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Composition analysis of medieval ceramics by laser-induced breakdown spectroscopy (LIBS)

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Abstract Laser-induced breakdown spectroscopy (LIBS) technique is expected to be one of the most preferred techniques in archaeology research since it does not disrupt the structural and chemical form of archaeological samples, and it is considered virtually nondestructive analysis method. In this work, LIBS is used for analyses of glaze, paint, and clay of medieval ceramics collected from East Plain Cilicia, Osmaniye Province during archaeological survey. Transparent glazed and colour-painted ceramics of the Islam and Byzantine pottery traditions are analysed to detect distinctive and common features of the chemical compositions of their glazes. The spectral lines of Islamic and Byzantine glazes indicate that their structures are same. However, strontium (Sr) is determined in the transparent glaze of Islamic ceramics. Elemental composition and homogeneity of paint on one of the sample are determined by LIBS analysis. Colour changes are related with composition differences of the paint content in the archaeological ceramic. In addition, the clay classification of archaeological ceramics taken from the Yapılıpınar mounds, Taşlıhöyük mounds, and Örenşehir ancient sites is done using PCA and PLS-DA chemometric techniques. According to the results of the classification, Yapılıpınar mounds terracotta ceramics differ from those of Taşlıhöyük and Örenşehir ancient sites.

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1 Introduction

Archaeological ceramic samples are the most common materials culturally found during archaeological works, which yield wealth of information about ancient cultures and societies [1]. Analyses of archaeological ceramics prior to the twentieth century were macroscopic examinations detecting the physical properties of ceramic such as body shape and size, fabric colour and texture, decoration colour, design, and functionality. At the beginning of the twentieth century, chemical analyses and petrographic studies began to be applied on archaeological artefacts [2]. The chemical and crystallographic characterizations of ancient ceramics motivated us to understand the technology of pottery production used in a given period time [3]. There are various analytical techniques such as instrumental neutron activation analysis (INAA) [4], Raman spectroscopy [5], Fourier transform infrared (FT-IR) spectroscopy [6], X-ray diffraction (XRD) [7], X-ray fluorescence (XRF) spectroscopy [7, 8], and proton-induced X-ray emission (PIXE) to determine chemical and structural composition of the samples in archaeological objects. Many of these techniques require sample preparation, which destroys the structural form of ancient ceramic sample because these techniques require sample mass relatively in large quantity for effective analysis. Therefore, archaeologists refrain to facilitate destructive analysis techniques, unless it is inevitable. Laser-induced breakdown spectroscopy (LIBS), also known as "Microemission Spectroscopy", is a spectrochemical elemental analysis technique [9]. Basically, laser pulses from Q-switched laser source are focused on

the target materials that produced laser spot size about micron scale using a suitable focusing lens. Radiations emitted from the plasma plume created by focused laser beam are contained information on the chemical composition of target material. In order to achieve stoichiometric ablation and invasiveness, the analytical performance of the LIBS technique can be improved reducing the thermal effects that created by nanosecond pulse duration. In our previous depth profile analysis of galvanized steel sheet, the effects of laser processing parameters, such as laser energy, laser spot size, and coating thickness were investigated to find out depth resolution by applying Taguchi optimization method [10].

The use of laser-induced breakdown spectroscopy (LIBS) has been investigated for a wide range of material analysis applications and the interest in LIBS has grown significantly due to numerous technical advantages which include small sample requirements, minimal or no sample preparation, rapid analysis time, multi-elemental capability, no requirement for vacuum, and online and stand-off detection over other analytical methods [11–14]. LIBS can be preferred in the archaeological sample analysis, because (1) it allows simultaneous analysis of main and trace elements, i.e. multi-element analysis, (2) it only ablates miniscule particles at the microgram level, i.e. the damage to the sample is minimal, and (3) it provides the flexibility of using a portable system and thus, enables in situ analysis (in the museums, excavation sites or historical buildings) can be used [15]. In addition LIBS technique can also be used along with other spectroscopic and imaging techniques such as Raman spectroscopy, laser-induced fluorescence (LIF), laser time-of-flight mass spectrometry, and hyperspectral imaging for analysis of archaeological samples [16–18]. Giakoumaki et al. performed combining LIBS and Raman techniques in a hybrid unit for the analysis of cultural heritage samples. They preferred to use the second harmonic (532 nm) of nanosecond pulsed Nd:YAG laser and emitted light (Raman scattering and plume emission) collected by same lens in the hybrid system for both LIBS and Raman analysis [19]. The use of the hybrid system eliminates disadvantages of these techniques separately as well as both element and molecular analyses of samples IS determined by the system. LIBS technique has a wide range of applications in archaeology and art. In these applications, painted works of art, ceramics, icons, sculptures, metals, glasses, marbles, stones and biomaterial objects are located [11, 20, 21]. LIBS technique is used for an in-depth analysis of multilayer archaeological samples, mapping of the sample surface to determine restoration work on archaeological samples, and in situ analysis of archaeological samples in museums by handheld or portable LIBS instruments, all of which have particular importance for archaeologists.

The materials used in decorative and functional ceramics are different. Materials used in the main body and decorations of ceramics vary according to the functionality and purpose of the ceramic product. Materials can be applied in a number of ways to decorate on ceramic surface such as adding a coloured slip and paint prior to firing, as well as adding coatings and paint after firing. While the glaze on the surface protects the paint and/or bulk layer, paint layer applied for decorative purposes as needed. Knowledge of the glaze, paint, and clay composition can provide important scientific information on a number of issues concerning archaeologists and art historians. The provenance of minerals can offer insights regarding possible trade routes and sociocultural interactions between different cultures [2].

