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CHARACTERISATION OF LUSTRE COMPOSITIONS FROM EGYPT BY LIBS AND IBA

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Ion Beam Analysis (IBA) and Laser Induced Breakdown Spectroscopy (LIBS) are particularly useful tools for analysis of artworks, systematic characterisation of luster were performed using IBA and LIBS. Spatially resolved elements distribution obtained by area scans in addition to spot analysis provided detailed information about the glaze and luster nano particles, the analytical results and the context of the luster were used to extract information about the luster technology. This work reports the analysis of ceramic samples decorated with luster, these sherds were collected from Al-Fustat site, the samples refers to Fatimid period in Egypt. The study aims to understand the technology of luster in Egypt through non (micro) - destructive techniques via the two different methods.

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1. Introduction

Luster is a nano particle metal-glass composite made of metal copper and /or silver embedded in the glassy matrix (Perez-Arantegui 2001). It gives the surface a particular colored aspect, often metallic in specular reflection and shines including the appearance of gold (Caiger-Smith 1985). The luster technique appears initiated for glazed ceramics at the 9th century in the Mesopotamian area under the abbasid dynasty (750-1055 A.C.) probably in Samara, Susa, Baghdad and Basra (Mason 2004). There were several well-known centres for producing luster-decorated cermic, and possibly glass, during the Islamic history; some of these were Baghdad and Basra in Iraq, Kashan in Persia, and Al-Fustat in Egypt. The first luster appeared in Egypt more precisely was in Al-Fustat where an important production center appeared under the Fatimids (969-1171A.C.) and then the technique diffuses in all Orient (Padeletti 2006).

The luster technique involves a sophisticated and innovative process which entails the reaction of the luster paint with the glaze surface at a relatively low temperature, this reaction results in the introduction of silver and copper ions into the glaze by means of ionic exchange with the alkali ions from the glaze (Kingery 1986). Luster is produced by the application of a raw paint over the glaze followed by a further firing process, the firing temperatures at about 550 °C in a reducing atmosphere this reaction involves an initial ionic exchange of the metal ions from the paint with the alkali ions in the glaze to form metal nano-particle, After cooling the remaining paint is washed off revealing the luster beneath (Pradell et al., 2004, 2005). The luster characterized with its color and transparency of the layers due to the absorption and scattering of light in the layer. A continuous metal layer is transparent for wavelengths below a given value and absorbs most of the light for larger wavelengths. The silver and copper nano particles are transparent for all wavelengths with the exception of the enhanced absorption at the surface. The

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position and width of this depends on the nature and size of the nano particles and the nature of the glassy media, either dissolved in the glassy matrix or forming crystalline compounds, also affects the final color of the luster layer (Padovani et al., 2003, 2004). The optical properties of luster depend on the nanostructures of the silver and copper on the surface, on the nature of the glaze and when applied over pre-existing pigments, on the interaction with the underlying colors (Borgia 2002). Some attempts have been performed to understand the ancient luster coloration but hardly gave a clear correlation between chemical composition and luster color (Robin 2003), and generally made some assumptions regarding nano particles shape, size and luster nanostructure. Hence, the aim of this paper is to establish a basis for understanding copper luster nanostructure linked to its color and characteristic shine and elements distribution up on the glaze surface.

Ion Beam analysis of luster decoration gives access to the distribution of elements in the first layers of the objects. Ion Beam analyses have been performed on sherds having a more or less pronounced metallic aspect with the ion beam impacting on apparently unaltered zones in order to characterize the composition and structural variability of luster decoration. Laser-induced breakdown spectroscopy LIBS is an analytical technique that enables the determination of the elemental composition of materials on the basis of the characteristic atomic fluorescence emitted from micro plasma produced by focusing a high-power laser on or in a material, LIBS requires no removal of sample from the object. Thus LIBS can be regarded as a nearly non-destructive technique and could be easily inserted in a series of investigation and intervention methods with high accuracy (Sava 2002, Radvan 1998) The absence of sampling and sample preparation, in combination with the fact that a single laser pulse measurement is complete in less than a second, offers unparalleled speed to the technique. The technique has the capability of providing depth-profiling information if spectra from successive.

2. Materials and methods

2.1 Samples

Nine fragments of glazed ceramics decorated with luster were chosen for this study, the samples refer to the Fatimid period (358-565 AH / 969 -1169AD) , every sherd has a body thickness less than 7mm with a homogenous yellowish color of the body and very fine texture, The all samples consist of a ceramic body covered with glaze layer; the samples are polychrome luster decorated with typical patterns of golden, brownish, olive lines and circles of luster. The olive green designs are very homogeneous although they do show some amber-brown spots. The samples are sherds originated from one the most important production centre located in Egypt, Al-Fustat (Fig. 1).

