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Elemental Analysis Study of Glazes and Ceramic Bodies from Mamluk and Ottoman Periods in Egypt by Laser-Induced Breakdown Spectroscopy (LIBS)

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Abstract

This paper reports on the elemental analysis of archaeological glazed ceramic artifacts, found in Al-Fustat excavation located in Old Cairo. The objects dated back to Mamluk period (1250-1517 AD) and through Ottoman period (1517-1805 AD). The semi-quantitative analysis on the multi-layered ceramic findings regard colored glazes decorations present on the surface and ceramic bodies were carried out by Laser Induced Breakdown Spectroscopy (LIBS). The qualitative elemental analysis results obtained by LIBS were confirmed with other analytical techniques such as Scanning Electron Microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS) and X-ray diffraction (XRD). The obtained results gave indications about the manufacturing process and the raw materials of the ancient ceramics belong the Mamluk and Ottoman periods in Egypt, that help in the conservation process. The analysis demonstrate the potential of the LIBS technique to perform routine, rapid, on-site analysis of archaeological ceramic, which leads to the quick characterization or screening of different types of ancient ceramics objects.

Key words: LIBS; Ceramics Artifacts; Elemental Analysis; Spectra; Plasma; Emission.

Introduction

Modern technology is now playing an increasingly important role in the preservation of culture heritage. Various analytical techniques have been used extensively in study of archaeological and art objects providing important chemical and physical insight to the structure and characterization of objects and materials. For example, polarized light optical microscopy (POM) and scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), atomic absorption spectrometry (AAS), proton induced X-ray emission (PIXE), inductively coupled plasma coupled to optical emission or mass spectroscopy (ICP-OES) and Raman spectroscopy are among the most widely used techniques in analysis, identifying and studying of archaeological materials and conservation. (Smith and Clark, 2004; Dome'nech-Carbo et al., 2008; Iordanidis et al., 2009; Neira et al., 2009; Giussani et al., 2009). However, one concern with most laboratory techniques relates to requirement for special sample preparation and handling procedures (Barclay, 2001). Amongst the most promising candidates are laser techniques. Spectroscopic analysis of ancient artifacts provides historians and archaeologists with useful information to reveal the history of ancient shards, particularly as the process of its production. A great importance is attributed to the determination of the composition of ceramic painted surfaces, with the identification of pigments and binding additives (temper) (Elsayed et al., 2008) such as quartz, rock fragments, powder or fragments of ceramic (grog), straw and shales. These components were added to the clay mainly to provide the paste a higher resistance, to support the temperature changes during firing, to accelerate drying and to reduce excess of plasticity or shrinkage (Arce et al., 2013) The data obtained by LIBS is necessary to date and

restore the ancient pottery, ceramic bodies and glazed coatings (Elsayed et al., 2008) Revealing the technical skills of ancient potters has been the subject of much research since it has been one of the most important issues for gaining a deep insight of bygone culture and also it is required in order to structure the conservation or restoration of a piece of art (Barclay, 2001; Zoppi et al., 2002).

In this context, laser-induced breakdown spectroscopy (LIBS) is a potential alternative to other spectroscopic, mass spectrometric, or X-ray techniques used in art conservation and archaeology related applications. Advantages of LIBS over quantitative techniques for elemental analysis applied on historical findings are mainly due to its low invasiveness comparing to other analytical methods, possibility to perform in-situ measurements, high discrimination, non-destructive (some micrograms of material are ablated with each laser pulse) as well as the fact that there is no need for sample preparation (Barclay, 2001; Muller and Stege, 2003; Brysbaert et al., 2006; Erdem et al., 2008).

LIBS has been used for the analysis of pigments, icons, polychromes, pottery, metals, marble and painted plaster and became a useful analytical tool in art and archaeology (Melessanaki et al., 2003; Lazic et al., 2003; Nikolov et al., 2004; Marco et al., 2005).

In this study, laser-induced breakdown spectroscopy (LIBS) was employed for the elemental characterization of selected ancient ceramic samples dated back to 13-18th centuries (Mamluk and Ottoman periods). These samples were excavated from Al-Fustat archaeological site in old Cairo. The results obtained by LIBS were confirmed by comparing the obtained results with other analytical techniques such as Scanning Electron Microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS) and X-ray diffraction (XRD). Information about ancient Mamluk and Ottoman ceramics technology such as materials composition,

kinds of surface glazes and evaluation of firing conditions and temperatures have been deduced from LIBS technique, which will help in restoration and treatment processes of these objects.

Experimental and samples description

Archaeological ceramic samples

The samples were collected from Al-Fustat excavation in old Cairo, the first capital of Islamic Egypt (641 AD) which continued occupation at least the first century of the Fatimid period (969- 1171 AD) (UNESCO, 2004). The samples belong to Mamluk and Ottoman periods.

Mamluk ceramic samples. The Fatimids were overthrown by the Ayyubids who ruled over Egypt from 1171-1250 AD and they were replaced by the Mamluks from 1250-1517 AD. Mamluk Rule ended when the Ottoman invaded Egypt in 1517 AD and annexed it to the Ottoman Empire. The Egyptian pottery in the Mamluk period may be divided into the following groups: monochrome-glazed wares,

underglaze-painted wares, luster-painted wares, slip-painted wares and blue and white wares (Fehervari, 1998).