Elemental analysis of the medieval ceramics of different clay body with structural in appearance was made using PCA and PLS-DA chemometrics methods in order to classification in our previous study [22]. These structural differences were porosity and clay colour even visible with the naked eyes. These ceramics called as frit, calcerous frit, and terracotta, according to analysis results, medium amount of Ti and high amount of Ca and Fe observed in terracotta samples terracotta, while frit ceramics contained Ti element (terracotta ceramics not contain) and low amount of Ca element. Using the basic difference and relative intensity of elements, all the analysed ceramics were classified successfully. Present study focuses on glaze, paint, and clay analyses of the medieval ceramics collected during archaeological surveys of the Osmaniye Province. In difference to previous published studies [22], this paper reports in comparison of only terracotta ceramics from different ancient sites from Osmaniye Province, Turkey, belonging to Islamic and Byzantine ceramic traditions. Moreover, this study examines surfaces of archaeological artefacts that glaze, paint and clay compositions of the Osmaniye medieval ceramics to detect distinctive features peculiar to the culture and society that produced. Selective samples of the Osmaniye medieval ceramics are mostly found from settlements such as, Örenşehir, Yapılıpınar and Taşlı 1 mounds and clay body of the terracotta ceramics were very similar. Selected samples are identified and classified in two major groups by macroscopic analyses belonging two distinctive cultures that prevailed in Plain Cilicia contemporaneously [23, 24]. The most prevalent differences between Islamic and Byzantine ceramic traditions were found in the analysis of transparent glaze. In the paint composition analysis, elemental variation of brown and green paint on the Yapılıpınar mound ceramic (Yplpnr Gzb 2008–14) was observed by using LIBS signal taken along the line on the sample surface. Differences between the LIBS signals of the individual elements were observed along the linear

measurements colour change of samples. In the clay composition analysis, the classification of archaeological ceramics that belong to Yapılıpınar and Taşlı 1 mounds, as well as to the Örenşehir site are performed by PCA and PLS-DA chemometric methods with LIBS spectral data to find the most important trends in data and to classify the samples. In all the ceramics, the same elemental composition was determined; the only difference was their relative intensities in different samples.

2 Materials and methods

Medieval ceramics collected during the archaeological survey of Osmaniye Province are very fragmentary but qualified enough to deduce information bearing specific features of pottery traditions that can be identified as Islamic or Byzantine. Osmaniye Province encompasses land of the east of Plain Cilicia, namely Yukarı Çukurova, which is bordered by the Amanus mountain range at east, Taurus Mountain range at north, Deli Halil Basalts at south, and Misis and Anazarbus ridges at west through which the Ceyhan River meanders to reach to the Mediterranean Sea. It was on the junction of major ancient routes connecting northern Highlands of Anatolia and Upper Mesoptomia, namely Euphratesia to the Mediterranean Sea and North Syria. A strategic location such as the East Plain Cilicia was to be the stronghold of ruling power. In early medieval period, for 300 years it was the military zone of the Arab armies. Inevitably, in successive centuries it became the battlefield of the Arabs, Byzantines, Crusades, and Armenian Barons changing hands frequently leaving materials of their cultures, which are mostly potsherds.

Fragmented ceramics collected during the Osmaniye archaeological survey belong to Byzantine and Islamic ceramic traditions. Ceramic fragments subject to present study are findings of the Taşlı 1, Yapılıpınar mounds, Örenşehir, and Mağaralı South settlement sites, and they are dated earliest to the tenth century and the latest to the thirteenth century; the samples dated earlier are identified as ceramics of Islamic culture and samples dated later periods as of Byzantine culture. Ceramics selected for the colour-glazed analysis belong to the eighth and the fourteenth centuries (Yplpnr Gz 2008–35, Tslhyk G 2006–32, Örens 2006–125, Mgr G 2009–30). These ceramics belong to Islamic and Byzantine ceramic traditions and have brown and green colour glaze on their surfaces. The selected samples for the paint analysis are identified as the incised (sgrafitto) decoration Byzantine ceramic dated to the thirteenth century (Yplpnr Gzb 2008–14). Ceramics used for clay composition analysis belong to Yapılıpınar, Taşlı 1 mounds, and Örenşehir settlement (Yplpnr Gz 2008–31, Yplpnr Gz 2008–32, Yplpnr Gzb 2008–14, Tsl Hyk G 2006–46, Orens 2006–84). Common features of these earthenware terracotta ceramics have clay colour range from buff, pink to red. All of the samples chosen for the analyses are glazed having decoration either painted or incised and most of them have white slip over body. Among chosen samples incised–sgrafitto decoration are all identified as Byzantine ware, whereas samples identified as Islamic ware are underglaze painted such as, Yplpnr Gz 2008–32, Orens 2006–84 and 10, and are not decorated in sgrafitto technique. Orens 2006–125 found at Örenşehir a settlement Islamic in origin is a unique sample having deep-cut decoration over applied white slip and green glaze, which is a feature of early ceramic tradition of Islam both Umayyad and Abbasid [25].

In this study, elemental components of the selected transparent and coloured medieval glazed ceramic sherds of Osmaniye Province are analysed using the LIBS technique. The aim of the glaze analysis is to detect distinctive and common features of the chemical structure of glazes of the Islamic and Byzantine ceramics. The analysis would help archaeologists to understand the cultural interactions between the two periods.