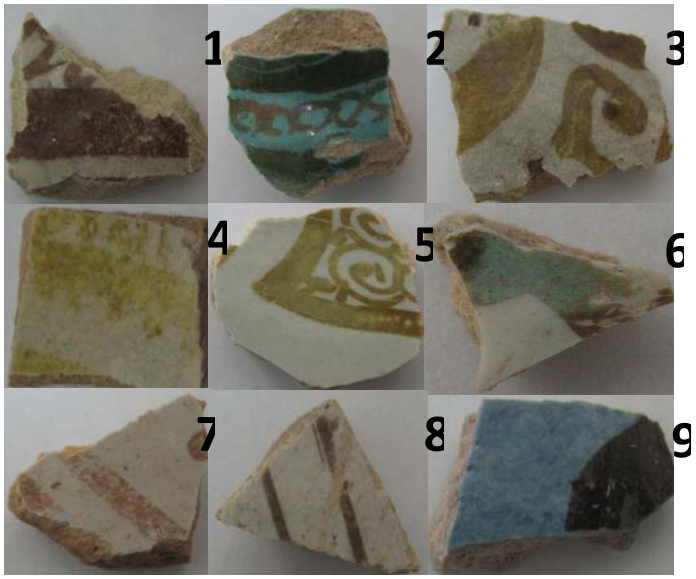

Fig.1. shows the samples glazed ceramic with luster layer from Al-Fustat, Egypt.

2.2 LIBS Setting

Laser Induced Breakdown Spectroscopy (LIBS) consists in atomic emission spectroscopy where a pulsed laser is used as excitation source. LIBS is a micro-destructive technique that can also be applied for stratigraphic investigations. The set-up used for the analyses reported in this paper is transportable [Simileanu 2008, 2011] and currently it is tested as remote controlled method of investigation and diagnosis [Angheluta 2011]. The method's fast acquisition of data allow us to analyze a rather large number of spectra in a short time, therefore LIBS is a very suitable method for the situations where fast results are required in on field conditions. The experimental set-up used in the current investigations is formed from an irradiation system (Q-switched Nd:YAG laser for induced plasma formation on the artwork's surface), an optical collection system and the analysis/interpretation software of the spectral data. The wavelength of the laser used to provoke the plasma formation on the irradiated material surface is 1064 nm. A focusing system with 60 cm focal length is used for the focalization of the laser beam on the investigated surface. The energy of the laser pulse used can be fluctuated from 10 to 300 mJ, which translate to energy density values on the sample surface in the range of 20 – 600 mJ/cm2. The emission is collected by an optical fibre, placed near the plasma plume, and transferred to the spectrograph. Lens systems lead to improved collection efficiency and the transmission through optical fibers assures high flexibility and compact design of the system (Fig.2).

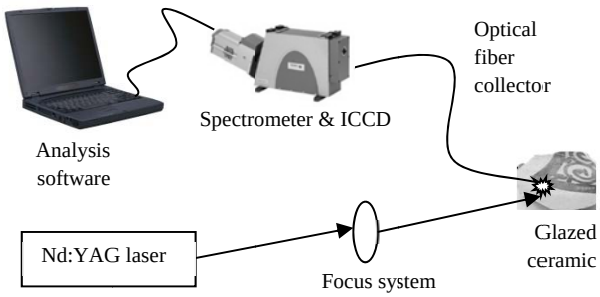

Fig.2 single pulse LIBS setup

2.3 Ion Beam Analysis (IBA)

2.3.1 PIXE

PIXE is one of the most sensitive micro analytical methods [Johansson 1995]. PIXE is non-destructive method used for multi elemental analysis both in vacuum and in air [Neelmeijer 2002], in vacuum mode can be advantageous for detection of low atomic number elements. Broad beam PIXE analysis with 1.0 MeV protons, the beam current was between 5 nA and 20 nA, the measurements were performed at Warsaw – Poland. The samples with different dimensions from 2x3 mm up to 10x10 mm were mounted for analysis - on different positions on the holder perpendicular to the beam direction. The final evaluation of data was performed for the spectrum resulting from subtraction of that taken for outside surace, this procedure made it is possible to perform qualitative analysis of the glaze and the luster layers.

2.3.2 μ-PIXE analysis

The scanning micro beam-PIXE (μ-PIXE) analysis allows identification of elements by taking high resolution elemental maps of the samples by scanning an area of 2 mm square with a narrow beam focused to 1 μm. A proton beam of 3.05 MeV from the 3 MV Tandetron accelerators at Forschungs Zentrum Dresden, Germany was used for μ-PIXE analysis. The analysis was performed in three steps: first the region of interest was selected with an optical microscope

equipped with a CCD camera, next the beam of 5 µm diameter was scanned across the selected area usually 105 X 105 µm to get an elemental map, and finally in the region of maximum abundance of elements typical for a given glaze composition the µ-PIXE spectrum was measured with good statistics (Sadek et al 2012).

