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MULTI-ANALYTICAL APPROACH FOR THE STUDY OF GLAZED POTTERY FROM AL-FUSTAT, EGYPT

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ABSTRACT

This work presents the archaeometric characterizations of glazed pottery from Al-Fustat by using multi- analytical techniques. Pot sherds investigated by colorimetry, Polarized Light Microscope OLM, XRD and SEM. In the studied samples, quartz added to the pottery body paste. In addition, additive materials commonly added to the raw materials such feldspars, mica, amphibole, pyroxene and calcite. Mineralogical and morphological analysis of the matrix indicate that the firing temperature carried out at 900 °C. Elemental analytical of glaze layer indicate lead glaze was used in the Fatimid glazed pottery. Source of glaze color identified in Fatimid glaze, since Fe used widely in the preparation.

KEYWORDS: archaeometry, firing minerals, polarizing microscope, SEM, vitrification

1. INTRODUCTION

Al-Fustat was built to be the first Islamic capital of Egypt, it established after the conquest of Muslims in 641 A.C. Al-Fustat name comes from the word Fustat, which means tent or pabyilion. Leaders chosen the location because of its obvious advantage, Because of the port facilities and location connect the upper Egypt and east-west routes by land and sea (Raymond et al 2000). On the east bank of the river Nile, south of modern Cairo Al-Fustat grew to form a permanent city out the Arab camp, set up Byzantine fortress of Babylon. The Abbasid governors stayed in the north suburb, Al-Askar, while the Tulunid dynasty built new quarter, Al-Qatai to serve as their capital. Al-Fustat survived after 969 A.C, when nearby Cairo became the capital of Fatimid Egypt. In 1168 A.C the town destroyed by fire to prevent its occupation by Frankish armies. Saladin rebuilt the city few years later and joined it with Cairo, it replaced to Al-Qahirah. The older site, Al-Fustat remained the main production center of ceramic, glass, pottery etc. in Egypt. Glazed pottery comprising of a mixture of natural materials mixed, shape to form desired shape by a variety processes, and transformed by firing to form asolid material resistant to attack by water by water. Glaze is a coating layer on the pottery surfaces, it is formed basically from silica, flux agents such as lead compounds or alkaline or both. Surface treatment applied to the dry pottery before or after the first firing, and later subjected to burning. Coloring agents added to the glaze mixture that gives a homogeneous color to the glaze surface, depending on presence of opacifiers in the glaze it becomes opaque or transparent. Glaze play important role in impermeabilizing the pot's surface (Rice 1987).

During the Islamic period's ceramics produced all over the middle east, however, one of the well-known production center was Al-Fustat (Mason 1990). Researchers take into consideration the investigations of glazed pottery, analysis achieved on key role in solving questions concerning dating and provenance of glazed pottery objects. It provides knowledge about the start raw materials of the body/glaze, manufacture and find out the details of glaze production techniques. From year to year, it observed the increasing role of archaeometric studies in the investigations of archaeological materials (Henderson 200). Various techniques used to identify the chemical compositions of archaeological ceramic from Egypt (Hill et al. 2004).

This work aims to present results of multiple analytical techniques to broaden the information's about glazed pottery technology used by potter's in Al-Fustat production center during Fatimid period. This work focuses on inclusions through the grain's boundaries that may be sharp or overlapping. The potential raw materials used in the pottery body, slips and glaze identified by different physical and chemical techniques.

2. MATERIALS AND ANALYTICAL METHODS

2.1 Samples

Twenty glazed pottery sherds were studied in this work; the fragments belong to the Fatimid period (969- 1169 A.C.), the samples were discovered in Al-Fustat excavations, and stored in Al-Fustat repository. All samples comprise of body coated with a glaze layer. The coating layer charged by colorants to give various colors; white, yellow, green, blue and black, these shards are parts from different type of objects fig.1