All ceramics are analysed using BAKI-LIBS^{TM} (BEAM ArGe laboratory prototype) experimental system shown in Fig. 1. In this study, Q-switched Nd:YAG laser with pulse 4.4 ns at 1064 nm wavelength (EKSPLA NL301HT) is used as an excitation source for the analysis of archaeological samples and all LIBS experiments are performed at the atmospheric environment. The laser is capable of delivering a maximum energy output up to 450 mJ and run at the maximum repetition rate of 20 Hz. The laser beam is focused on a spot size of about 200 μm diameter on the sample by a BK7 lens with 150 mm focal length, however the diameter of heat-affected zone area is approximately 400 μm. The laser and spectrometers are triggered and synchronized using a delay generator (DG535, Stanford Research Systems). The timing of the experiment is previously adjusted to provide an optimized S/N ratio and nearly constant temperature in order to verify the existence of local thermodynamic equilibrium (LTE). Delay generator is set to 1-μs delay time and 10- μs gate width in the optimized experimental conditions. The emitted light from plasma is collected with a lens coupled to a 600-μm-diameter fibre bundle that is split into seven channels in a crossed Czeny–Turner-type spectrometer system. The resolution of BAKI spectrometer^{TM} containing a linear CCD detector having 3648 pixels is 0.07 nm and the channels are customized from 200 to 900 nm wavelength range [26]. The spectrometer software includes the NIST [27] database and experimental spectral data from certified reference materials for wavelength

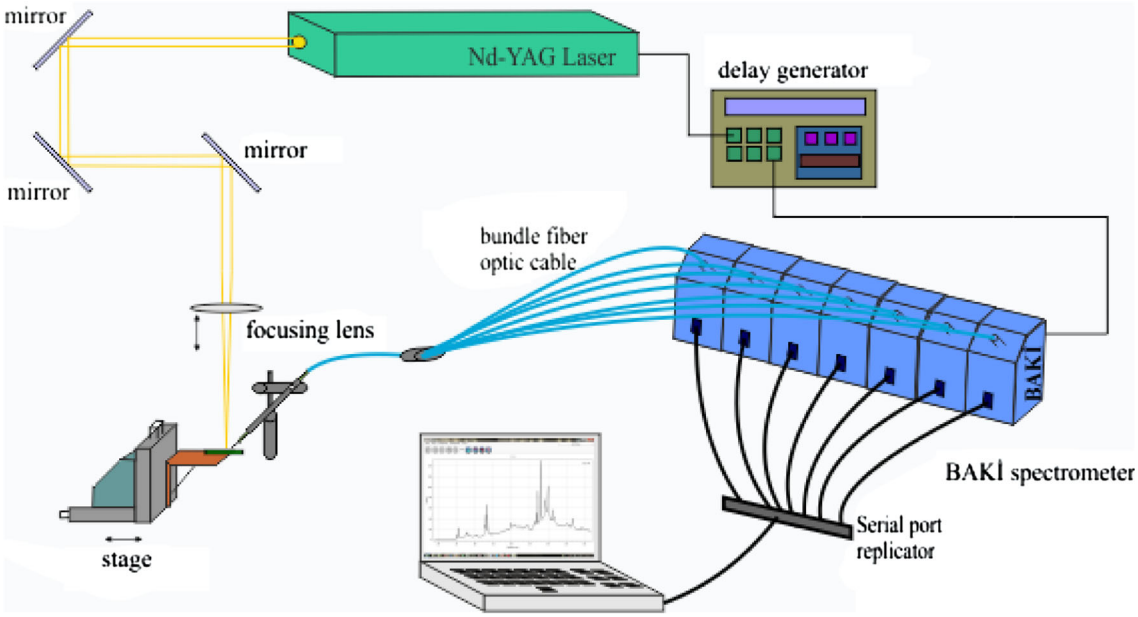


Fig. 1 Schematic representation of BAKI-LIBS^{TM} (laboratory prototype) experimental system for the analysis of archaeological ceramics

identification of emission lines. In the published previous studies BAKI-LIBS^{TM} set-up was also used, an interesting application to analyse the amount of diffusion depth of stellite powder into the copper plate for providing a depth profile of elemental composition of the penetrated region of the laser welding [28].

All the experiments in this study, afore mentioned LIBS system was used, but different experimental parameters were applied for each of the glaze, paint, and clay analysis to minimize the impact of the plume expansion on the sample depend on the matrix specifications. Therefore, system was optimized for each analysis. LIBS measurement for glaze analysis, 10-mJ pulse energy of Nd:YAG laser, taking average over 10 shots, is applied on the ceramic surface. Our LIBS system has a motion control unit, which allows us to take measurements along a line on the sample without removing it from the LIBS system. Along the line for paint analysis, 26 spectra at 1-mm intervals are recorded on the archaeological ceramic, which contained green and brown paint, in order to determine content and homogeneity of paint on the ancient ceramic. For each measurement of the paint analysis, 30 mJ pulse energy of Nd:YAG laser, averaging over three shots is applied on the ceramic surface. In the archaeological clay analysis, each spectrum was recorded with the laser energy of 30 mJ averaging over ten shots by using the BAKI spectrometer^{TM}. Five LIBS data from each of the five selected pieces of the ceramic were recorded and measured. Assessments were performed based on the average of the data. All of the data collected were used for the classification of ceramics.