3. Results and discussion

A series of analysis in the point mode and area scan were carried out to determine the chemical compositions of the luster and the glaze used as ground of the luster layer.

3.1 Glaze:

The LIBS and IBA results of the all glaze samples indicate that the samples are typical composition of the opacified lead glazes base , that the glaze is composed of lead as flux and the glaze was whitened with particles of tin (Sn) introduced into the glaze materials, with other elements such as aluminium, potassium and calcium. There is an agreement between LIBS and IBA results, however, LIBS can identifies more elements, especially light elements and traces. µ-PIXE can scan samples and more procedures via software's convert the data into maps, which shows the distribution of elements and homogeneity of the glaze compositions that show the mixing and preparation of raw materials were enough. The composition of glaze used is lead-alkaline with high content of lead, with a considerable amount of Tin Sn for opacification, Ca and K (Sadek et al 2012).

3.2 Luster:

The SEM shows the luster homogeneity and distribution of luster metal particles up on the glaze, nevertheless there is missing parts in the luster layer due to deterioration factors, the luster crystals size about 50 - 200nm. The luster metal particle sizes range between 5 nm and 50 nm and forms a layer of varying thickness between 100 nm to 1 µm (Fig.3).

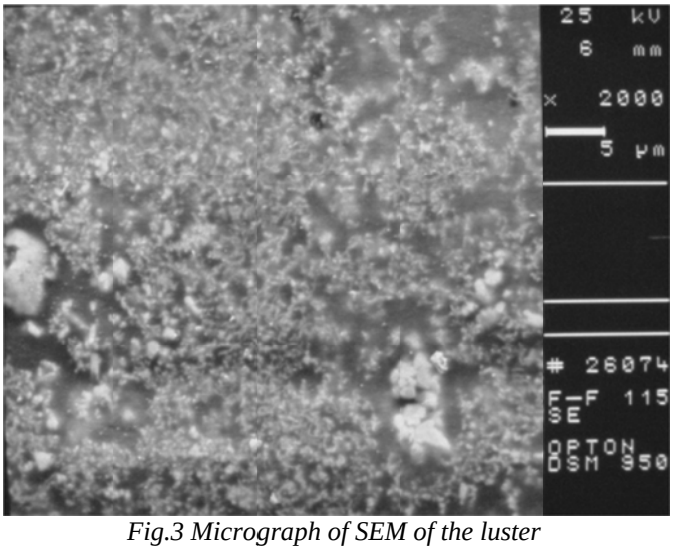

Fig.3 Micrograph of SEM of the luster

3.2.1 Ion beam analysis:

PIXE and µ-PIXE has been performed directly on the luster on the outside surfaces of the samples, the analysis were followed by procedures to get spectra. The IBA results show that silver and copper are present in the all samples golden, reddish and greenish luster. The elemental analysis carried by IBA shows, besides Ag and Cu, other elements of the substrate's opaque glaze

such as Al, Pb, Sn, Al, Fe and Pb, due to penetration of IBA beam through the cracks present in the luster.

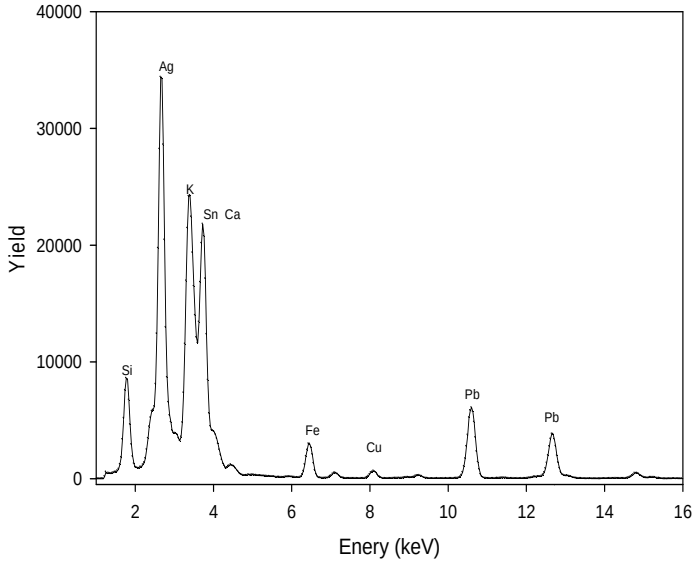

Fig.4 Shows PIXE pattern of Luster.