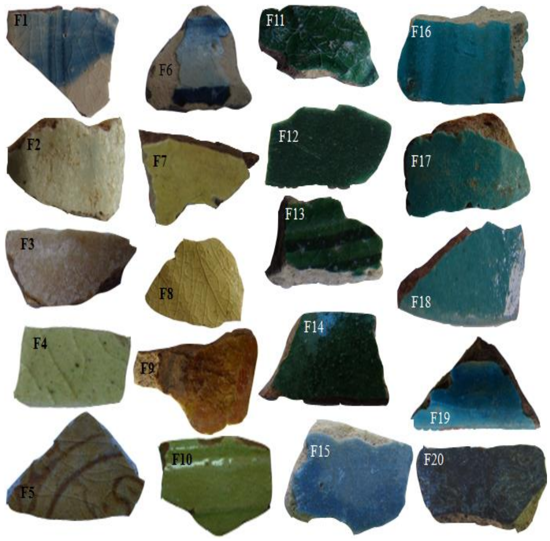

Figure 1. Shows the studied glazed pottery from Al-Fustat, Egypt.

2.2 *Analytical methods*

2.2.1 Color measurement

The colorEye XTH is portable unit with switchable aperture sizes (10mm and 5mm), this provides accurate and flexible measurements of both large and small samples. In the D65 standard illuminant, the observer used for obtaining values for luminance L*, a* and b*. These values derived from the tristimulus values and give visualized ideas of the color changes of the samples surfaces. The colorimeter calibrated prior to each use the calibration carried out to a white paper sheet as standard surfaces. Measurements applied on both pottery body and glaze layer.

2.2.2 Polarizing Light Microscope (PLM)

The polarizing microscope studies the optical properties of the thin sections, it describes the nature of fabrics; size, shape and color of the grains. The pottery body examined by PLM in order to interpretate and compare between fabrics types. Furthermore, identification of the geological sources of raw materials used for ceramic production by investigation of thin-sections. Sectioning of glazed samples is a challenge because cutting and polishing may lead to break and fall down of the glaze layer, precautions taken during preparation of sections. The thin-sections slices prepared by gluing the samples to a slide of glass, thinned by successive polishing to 0.03 mm thickness. The sections studied in both light and crossed polarized transmitted light, the samples prepared and investigated by Optiphot2 Nikon

2.2.3 X-Ray Diffraction

The samples studied by XRD in order to identifies mineral phases and chemical compounds of burnt clay body, crystalline phases identified by XRD in particular for homogenous single phase materials. XRD patterns is set related to the crystalline phases. A particular inclusion can examine apart, identification of specific phases in ceramic that give indication about firing temperature and raw materials used in production of glazed pottery. the sample scraped from ceramic body edges of the sherds. Several milligrams of each sample powdered on average 1-3 µm size sufficient to avoid significant line broadening associated with small particles less than 0.1 µ (Eiland et al 2001). XRD measurements performed by X-ray Diffractometer Siemens D500.

2.2.4 Scanning Electron Microscope (SEM/EDS)

The scanning Electron Microscope is a powerful tool that creates images using Electrons instead of light energy. SEM/EDS describes internal morphology and fabrics by detailed examination of the ceramic body, for defining and/or comparison of proposed fabric types (Barclay 2001). The Environmental Scanning Electron Microscope used in this work Philips XL30 FEG equipped with secondary electron (SE) and back scatter electron (BSE) detectors and EDS. ESEM used to investigate and analysis the glazed pottery.

3. RESULTS AND DISCUSSION

3.1 The body

3.1.1 Colorimeter

For each sample three readings carried out on fresh edges of the samples, the results expressed as L* (lightness), A* (redness) and B*(yellowness) values. The measurements show limited heterogeneity. In addition, presence of light minerals such as calcite and quartz have high value of L* and less A* and B* and converse when the body is black or reddish as result to iron oxides or because the body not well fired.