3 Result and discussion

3.1 Glaze analysis

From ancient times until today, ceramics have been covered with glaze in order to prevent the liquid absorption and corrosion, as well as decorative purposes. Silicon dioxide (SiO_2) is used as the primary glaze material, as it has a lot of feldspar and silicate glass form. Also several metal oxides are used to colour the glaze content [29]. The first glazed clay objects were produced in Mesopotamia [30]. Paynter and Tite demonstrated that Mesopotamia glazes and glasses have very similar elemental composition. They proposed the material used for glazing is the same one used for glass production [30].

LIBS can be accepted as an minimally invasive technique due to the microsampling character of measurement that a few micrograms of material are ablated with each laser pulse caused only microdamage on the sample. Nanosecond laser pulse duration creates a heat-affected zone (HAZ) that is observed around of the laser spot size. The analytical performance of the LIBS technique can be improved reducing the thermal effects in order to achieve stoichiometric ablation and invasiveness. The fluence (power density) is reduced to obtain lower ablation and better depth resolution; however, larger laser spot size is occurred on the sample surface. The optimized experimental parameters or shortening of laser pulse duration (picosecond or femtosecond) decreases the size of the heat-affected zone and leads to more controllable material modification and removal. If the laser pulse energy is used

sufficiently low to minimize the impact of plume expansion on the samples, LIBS is also applied for characterization the depth and composition of individual layer of the multilayer materials. Depth profile analyses of the elements depends on the relative intensity which can be helpful to determine thickness of the thin film coating, glaze and paint. Clay and glaze contributions to plasma emission make it difficult to distinguish the LIBS measurements of glaze analysis because calcium (Ca), aluminium (Al), silicon (Si), and magnesium (Mg) are found in the content of both but vanadium (V) and lead (Pb) are found only in glaze content. Iron (Fe) spectral lines in all of samples clay and brown glazes were observed except from transparent glazes. There are no spectral lines of Pb or V elements detected in the cross-sectional analysis of the clay. In the glaze analysis laser pulse energy is set as possible as low to avoid interference of the layer beneath the analysed one. During the LIBS measurements laser pulses are interacting with a very tiny area of the material. Optical microscope (Olympus BX51 M) image of the crater produced by 10 pulses on the archaeological artefact sample that used transparent glaze analysis are shown in Fig. 2. The diameter of the average laser spot size is approximately 200 μm, while HAZ size is about 400 μm, and thus it reveals that LIBS technique has major advantages for analysis of cultural heritage.

When the laser beam is repeatedly striking at the same spot, crater edges are covered with a molten material as a film formed through melt expansion by the vapour pressure. Therefore, clay analysis is performed from the cross section of the ceramic sample to avoid primary layer contribution to underneath layers.

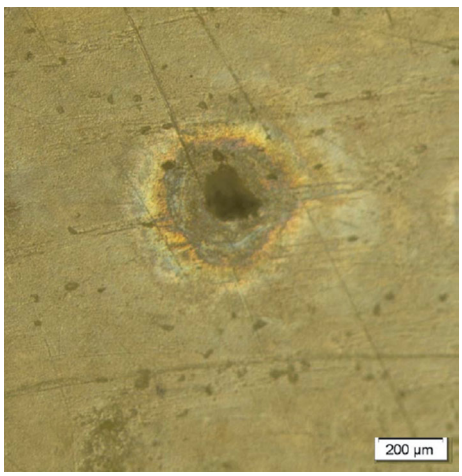


Fig. 2 Microscope image of laser spot dimension on transparent glaze (Byzantine ceramic) after 10 pulses at 10-mJ laser energy, the averaged spot diameter is approximately 200 μm while HAZ size is about 400 μm

In this study, transparent glazed and colour-painted ceramics of the Islam and Byzantine pottery traditions are analysed to detect distinctive and common features of the chemical compositions of their glazes. LIBS spectra of transparent glaze ceramics are shown in the Fig. 3. Mg, Si, Al, Ca, K, V, Na and Pb are determined as major elements in the archaeological glaze. Sr element is observed in the transparent glaze on Islamic ceramic but not in Byzantine transparent glaze. The existence of strontium content in the glaze would imply that its source could be ash glaze, limestone, or plants [31, 32]. Also ceramic clay structure of Islamic ceramic has no Sr element therefore Sr element contribution comes from the glaze. According to the results of LIBS measurement taken from glaze surface, the LIBS technique comes into prominent analysis of individual layer in ceramics. Southern Chinese ceramics employed two types of high fired glaze: limestone glaze and ash glaze. Ash glaze was the dominant high fired ceramic coating from third century AD until the fourteenth century AD in China, and on the other hand, limestone glaze was widely used from the middle of the fourteenth century AD onwards [33]. The glaze is called ash glaze or limestone glaze depending on the fluxes involved for making these glazes. Both ash glaze and limestone glaze contains botanic ash; but for the limestone glaze calcium carbonate is the major component. These results indicate that Islamic and Chinese ceramic glazes have similar content or produced by the same technique unlike Byzantine transparent glaze. It is known that Chinese import ceramics were highly demanded in markets of the Arab World, which led local potters to imitate both the technique and decoration of Chinese ceramics [34, 35]. Similarly, Madkour et al. observed Sr in the clay body of the Mamluk sample. They performed an analysis on Islamic ceramics produced in Egypt during the region of Ottoman and the Mamluk while only the production and raw material of ceramics belong to the Islamic period that was emphasized in the analyses [36]. Also, in the transparent glaze compositions of both cultures, significant amounts of lead were observed. Tite et al. [37] have mentioned in the review article that transparent high lead type glazes were extensively used in the Islamic and Byzantine cultures. First transparent high lead glazes have been produced 45–60 % PbO with an alkali content less than 2 % Na2O-plus-K2O and an alumina content 2–7 % Al2O3 [34]. Melessanaki et al. also observed a similar glaze composition on Byzantine ceramics [38]. They determined a significant amount of Pb element in glaze content. In our LIBS measurement, the same elements (Pb, K, Na, Al, V) were determined in the transparent glaze composition; however, Pb and Na emission line intensities in Islamic transparent glaze were higher than that that of Byzantine transparent glaze. Variety of metal oxides including vanadium, chrome, antimony,