The first sample no.1 belongs to so-called underglaze wares with floral decoration with dark blue and turquoise under clear glaze. The body is faience or so-called white frit ware "Stone Paste". This type of clay was used for the production of a new type of Islamic ceramic since the 12th century (Tite and Mason, 1994). Sample no. 2 is a fragment of a blue and white wares and the body is a local imitation of Chinese porcelain where the potter had to hide the local clay body with an opaque white glaze by mixing tin oxide with a lead glaze-covers the earthenware body of these wares at the beginning of 14th century (Atil, 1990; Watson, 2004). The last sample in this group, sample no.3, belongs to slip-painted wares or enameled wares with yellow, dark yellow and brown colors. The body is a red earthenware (Figure 1) shows real pictures of these samples.

Ottoman ceramic sample. The golden age of Ottoman pottery coincided with the apex of the Ottoman Empire and with the region of Sultan Sulayman the Magnificent (1520-1566 AD). The major pottery centre was at Iznik. Red earthenware pottery; the so-called (Miletus) ware was produced for long time before the introduction of its famous faience tiles and vessels (Porter, 1995; Hillenbrand, 1999). Sample no.4 dates back to this period and it is a fragment of blue and white wares and the body of this sample is a faience or white frit ware.

Analytical techniques

Laser experimental set up. The experimental set-up used for LIBS measurements is shown in Figure 2. The output of Q-Switched Nd:YAG laser (Continuum SurlaiteII) operates at its fundamental wavelength (1064 nm) was used to generate the plasma. The laser was running at a repetition rate of 1 Hz. Individual laser pulses

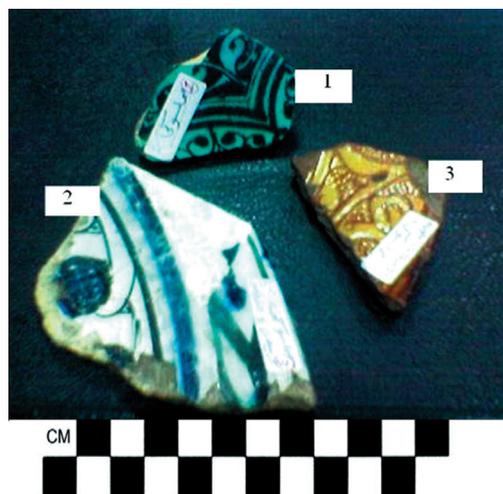


Figure 1. Samples from Mamluk period.

had a pulse length of approximately 10 ns, and pulse energy of 30 mJ. This pulse energy was sufficiently low to minimize the impact of the explosion on the samples. A laser beam delivery system based on the mirror and lens optics was used as shown in Figure 2. The laser beam was focused on the sample surface using a 100-mm focal length lens, producing a crater of approximately 100 μm in diameter. The light emitted from the plasma was collected by a one-meter length wide band fused-silica optical fiber, connected at its other side to a spectral analysis system. This system consisted of an echelle spectrometer (PI - Echelle, Princeton Instruments, USA) with a gateable, intensified

Charge Coupled Device, ICCD, (Princeton Instruments) attached to it. The emission signal was corrected by subtracting the dark signal of the detector through the LIBS software. A gate width of 10000 ns and delay of 1000 ns were chosen for maximizing spectral line intensity while maintaining a good temporal resolution. The gate width and delay time have been selected, after the implementation of an optimized to maximize the ratio of the intensity of the spectral lines to noise. The choice of gate width and delay time for the spectroscopic data acquisition is accomplished by computer-controlled system. Upon these conditions it was possible to observe the produced plasma at