3.1.2 Polarizing Light Microscope (PLM)

Thin sections investigation under the PLM revealed that all studied potshards texture is non-homogeneous, this appears through roundness and shape of grains in the pottery pastes. Quartz is the main additive in studied sections; it is abundant and comprises about 45 -70 % of the matrix The shape of quartz grains used to determine the sources of sand, most of the grains characterized by its angular and sub-angular edges, thus, supports the hypothesis of grinding sand during the production processes. Traces of potassium feldspars; microcline and orthoclase determined in the samples, this assure adding of small amount of rocks powder to the pottery paste or these minerals are present associated with sand. These minerals usually occur in magmatic and metamorphic rocks which found only in volcanic rocks and form at low temperature fig.2. Isotropy of the matrix observed in the samples point out to uniformity of the firing atmosphere (i.e. oxidizing or reducing). Color pattern showed by a part of shards confirms this hypothesis (Sadek 2012).

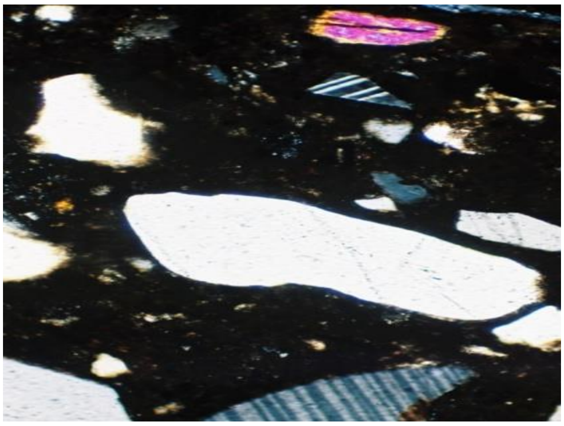

Figure 2. PLM of plagioclase, pyroxene and twinning of the microcline.

Quartz shape is rounded and its size varies from 200 µm to 2 mm. As a result of thermal transformations, quartz grains exposed to intergrowth fig.3. The optical properties of thin-sections suggest that firing temperature carried out at 700 - 800 ºC. Above 850 ºC carbonates decomposes and the clay particles become sintered. The firing temperature of secondary minerals formation affected by firing kiln such as pit or kiln firing but it decomposes around 875 ºC in pit firing conditions (Maritan et al 2006). Secondary calcite observed by PLM inside pores, it occurs in ceramics because of post burial deposition processes due to de-carbonization of ceramic body in humid soil, crystallization of secondary calcite occurred during burial fig.4 (Cultrone 2001). Under the polarizing microscope, the slips appear as a thin layer with variable thickness between 10-40 μm up to a maximum of 100 μm in a sample. The potsherds characterized by presence of one or multiple layers of slips applied underneath the glaze fig.5.

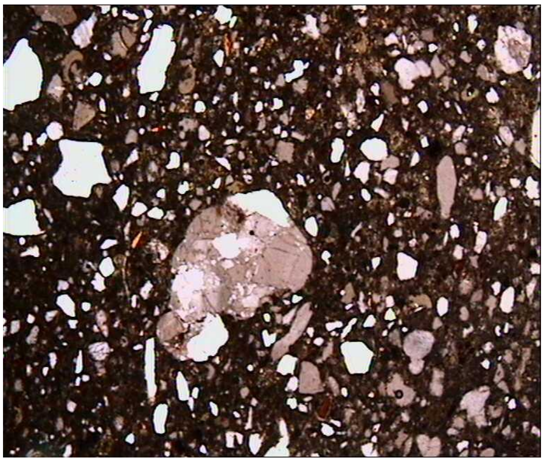

Figure 3. PLM shows simplistic intergrowth of quartz.

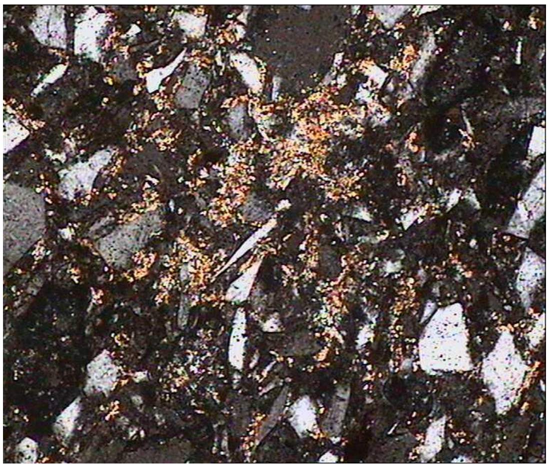

Figure 4. PLM shows presence of secondary calcite.