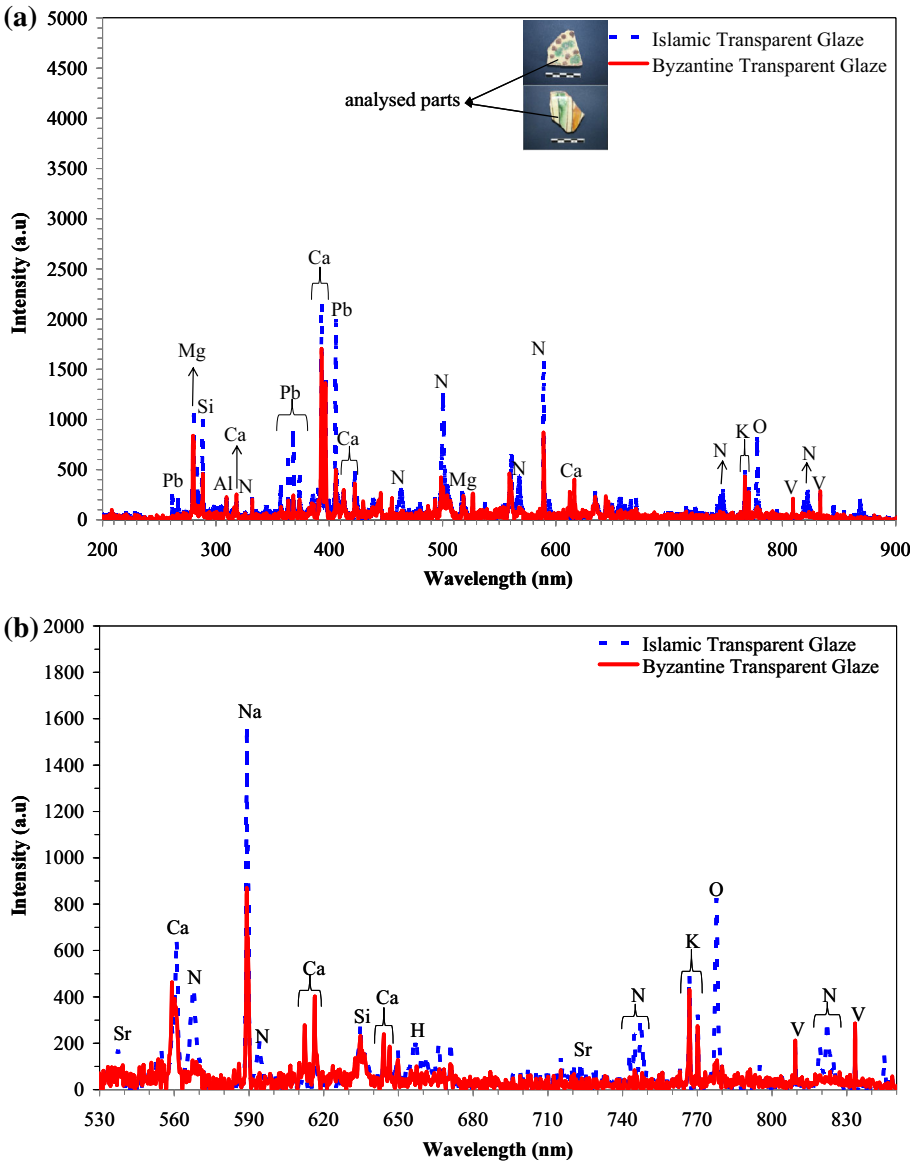


Fig. 3 **a** Emission spectrum of Islamic and Byzantine ceramic transparent glazes from 200 to 900 nm, **b** Enlarge spectrum of Islamic and Byzantine ceramic transparent glazes from 530 to 850 nm

iron or rutile is used in the alkaline glazes to obtain bright yellow colours. Vanadium has observed only glaze content in the surface of the sample which is a refractory metal that has melting points above 2000 °C and yield noticeably ore subdued colours at higher temperatures. Also, Colao et al. [39] observed vanadium on the LIBS analysis of Roman sculpture surface, and they did not detect it in the internal part of the sculpture, but concluded that this element probably is coming from the material used for the mould. This result shows in that period vanadium was used for colourant as well as heat shield and tool coatings for glaze of the ceramics and sculpture surface.