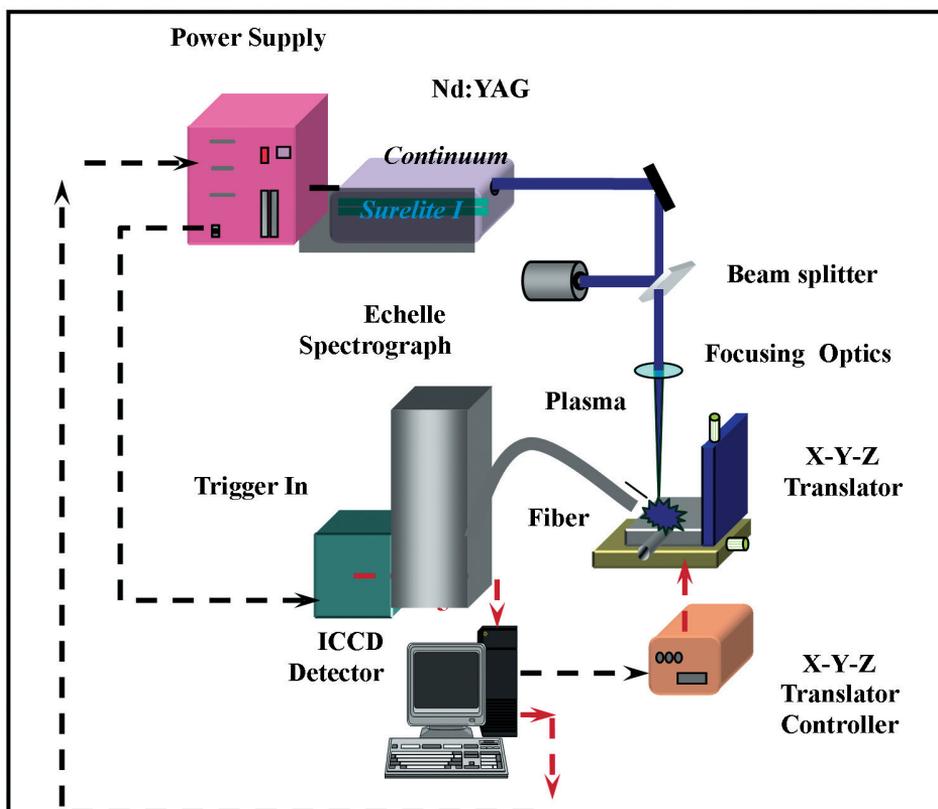


Figure 2. The schematic diagram of the Laser Induced Break-Down Spectroscopy; experimental arrangement used for identification elements of the colored glazes, and ceramic bodies of Mamluk and Ottoman ceramics.

Local Thermal Equilibrium (LTE) necessary for plasma modeling. The analysis of the emission spectra was accomplished using the commercial software (GRAMS/AI v.8.0, Thermo-electron co.). The reproducibility of measurements strongly depends on the experimental conditions. The average energy of laser pulse could be precisely adjusted to maintain a pulse-to-pulse variation of approximately 2%. To improve LIBS precision, spectra from several laser shots have to be averaged in order to reduce statistical error due to laser shot-to-shot fluctuation. The measurements have been taken at five locations on the sample surface in order to avoid problems linked to sample heterogeneity. Fifty laser shots were fired at each location and saved in separated files and the average (average of 250 spectra) was computed and saved to serve as the library spectrum.

X-Ray diffraction analysis (XRD). Mineralogical investigation was carried out through X-ray diffraction analysis, which is an effective tool to identify the mineralogical constituents of the clay bodies samples. Representative powdered samples were studied using X-ray diffractometer (Philips, PW 1840) with Ni-filtered CuK α radiation at operating conditions of 40 kV/30 mA and a scan speed of 2° (2 θ)/min.

Scanning electron microscopy (SEM/EDS). Since the 1970s, scanning electron microscopy (SEM) combined with energy dispersive X-ray microanalysis (EDS) has become widely used for the analysis of archaeological artifacts, including ceramics. This non-destructive examination and analysis of ceramic body fabrics and surface finishes, such as slips and glazes (Schleicher et al., 2008; Mangone et al., 2013). Samples of colored glazes were examined by (SEM/EDS) Philips XL30 ESEM (Environmental Scanning Electron Microscopy) and JEOL JSM-5400 (Low Vacuum).

Results and discussion

Ceramic bodies

LIBS analysis of ceramic bodies. The principal difficulty in the quantitative analysis of LIBS glaze and ceramic body is relevant to sample inhomogeneity, which in the possession of a single pulse is applied. This could be partially overcome by averaging over different analytical lines of the elements acquired in different spectral parts, i.e. sample points. Another analytical difficulty is due to interference of the layer beneath the analyzed one, which might be also ablated by laser. Although the laser pulse energy was kept low, it was noticed that in all LIBS measurements on glaze, it is even more difficult to distinguish the glaze from body because all the major elements of body such as Si, Al, Ca, Mg are also present in the glaze and some ion migration toward glaze occurs also during the ceramic firing. But in LIBS measurement of glaze, a significant amount of Na, K, Pb, and Sn present only in the glaze of some samples was observed in addition to, Cu and Fe. The reproducibility of measurements strongly depends on the experimental conditions. This means that for accurate evaluation of the elements, specifically the plasma parameters has to be kept as constant as possible. By measuring the electron density and plasma temperature on line, the plasma reproducibility can be assessed. For this control and monitoring mechanism the following procedure is easy to follow:

Our analytical procedure of LIBS spectra previously corrected for instrument spectral response is based on the assumption of local thermodynamic equilibrium (LTE) conditions. To verify the LTE, the electron density N_e and electron temperature T_e must first be estimated. The plasma temperature was calculated through Boltzmann plot applied on an element with sufficient number of well defined atomic lines. Measuring the profile of Stark expand atomic emission lines is considered one of the strongest

spectroscopic techniques to determine the density of electrons with a reasonable degree of accuracy. LIBS technique has been demonstrated to be quite useful tool for the investigation of elemental composition of ancient ceramic. It provides non-destructive (micro-destructive) and analysis of both the surface glazes and the ceramic bodies. The optical microscope picture for a glaze surface sample (as an example) shows a laser spot diameter on the surface of about 100 μm diameter as illustrated in Figure 3. A tiny amount of the ablated material from the surface of the body and glaze was noticed that can not be noticed by naked eye.

