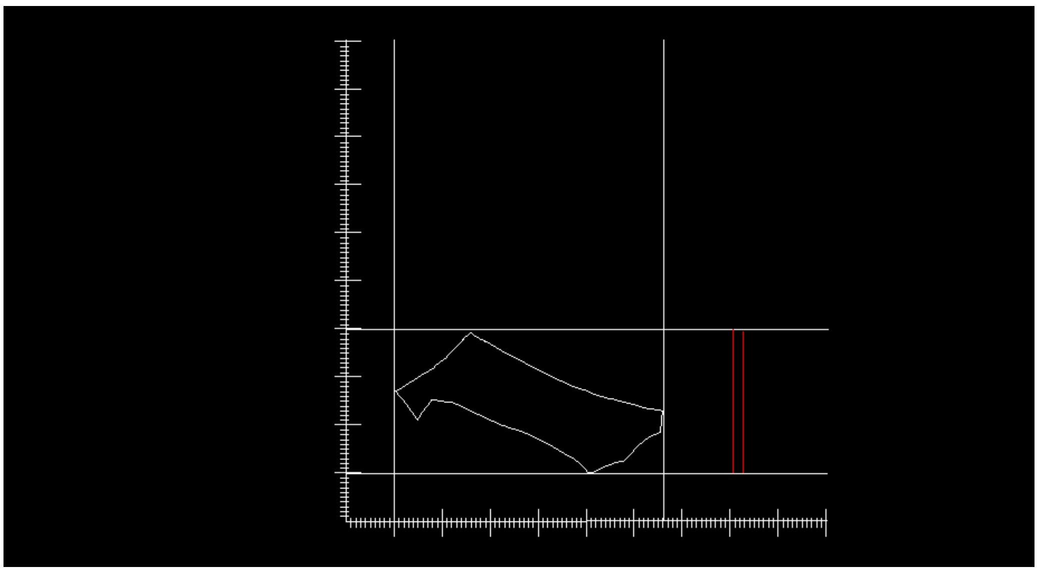


Figure 25: Sample no 4

Al 5

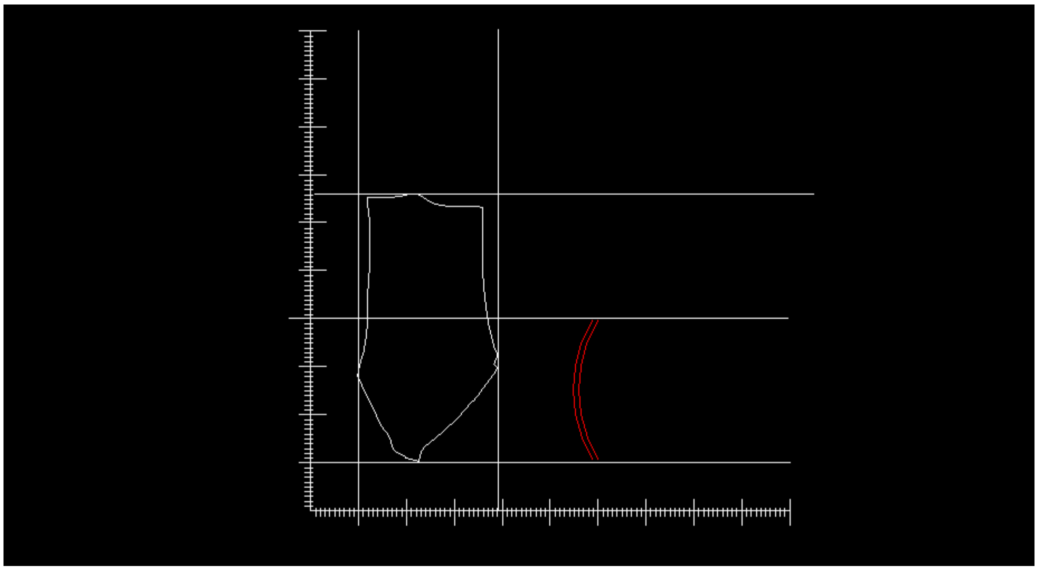


Figure 26: Sample no 5

Al 6

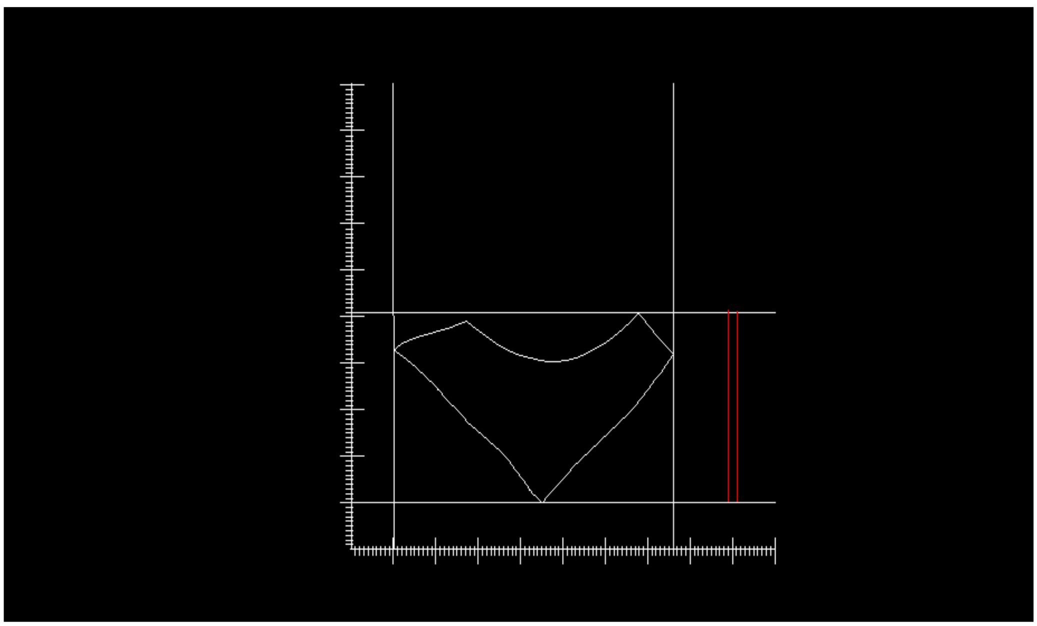


Figure 27: Sample no 6

Al 7

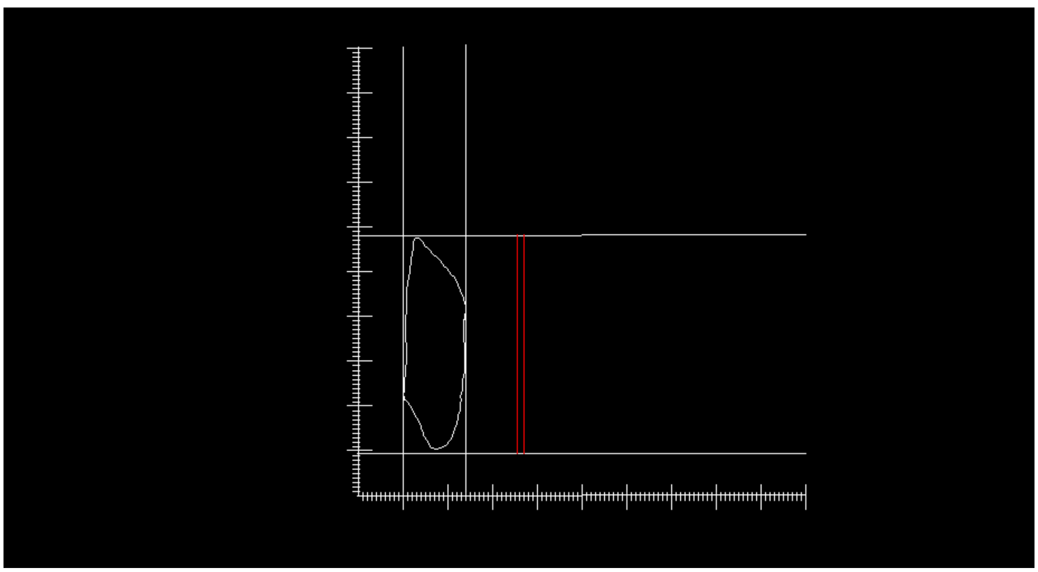


Figure 28: Sample no 7

Al 8

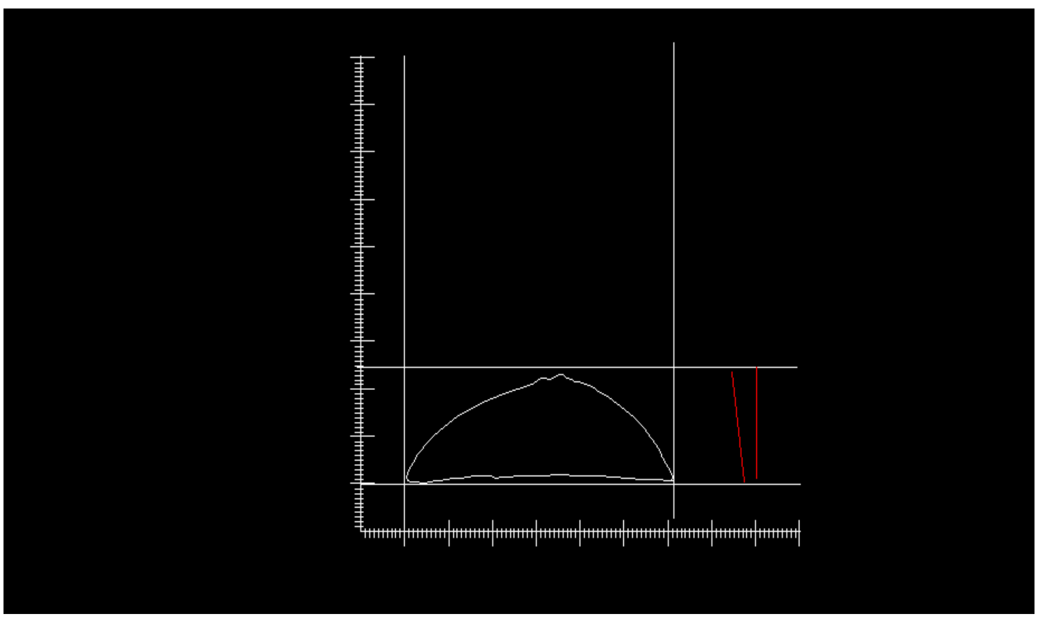


Figure 29: Sample no 8

Al 9

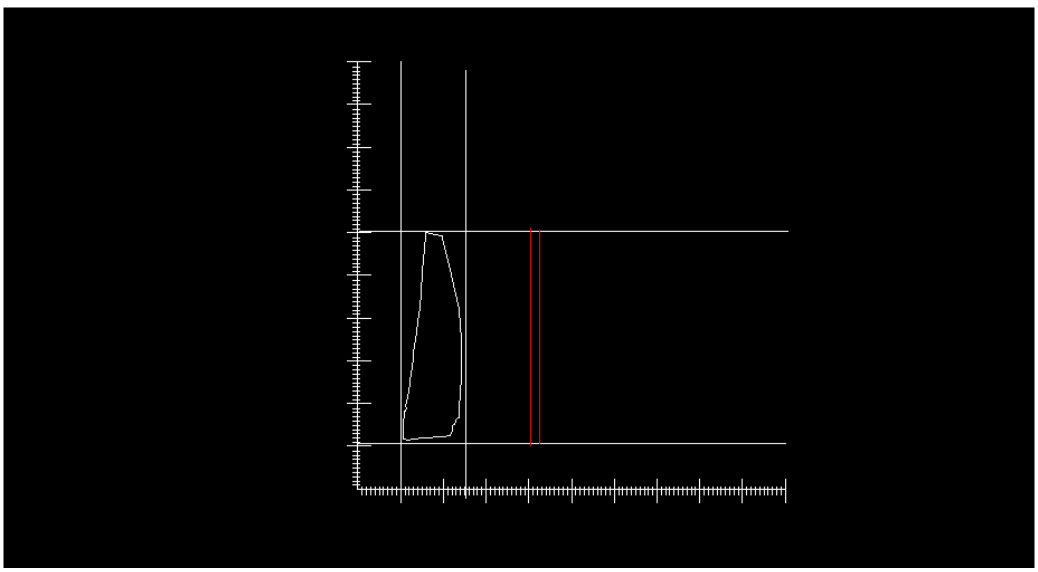


Figure 30: Sample no 9

Al 10

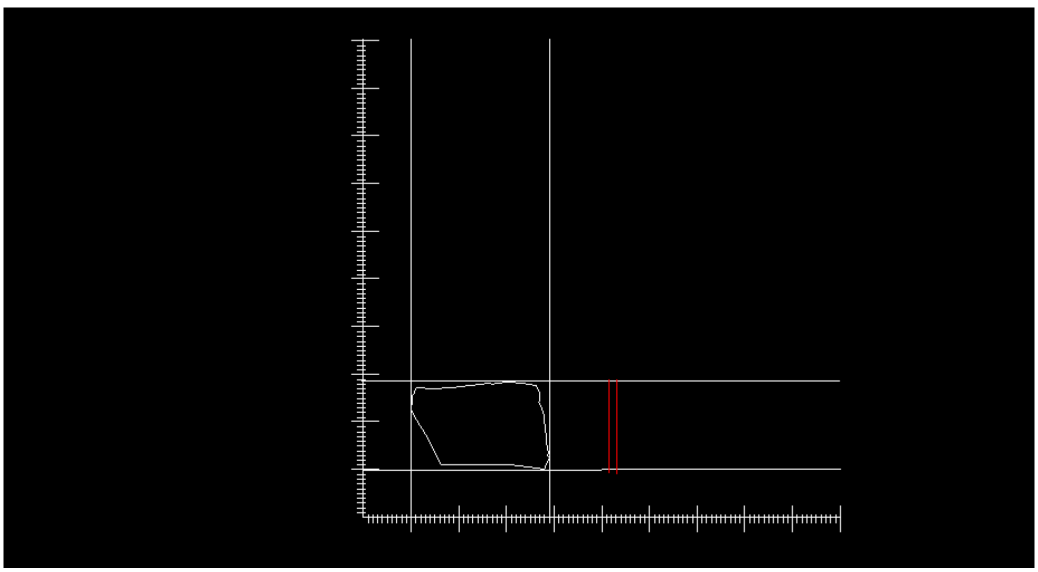


Figure 31: Sample no 10

CHAPTER 4

CONCLUSION