Colour-glazed and paint ceramics are often used for domestic utensils such as kitchenware, pots, bowls, plates, jars, urinals, and candle lamps [40]. Metal oxides are used to colour the glaze. Green, yellow, and brown lead glazes are related to metal ion colourants: green lead glaze is determined with the presence of $Cu2^{+}$ or $Fe2^{+}$, while the brown colour is related to $Fe3^{+}$. We observed iron and copper elements in brown and green coloured glazes, respectively. These results are common for ceramic production in both Byzantine and Islamic periods. However, we detected zinc (Zn) element in the brown glaze ceramic from Yapılıpınar mound (Yplpnr Gz 2008–35), which belongs to the Islamic period (Fig. 4). While zinc (Zn) is not found in brown-glazed ceramic clay body analysis, it has been identified only in the surface analysis. While brown glaze is preferred in the interior surface of cooking containers in both thirteenth and fourteenth centuries, green glaze applied on the surface of the containers were used to store liquid. Melessanaki et al. [38] performed the LIBS on Byzantine green glaze ceramics. They observed copper and

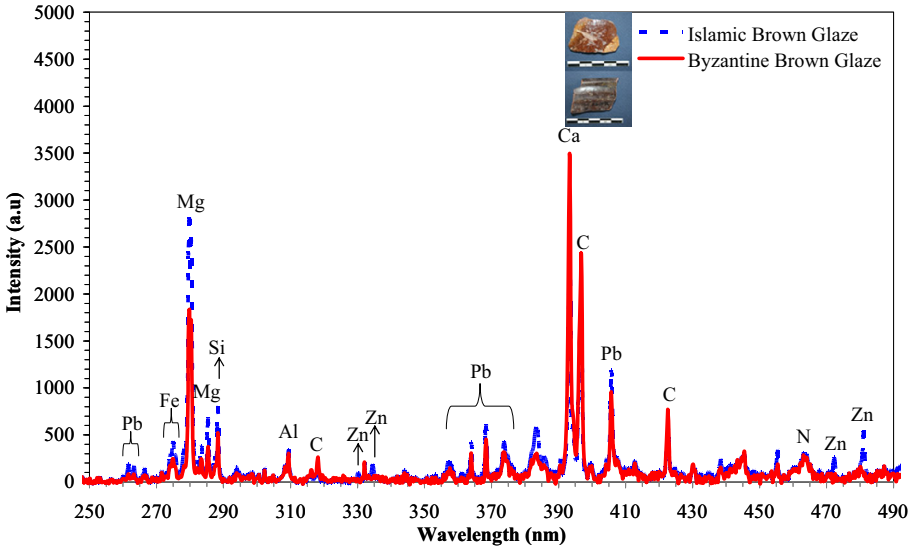


Fig. 4 Emission spectrum of the Islamic and Byzantine brown glaze samples

tin elements in green glaze and proposed that bronze (copper and tin) was used to identify the source of tin in the green glaze. Colao et al. [39] observed a significant amount of tin and lead in all of the glazes. On the contrary, we only observed lead in our samples. They suggested that use of glazing mixtures based on silica sands and claimed, where lead was used to decrease the melting point and tin was used for opacifying [39]. Examined ceramic samples, especially Byzantine ones, have a glossy surface. Spizzichino et al. [41] performed quantitative element analysis of lustre to demonstrate the differences between Hispanic and Italian findings. They just observed cosalite (Pb2Bi2S5) in Italian lustre and found Pb and Sn in Hispanic and Arabian lustres in higher concentrations than the Italian lustre. Also, they observed Si and alkali metals in both of them but lower concentration in Hispanic and Arabian lustres.

3.2 Paint analysis

Metal oxide sources had been used to obtain paint composition in the ancient ceramics [29]. Paint was used for decorative purposes on the surface of archaeological ceramics; and it contains different elements to produce specific colours. We performed a paint analysis on the painted Byzantine ceramics.

In the LIBS results, Cu and Fe were observed in green and brown paints, respectively. As shown in Fig. 5, normalized intensity of Fe is increased at eighth pulse shot as laser shot focused on the dark (brown) line that was made as a decoration on ceramic. The 324,75-nm wavelength emission line of copper element is partially seen after the eighth pulse shot, because the green paint on the ceramic is not homogeneous. Pigment identification on an icon and miniatures was performed using LIBS and Raman techniques by Burgio et al. [17]. In their study, not only determined intense emission of Cu element but also emission lines of Mg, Si, Al and As elements to the LIBS analysis of green paint on the miniatures suggested that the green paint based on a copper compound. In addition they performed the element compositions of brown paint on the icon, Fe, Al, Si and Pb elements were determined on brown paint so they suggested presence of red earth (iron based pigment). Also, on the LIBS analysis of Mamluk period, Islamic ceramics produced in Egypt, Madkour et al. [36] indicated that the source of brown and yellow colour was iron oxide and the source of the turquoise blue glaze was copper oxide that used in different Islamic periods to produce this colour in lead alkaline glaze. Although our sample is Byzantine ceramic, the result indicates that same element was used for the same colour glaze or paint.

3.3 Clay analysis

Ceramic samples for clay analysis were taken from three different ancient settlements which are Örenşehir, Yapılıpınar, and Taşlı 1 mounds (Yplpnr Gz 2008–31, Yplpnr Gz 2008–32, Yplpnr Gzb 2008–14, Tslhyk G 2006–46, and Orens 2006–84). One of the LIBS spectra of the samples is shown in Fig. 6. Fe, Mg, Ca, Si, Al, K and Na elements were determined in the clay composition of all ceramic samples, but they were observed in different relative intensities in each ceramic sample. For this reason, researchers prefer chemometric analysis methods thereby raw and hidden information were obtained from data [42]. Though, the LIBS spectra contain significant information about a sample's composition, they are usually complex. Multivariate techniques are used to distinguish materials from each other, especially for geological samples [43].