Three types of Mamluk ceramic objects were analyzed by LIBS technique. Spectra of ceramic bodies of samples no. 1, 2, 3 are shown in Figures 4, 5, 6. As shown from the characteristic emission lines spectrum of bodies samples no. 1, 2, the clay bodies of these samples contain a relatively high ratio of calcium. This indicates that the clay used was calcareous clay while the characteristic emission lines spectrum of body sample no. 3, as shown in Figure 6, indicated that this sample contained higher ratio of iron, this will prove it later. This explains the reddish brown color of this body sample. Body sample no. 4, as illustrated in Figure 7 contains high ratio of silicon, calcium and magnesium.

XRD analysis of ceramic bodies. Mineralogical analysis obtained by X-ray diffraction of ancient ceramic bodies can provides useful information about raw materials and determine the technological processes related to manufacture (Iordanidis et al., 2009). The ceramic samples were analyzed by XRD, in order to map the mineralogical changes of the ceramic material through the firing process (Hein et al., 2007). The presence or absence of specific mineral assemblages is often used for the estimation of the firing temperature of pottery, as each phase is stable within a definite interval of temperature: thus, recognition of a suitable number of phases

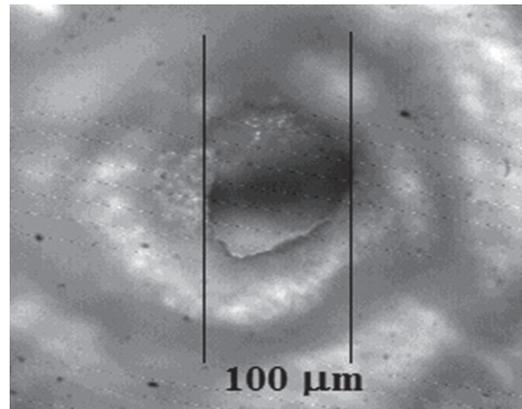


Figure 3. Optical microscope picture of the crater produced by LIBS technique.

may allow one to determine a temperature range encompassing the original firing temperature. However, one should take into account that phase transformations in fired clays may also occur during cooling (Mirti, 1995; Iordanidis et al., 2009).

The elemental analysis obtained from LIBS for ceramic bodies observed a good agreement with Mineralogical analysis obtained from XRD as shown in Table 1. The obtained results by both techniques indicates that silicon oxide /quartz was the predominant mineral and it was observed in all samples. The quartz was added in the form of sand to the original clays as a temper or degreaser component in order to facilitate the mould of the pastes (Arce et al., 2013). Sample no.1 contains quartz as a main component as well as tridymite (SiO_2), wollastonite (CaSiO_3) and diopside [$\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$] as traces, which are beginning to form at 870 °C, 900 °C respectively. Diopside which can be detected from 850 °C indicating that the firing temperature of this sample was between 800-900 °C (Guiraum et al., 1995).

In sample no. 2 calcite was existed as a trace component, that begins to form from at 600-800 °C, and it decomposed completely on firing around 800-850 °C (Rice, 1988; Thierrin,

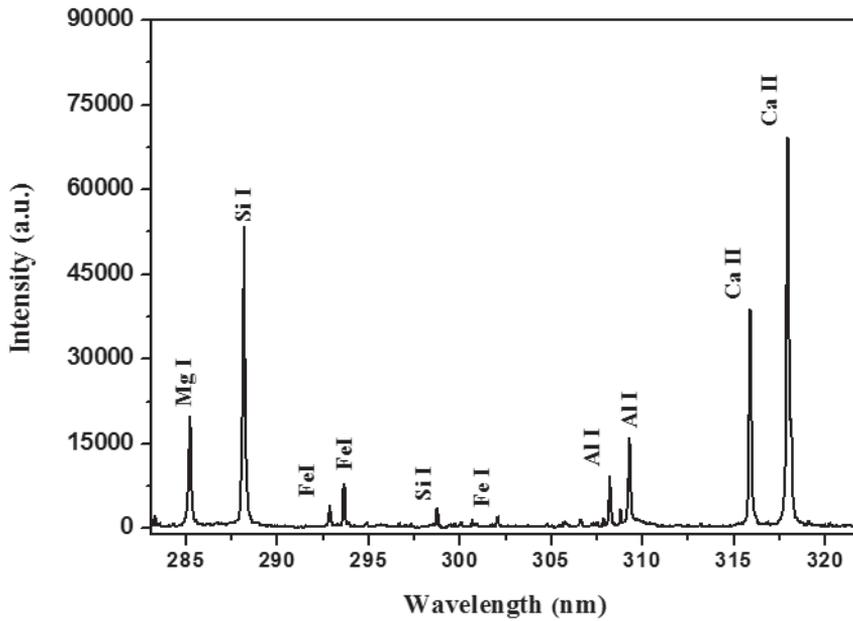


Figure 4. Characteristic spectrum of ceramic body Mamluk sample no. 1.