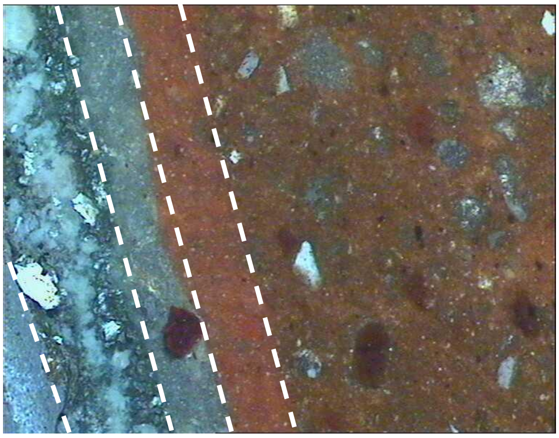

Figure 5. PLM shows multilayers of slips covering ceramic body and slip layer under glaze.

Black parts in the glaze identified by polarizing microscope, may refers to application of the glaze components to unfired body and due to incomplete oxidation of the ceramic body under the glaze (Tite et al 1998). Thus, prevent the oxygen to reach the clay during firing. In addition, formation of air bubbles in the glaze layer, however bubbles appear as result of organic matter burning in the glaze liquid, the gas bubbles can't immigrate towards the surface because the viscosity of the glaze liquid is too viscos fig.6.

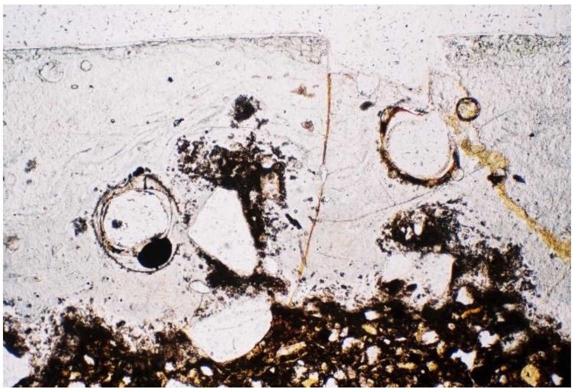

Figure 6. Microscopic image of thin-section shows blackening of glaze layer and air bubbles in the glaze layer.

3.1.3 X-Ray Diffraction

Mineralogy of pottery body depends on the chemistry of starting clay and firing temperature, with additional roles played by firing length and the amount of oxygen in firing atmosphere. New phases observed in the pottery body, in this section analysis common minerals detected in the bodies of studied samples are quartz, feldspar, hematite, biotite, calcite and opaque minerals, these observations confirmed by XRD analysis, quartz was present in all ceramic samples. Using calcareous and non-calcareous clays at the same firing temperature determines the formed phases of numerous Pb-K feldspars, related to the breakdown of illite which make many K^+ ions available for the nucleation and growth of K feldspar (Molera et al 2001). XRD patterns for samples are quartz and identical traces of calcite, feldspars are present; the interesting difference in raw materials shows that a different suite of minerals used for the paste. Gehlenite $Ca_2Al(AlSi)O_7$ occur in XRD spectra suggests a firing temperature above 800 ºC, where the identical minerals phases suggest a firing at a maximum temperature of 850 ºC fig. 7.

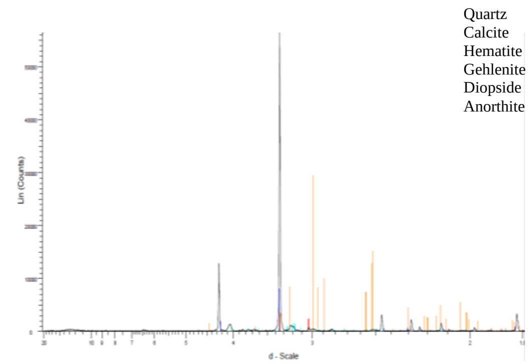

Figure 7. XRDR pattern of ceramic body.