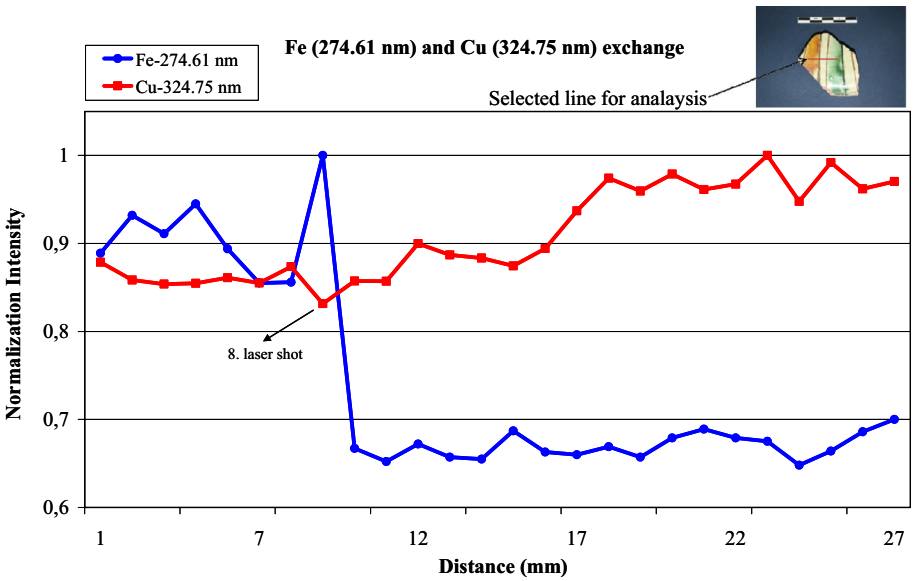


Fig. 5 Normalized intensity variation of Cu and Fe elements in the green and brown paint layer on archaeological ceramic, that points 1–27 shown in the *x* axis correspond to a scan from *left* to *right* along the "*red*" line indicated in the image

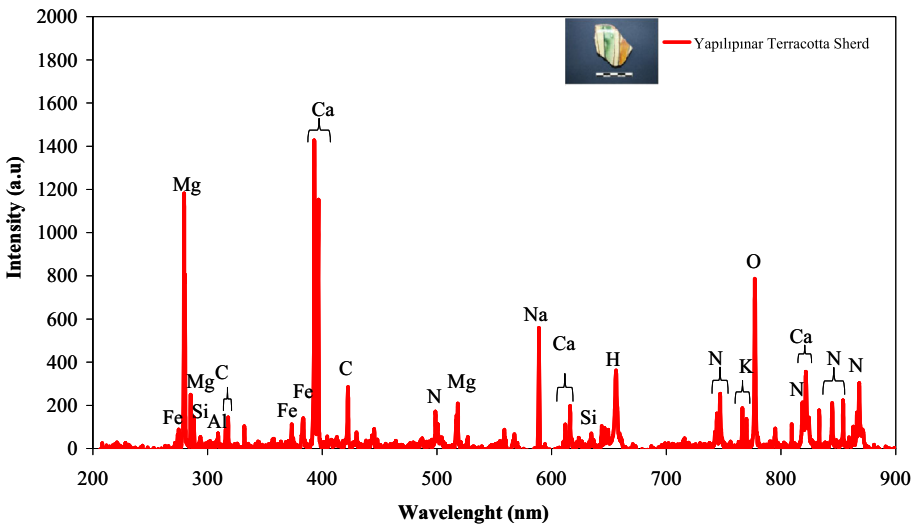


Fig. 6 Emission spectrum of Yapılıpınar ceramic sample

PCA and PLS-DA are two chemometric techniques, most commonly used in studies with regard to geological findings, and they are particularly preferred in LIBS measurements. Erdem et al. [44] used LIBS technique in the compositional analysis of pottery; and they explore correlations in spectral data, by using chemometric techniques that would possibly enable discrimination among different sherds dated from the early to middle iron age in eastern Turkey. PCA is a cluster method that aims to identify variations in the data set. We used PCA to determine variance between each sample, and PLS-DA to identify the optimal variance between each class. The cross-validation models are also performed in kidney stone analysis and classification in our previous work [45]. PCA and PLS-DA analyses are performed using commercially available chemometric software LIBS Graphical Development Tool (LIBS GDT, Applied Spectra) [22, 45]. The chemometric software is used to classify the ceramics, which are different clay structures such as fritware, calcerous fritware, and terracotta sherds. Ti element was detected in fritware ceramic clay but not in clay of terracotta sherds. Also, emission intensity of Ca element in terracotta sherds is higher than in the fritware clay [22, 42].

We used PCA to group the clay structure of archaeological ceramic samples, as shown in Fig. 7. In PCA analysis, all LIBS data were used to clearly visualize the variations in the data. The three most important principal components (PCs) were shown on a 3D score plot. In the PCA graph, the clay samples were identified as terracotta sherds, but these samples were found in different ancient sites (S1, S2 and S3 belong to the Yapılıpınar mound, S4 Taşlı 1 mound, and S5 belongs to Örenşehir settlement).