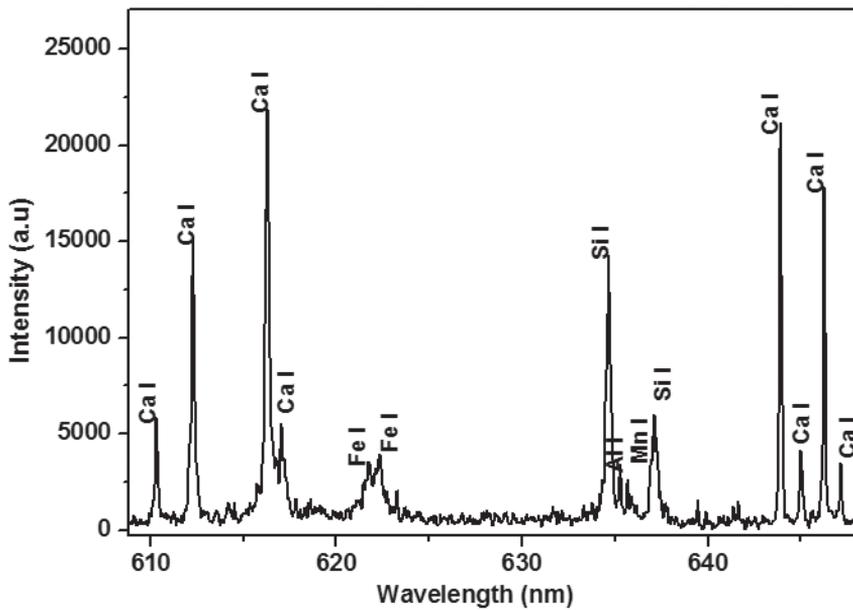


Figure 5. Characteristic spectrum of ceramic body Mamluk sample no. 2.

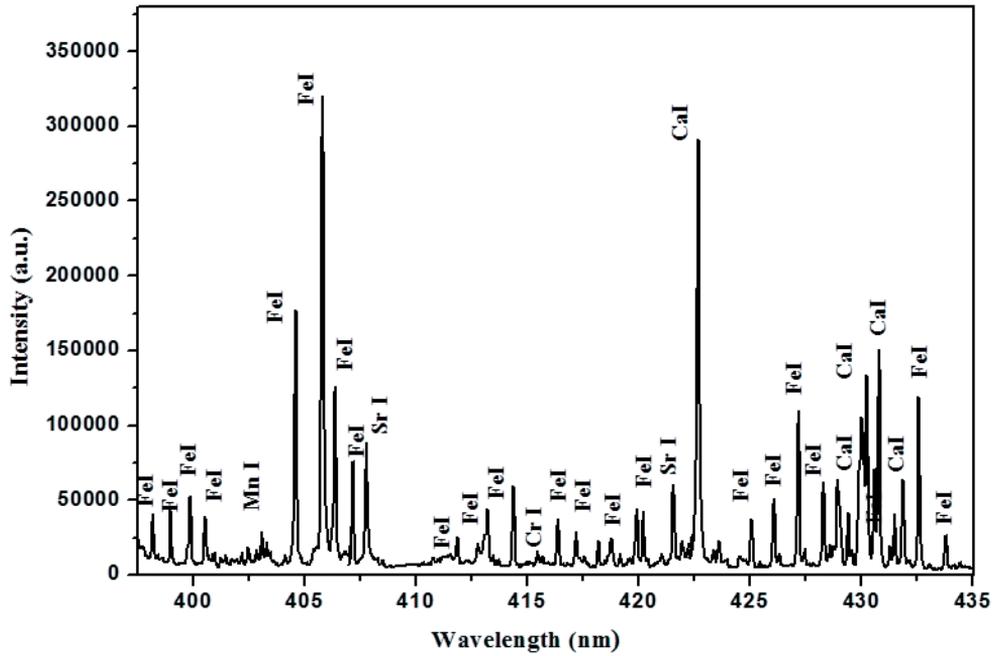


Figure 6. Characteristic spectrum of ceramic body Mamluk sample no. 3.

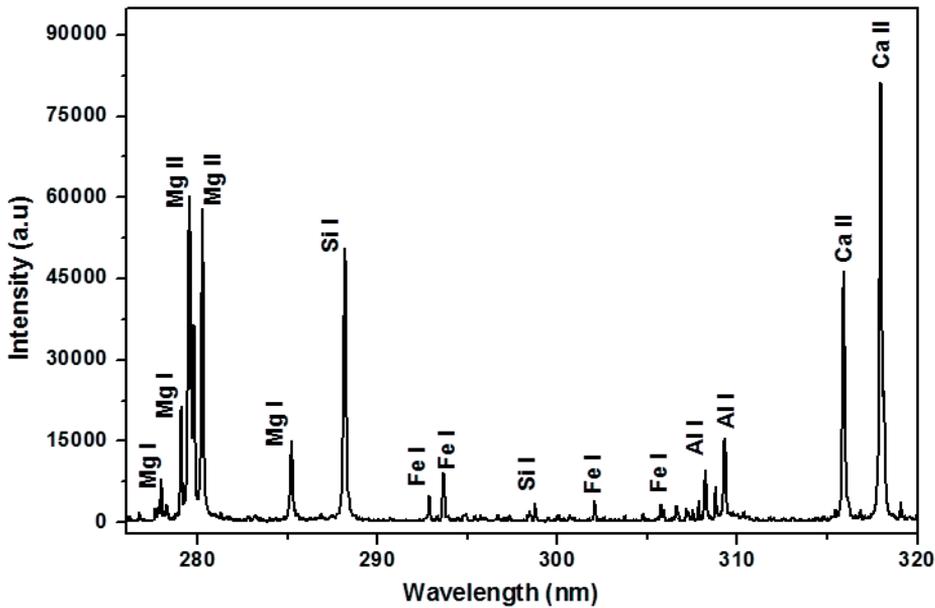


Figure 7. Characteristic spectrum of ceramic body Ottoman sample no. 4.