3.1.4 SEM

The visual aspect of SEM backscatter detector provides information's on the boundaries between different areas, decorative or microstructural and highlight areas of chemical compositions variation in glazes and inclusions. Samples registered to analyze the particle size distribution, microstructure and to corroborate the presence of minor phases, whose species are not easy to identify by XRD. Pottery body in the studied samples reveal high amount of quartz fig.8.

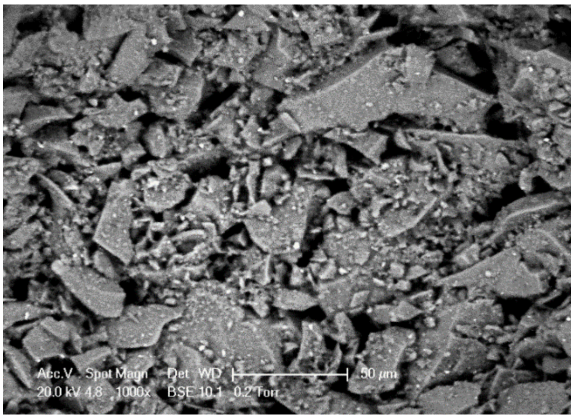

Figure 8. SEM micrograph shows inclusions deformation in the body

3.2 The glaze

3.2.1 Colorimeter

Three measurements carried out to each sample, measurement on glaze show difference in (L*, A* and B*) values. The values are not only indicating the color hue but also the most important function is to indicate deterioration and chemical compositions changes of the glaze layer that can't noticed by eye.

3.2.2 SEM

Scanning Electron microscope used to study the glaze layer, detailed SEM examinations show that the glazes air bubbles that confirmed by thin section investigation in some shards. Glaze thickness layer ranges from 200-300 µm. Air bubbles caused by partial vaporization of the glaze when the firing temperature increase. SEM observations shows intervention zone between glaze and ceramic body that confirms the obtained results from polarizing microscope confirming that glaze compositions applied to unfired body fig.9,and one firing techniques used for preparation of the glazed pottery studied inj this work.

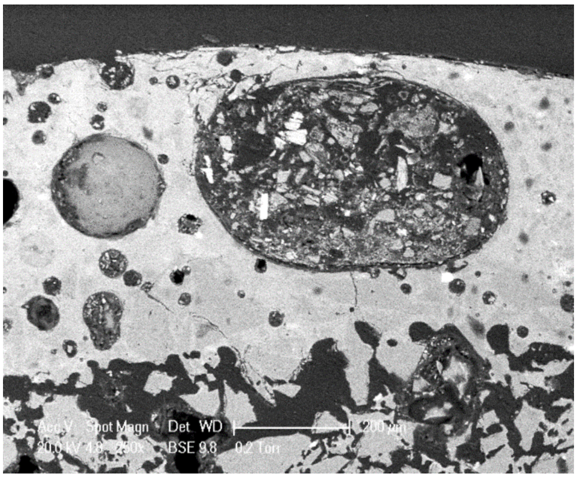

Figure 9. SEM image shows air bubbles in the glaze layer and intervention between glaze and ceramic body.

3.2.3 SEM/EDS

ESEM used to identify the chemical analysis of ceramics, SEM-EDS is the quantitative technique that detect elements down to around 0.5%. SEM provides information about chemical variations in glazes. The chemical analysis of the glazes displays high concentration of SiO_2 between 40-80%. Alumina Al_2O_3 shows variations within the range of 1-10 %. Glazes also contain potassium and sodium corresponding to 1-8% K_2O and 1-12% of Na_2O. Calcium content corresponds to 5-15% CaO. The lead oxide contents of the studied glazes samples vary from 10-50 %. Lead oxides used in the Fatimid glazes which provides elasticity and helps the fit of the glaze (Henderson 2000).