In this study 13th century window glass samples obtained from Vaulted (Tonozlu) Galleria, in Alanya Castle were examined to determine their raw material compositions and production technology. As far as we know this is the first study for 13th century window glass obtained from Alanya Castle.

In the analysis, two spectral methods, XRF and ICP-OES were used to determine major, minor and trace elements quantities. Those methods provide analyzing almost all elements simultaneously and with rather law error. The error of the analysis was about 3%.

XRF and ICP-OES data reflected the typical composition of soda-lime-silica glass with percent compositions of 10.7 Na_2O: 7.7 CaO: 65.3 SiO_2 as average.

Six samples have almost the same amount of alumina (about 3.4% as Al_2O_3), two samples have quite different values (5.8% and 1.9%). Presence of same amount of Al_2O_3 showed that one type of quartz sand was used for their production. Two samples may be imported to the site elsewhere or they may be produced in different workshops.

The fluxing agent sodium oxide (Na_2O) could be obtained from Natron (or another similar mineral Trona) naturally occurring mineral containing high percentages of Na_2CO_3. The use of this mineral is also indicated by the presence of minor amounts of MGO and K_2O for all samples with the exception of one sample. In this exceptional sample production using the plant ash is more probable.

Turkey has plenty amount of Trona mineral in various locations such as Beypazarı (Ankara)

Most of the samples had shown casting character as production technique.

Color producing elements were found to be Fe, Mn and Cu.

In the further studies, other window glasses obtained from other archaeological sites will be analyzed and their elemental composition will be determined to understand window glass technology in Anatolia.

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