Table 1. Shows XRD and LIBS analysis results of Mamluk and Ottoman ceramic bodies.

No.	Color of Body	Identified minerals by XRD			Identified elements by LIBS		
		Major	Minor	Traces	Major	traces	
1	White frit	Quartz SiO ₂	-	Tridymite Wollastonite Diopside	SiO ₂ CaSiO ₃ Ca(Mg,Al)(Si,Al) ₂ O ₆	Si, Ca	Mg, Al, Fe
2	Buff	Quartz SiO ₂	-	Calcite	CaCO ₃	Si, Ca,	Fe
3	Red	Quartz SiO ₂	Hematite Fe ₂ O ₃	Wollastonite Diopside	CaSiO ₃ Ca(Mg,Al)(Si,Al) ₂ O ₆	Si, Ca, Fe	Al, Mg
4	White frit	Quartz SiO ₂	-	Dolomite Tridymite Wollastonite Diopside Calcite	CaMg(CO ₃) ₂ SiO ₂ CaSiO ₃ Ca(Mg,Al)(Si,Al) ₂ O ₆ CaCO ₃	Si, Ca	Al, Mg

1995; Cultrone et al., 2001; Tschegg et al., 2008). The existence calcite indicates that the firing temperature was around 800-850 °C and the clay used for manufacture of this object was calcareous clay. The results obtained for sample no. 3, show that hematite was existed as a minor compound, which was formed through firing process between 850-950 °C. Both of wollastonite and diopside were exist as traces. This result gave estimation for the firing temperature that was around 850-950 °C (Thierrin, 1995) and the clay used was iron clay. The XRD results of sample number 3 showed that the body of this sample contained a high ratio of hematite Fe₂O₃ that confirmed the data obtained by LIBS technique as illustrated in Table 1 and Figure 6. Sample no. 4 contains quartz as a major compound and dolomite, tridymite, wollastonite, diopside and calcite as traces compounds. From these results, it was able to estimate the firing temperature of this object that was between 800-900 °C. In Table 1 the data obtained for sample no.4 by XRD was confirmed with spectra obtained in Figure 7 by LIBS.

Colored glazes

LIBS analysis of colored glazes. Glaze is silica based mixture often containing pigment applied on the surface of a ceramic objects and often fire over 1200 °C producing a decorative, impermeable, glassy coating (Lazic et al., 2003). Selected spectra from glaze layer of sample 1 is shown in Figure 8. The characteristic emission lines in this spectra, showed that the glaze of this sample contains silicon, lead, sodium, magnesium and aluminum. This indicated that flux, used in this sample was lead-alkaline glaze which usually used to decrease the firing temperature. The characteristic emission lines of glaze sample no. 3 spectrum, shown in Figure 10 indicated that the flux used in this sample was lead only. In this case lead may be added in the form of red lead oxide, Pb₃O₄ (Al-Hassan and Hill, 1986). The fluxes used in samples no. 2, 4 that contain high ratio of sodium and magnesium, were alkaline fluxes as shown in Figures 9, 11 respectively. The analysis of the LIBS spectra obtained from sample no. 1, showed that the source of turquoise blue glaze in this sample was copper oxide, that used in different Islamic periods to produce this color

in lead-alkaline glaze. As illustrated in Figure 8, this sample contains sodium, magnesium beside lead while analysis of the LIBS spectra obtained from samples number 2, 4 showed that the blue color in these samples was due to mixing copper oxide with alkaline glaze only (sodium and magnesium) as shown in Figures 9, 11. LIBS data indicated that the source of yellow and brown colors in the glaze of sample no.3 was iron oxides as illustrated in Figure 10. These oxides were used in the form of hematite mineral Fe_2O_3 to obtain yellow and brown colors in ancient glazes (Al-Hassan and Hill, 1986).

The results of LIBS measurements showed that samples no. 2, 3 contain Sn which was used in the form of tin oxide SnO_2 as opacifying agent to obtain the opaque white glaze in these samples, Figures 9, 10. Tin oxide was used in the production of Islamic opaque glazes from the ninth century AD, and subsequently in enamels

applied to Islamic and Venetian glasses from the 12th century AD onwards (Downi, 2002; Tite et al., 2008). Tin opacifiers were first introduced in Basra, Iraq in the first of the eighth century AD and were developed later in Iraq and Egypt and subsequently this technology spread to the rest of the Islamic world and also Europe (Mirti, 1995; Mason and Tite, 1997). The results also showed that some bodies and glazes contain alumina Al_2O_3 that was used in glaze recipes for two reasons, the first as a bonding material and the second to prevent the glaze flow off the ceramic through firing process (Downi, 2002).