White glaze: Calcium and lead identified in the white glazes, the main components are SiO_2, 30 % of PbO and 5 % of SnO_2. The ratio between the amounts of these elements and other important oxides, such as Na_2O, K_2O and CaO what differentiates the productions. Tin oxide first dissolved in silica and lead matrix, during the firing process of the glaze at 650 ºC, it recrystallized in the cassiterite SnO_2 structure (Molera et al 1999).

Green glaze: the studied samples are lead-alkaline glaze, high ratio of lead used as flux for advantages of application and possibility to get more hues of the same color. Cu and Fe with different concentration levels responsible for the color in green glazes. Using raw materials in different ratios of those two colorants amount potters obtained different hues green glaze, however, oxidation-reduction conditions played important role in the obtained hue, therefore it is very difficult to estimate the raw materials used in green glasses production fig.10.

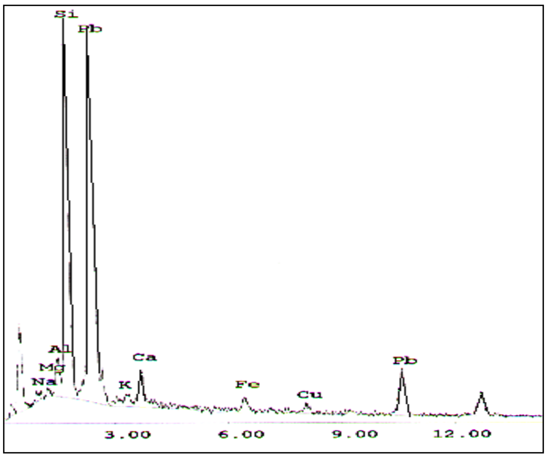

Figure 10. SEM/EDS pattern of green glaze.

Blue glaze: it is one of the most common color in glazed ceramic in Al-Fustat center. Analysis performed on surface in order to identify the blue glaze compositions, it shows the typical elements detected associated with copper (6% of CuO) in the glaze when copper is present in the presence of lead oxide and low alkali (Sadek 2005).

Yellow glaze: differences are noticed in the studied samples, the pigment comes from the same compound, which is a lead- antimony ($Pb_2Sb_2O_7$) composite called Naples yellow. (Sakellariou et al 2004). Another group of samples appear to have higher amount of Fe and Mn, this is a justification for the orange. Some samples contain high amount of Sn and low Sb, thus shows that Sn^{4+} have replaced the ion Sb^{3+} in the lead – antimony compounds, changes in the molecular structure (Rosi et al 2009).

Black glaze: investigated sample estimated as lead-alkaline glaze, however, with varying concentration of Pb and K. Mn found as the main coloring agent, the results presented, Fe play important role in the black coloration.

4. CONCLUSIONS

This work present multi-analytical techniques carried out on glazed pottery from Al-Fustat, that allows to define the production technologies used during the Fatimid period in Al-Fustat center. This study proved that Fatimid glazed ceramics have an intrinsic value that produced. The ceramic body of all Al-Fustat samples shows wheel-throwing and various paste colors, varying from reddish to grey; in some samples, polarizing microscope provides important information about the tempers in the body matrix. PLM also shows that the potters applied multi layers of slips, which consider a unique technique in the Islamic ceramic in Al-Fustat. The micro-structural, chemical and mineralogical evidence, together with the chemical similarity between glaze and ceramic body without lead contribution, suggests that the glaze produced by using of lead compound that acted as a flux, on unfired body and in similar firing conditions. Lead compound causes partial melting of the clay body and chemical diffusion phenomena, as testified silicon, aluminum and sodium are occurring. The glazed ceramic from Al-Fustat defined as high lead-glazed ceramic, due to its content (up to 60% in PbO), the variability of which is related to firing temperature. the body glaze interface, characterized by many micro-sized (< 5mm), the colors of the glaze, variable according to the ratio of colorants and firing atmosphere.

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