3.2.2 µ-PIXE mapping of luster

PIXE is relatively inaccurate for light elements (Si, Na, etc.), but well adapted to heavy elements (Cu, Sn, Ag, Pb, etc.). For the mentioned reasons and the advantages of µ-PIXE, it was used for mapping of the luster metal particles. Elemental maps for Ag, Cu, Sn, Pb, K, Si, Ca, Mn and Fe were carried out and the data were converted by RHEIMS software, from data collected. µ-PIXE maps show the distribution of Cu and Ag; it shows a good homogenous distribution of copper but heterogeneity of silver distribution. On the other hand there is an inverse correlation between Ag and Cu as shown in (Fig.5). In the golden luster samples the µ-PIXE shows higher content of Ag on the surface and opposite to that, the greenish luster in general does not have much Cu.

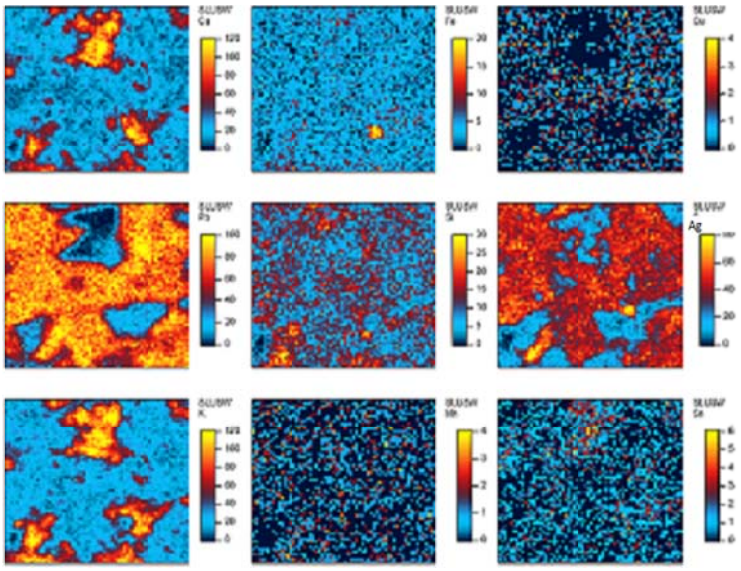

Fig.5 2D elemental distributions measured by µ-PIXE on luster.

3.2.3 LIBS

A series of single pulse of LIBS has been performed in order to identify the chemical compositions of the glaze and the luster. A significant amount of tin and lead were identified by LIBS in the all measured samples, and the compositions indicate that lead-based glaze with K and Sn was used in the preparation of the glaze layer. In the case of the reddish luster both copper and iron were found responsible for the hue of the luster. Cobalt and nickel were present in the blue decoration glaze. The main difficulty of LIBS analysis of luster is the interference of the glaze that could cause confusion in the results; this is why a microscope was used together with the laser beam, in order to select the right position for elements identification.

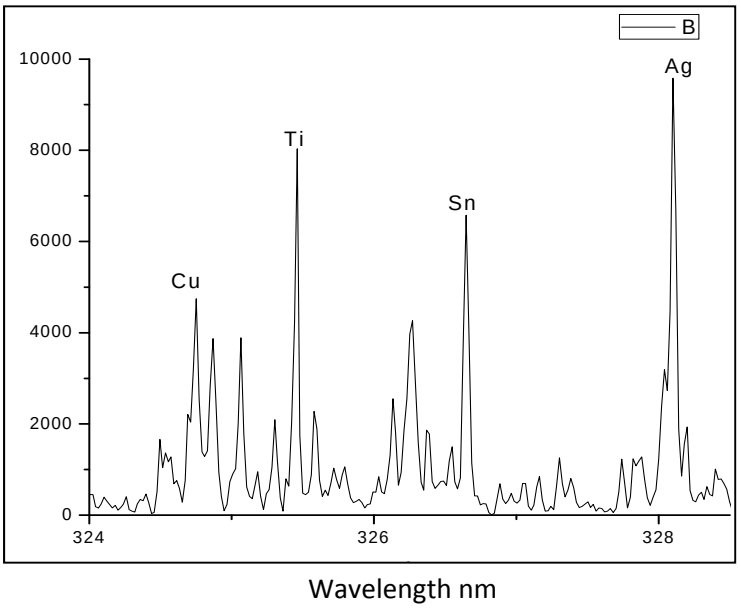

Fig.6 LIBS spectra obtained from golden luster

4. Conclusion

The archaeometric study of the Islamic luster from Egypt using IBA, SEM and LIBS was successfully applied and significant results were obtained from the study of metallic luster decoration, the conclusion could summarize as following:

- The use of copper and silver mixture gave a large variety of colors (in various proportions leads to obtaining different colors or tones for the decoration).
- Silver gives yellow or green luster, and copper gives amber, brown and red luster.
- The greenish luster has a homogeneous color. However under the SEM, silver always appears heterogeneously.
- Golden luster samples are composed of both silver and copper, while red luster generally contains only copper (high concentration of copper).
- The luster particles are very fine that the preparation procedures were good enough.

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