EDS analysis of colored glazes. The results determined by EDS for sample no. 1 revealed high proportions of silicon and lead with relatively low concentrations of aluminum, calcium, sodium, potassium and iron. Furthermore copper was used for a source of the blue color in this sample. EDS results obtained for samples

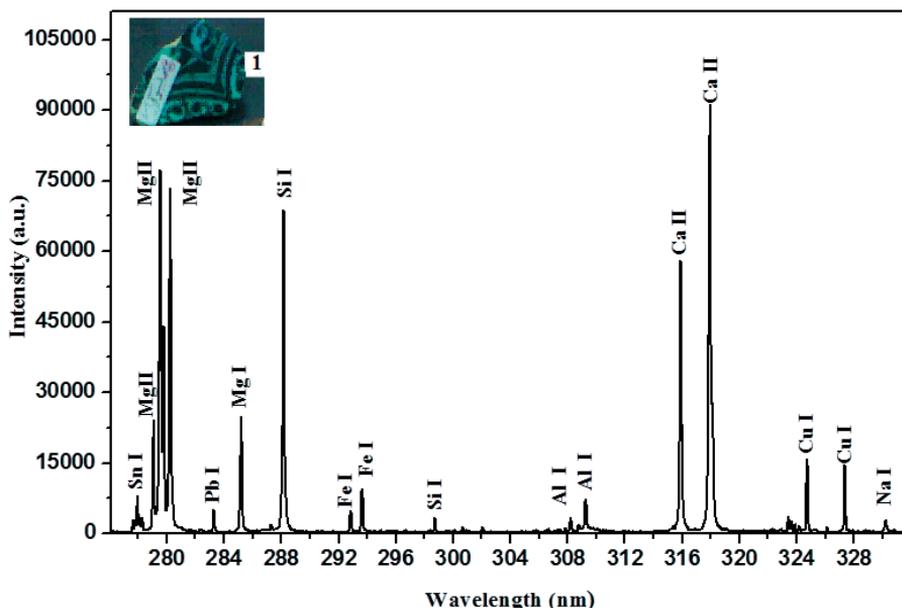


Figure 8. Characteristic spectrum of glaze sample no.1, dark blue and turquoise colors.

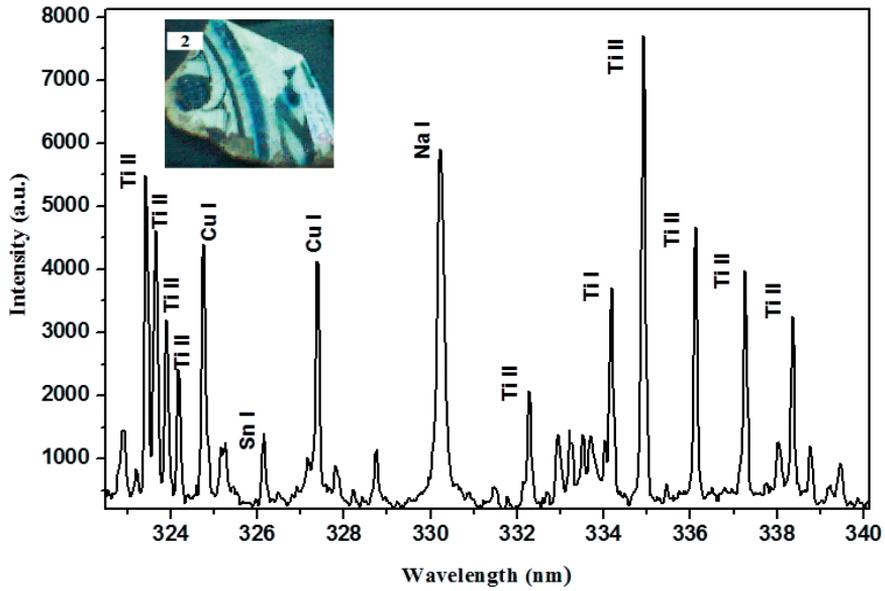


Figure 9. Characteristic spectrum of glaze sample no. 2, blue and white colors.

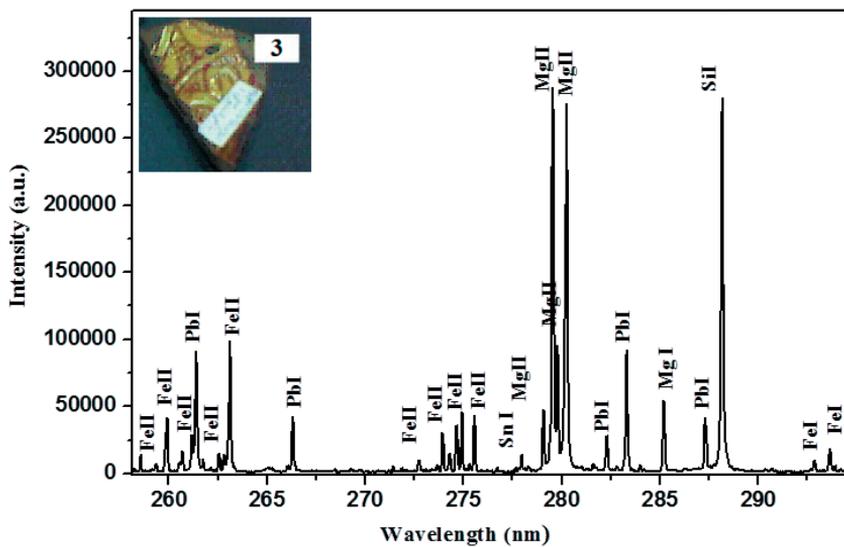


Figure 10. Characteristic spectrum of glaze sample no. 3, yellow and brown colors.