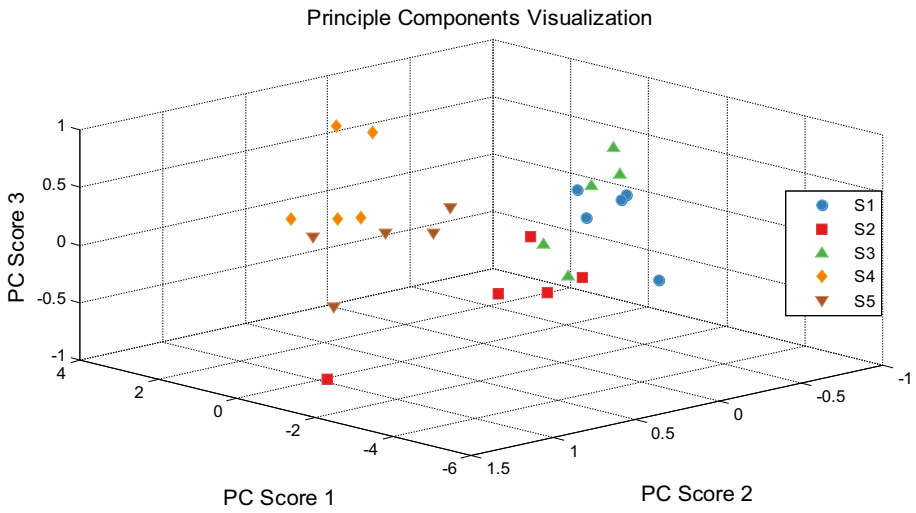


Fig. 7 PCA result of the Yapılıpınar mound, Taşlı 1 mound and Örenşehir ceramic sherds. In the PCA graphic, S1, S2 and S3 belong to Yapılıpınar mound, other ceramics S4 and S5 belong to Taşlı 1 mound and Örenşehir settlement, respectively

Yapılıpınar sherds are clustered separately from the other sherds that belong to Taşlı 1 mound and Örenşehir settlement. Örenşehir ceramics are situated between the clay structure of Yapılıpınar and Taşlı 1 mound ceramic are seen in the PCA card. Result of the analysis highlight the significance of the geological location of Örenşehir settlement. If ever Örenşehir people had produced the ceramics they utilized, then they might have benefited and might have been influenced from workshops of other mounds mentioned above. Yet, there are no archaeologically discovered kilns of the medieval pottery producing workshops in East Plain Cilicia. General consensus in identifying certain types of medieval ceramics, particularly, those of the sgrafitto decorated ware, are to be identified as productions of Port Symeon (Antioch), of Cyprus and or of Zeuxippus (Constantinople). Similar situation is valid for the Islamic ware, for example they are either of Raqqa or of Nishapur [46]. We used the PLS-DA multivariate technique to obtain confusion matrix of materials. In Fig. 8, PLS-DA results show that representative classes are not mixed with one another; and results are obtained with 100 % overall separation. According to PLS-DA analysis, we created a representative model to identify different sample classes. The model is tested by means of spectral data of specific sample classes and is validated to get involved in correct classes of the analysed samples.

4 Conclusions

In this study, we analysed three different aspects of archaeological ceramic samples, glaze, paint, and clay, using the BAKI-LIBS^{TM} system. Ca, Al, Si, Mg, K, V and Na elements are determined in the first layer, glaze, that the elements had been used in archaeological ceramics of both the Islamic and Byzantine eras. Strontium (Sr) element was observed in Islamic transparent glaze but not in Byzantine transparent glaze as seen Fig. 2. At that time, Islamic ceramic manufacturers also preferred the use of Sr in

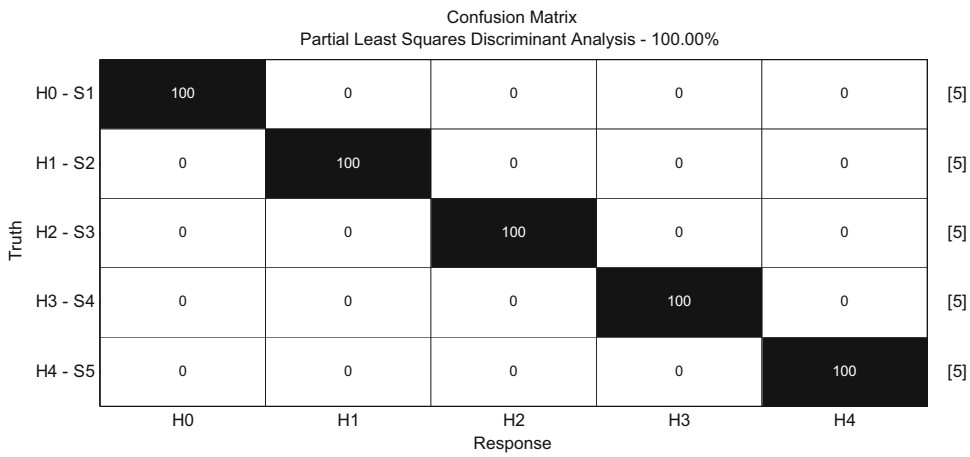


Fig. 8 PLS-DA result of the Yapılıpınar, Taşlıhöyük mounts, and Örenşehir terracotta sherds

transparent glaze structures. In addition, the use of zinc (Zn) in brown-glazed ceramic structure also had been preferable by manufacturers. In that periods vanadium (V) was used as a colourant in the glazes as well as for heat shield and tools coating. Paint layer is built on ceramic, and different elements are used to obtain different colours, e.g. copper for green and iron for brown. We also made a classification of archaeological ceramics belonging to different ancient sites using LIBS measurements according to PCA and PLS-DA results. Yapılıpınar clay ceramic samples are grouped separately from Taşlı 1 mound and Örensehir clay ceramics.

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