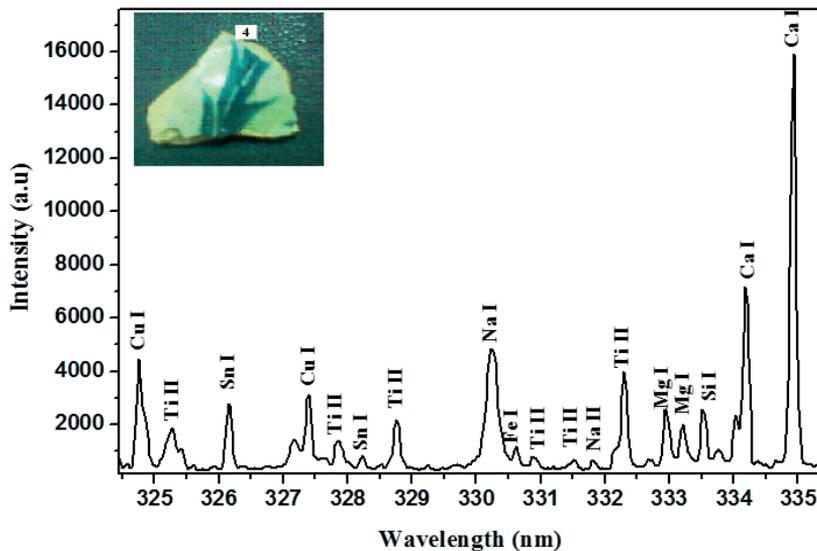


Figure 11. Characteristic spectrum of glaze sample no. 4, blue and white colors.

no. 2 determine high amounts of silicon beside alkalis mainly sodium and potassium which used as fluxes where lead is absent in this sample. Calcium concentration was relatively high in this sample, whereas aluminum, iron and tin present as trace elements. Sample no. 3 contains high percent of silicon, lead beside aluminum, while potassium, calcium and tin present as traces. The source of the yellow and brown colors in this sample was iron. The results of EDS for sample no. 4 showed high percent of silicon, potassium and calcium as well as low proportions of magnesium, aluminum, sodium, titanium and iron. The EDS results are illustrated in Table 2. The elemental analysis results obtained for colored glazes by EDS were in a good agreement with the elemental analysis obtained by LIBS technique.

Conclusions

The elemental composition of both glazes (decorative layers) and bodies of the archaeological ceramic samples were obtained

by LIBS measurements. The obtained results helped to classify the materials used and hence get more information about the ancient technology used for manufacture these samples. The obtained results showed the clays used through Mamluk period were two kinds, the calcareous clay that contains calcium beside quartz as a main component and the other was iron clay (earthen ware clay). The LIBS measurements of colored glazes showed that there were different kinds of fluxes (components which used to reduce the firing temperatures) used through Mamluk and Ottoman periods. Lead flux that indicated by the presence of red lead oxide, Pb_3O_4 and alkaline flux that indicated by the presence of sodium, potassium and magnesium components in the samples. The obtained results showed that the source of yellow and brown colors in glazes refer to presence of iron oxides while the blue and turquoise colors in glazes refer to copper oxides. The results obtained from LIBS were in a good agreement with that obtained from traditional techniques such as XRD and EDS. This study showed that LIBS is a promising

Table 2. Shows EDS analysis results of colored glazed layers of Mamluk and Ottoman ceramics samples.

Sample 4		Sample 3		Sample 2		Sample 1	Element %
Blue	White	Brown	Yellow	Blue	White	Blue	
-	0.36	-	-	8.48	8.37	4.96	Na
0.04	1.26	-	-	3.68	1.88	0.80	Mg
3.09	2.52	3.66	4.39	2.67	1.29	2.58	Al
65.87	64.99	19.67	24.97	64.98	68.19	60.98	Si
0.60	1.56	0.13	1.20	2.09	0.98	0.23	S
15.58	13.63	0.47	1.36	4.97	5.22	3.00	K
-	-	0.54	1.12	2.08	0.56	-	Sn
1.08	0.82	-	-	-	-	-	Ti
8.19	9.53	1.00	1.73	11.05	11.12	2.57	Ca
4.54	3.10	2.64	2.85	-	1.53	1.80	Fe
-	0.77	-	-	-	0.85	3.27	Cu
-	-	71.89	62.38	-	-	19.82	Pb
100	100	100	100	100	100	100	Total

technique allow quick examination of a large number of samples and it could be used in the excavation sites or at museums as compact and user friendly instrumentation could make it powerful tool for the analysis of large variety of materials leading to quick characterization and classification of archeological finds.

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