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Identification of porcelain pigments by Laser Induced Breakdown Spectroscopy

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Laser induced breakdown spectroscopy is a valuable method for identification of elemental compositions of solid materials, LIBS has many advantages such as the ability to obtain rapid elemental analysis, possibility to work in situ, non-destructive. For its significance results, LIBS represented as a unique instrument in archaeology, in this article LIBS applied as first analytical method on porcelain from Egypt, for identification of pigments used for decoration, for dating of the studied object.

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1. Introduction

Nowadays, it is important to use optoelectronics to underline the contributions of these technologies make and have made in the field ofarchaeometry and conservation science in obtaining the largest amount of significant information in any way without altering, modifying or compromising the integrity of the objects been studied. Even though this has been a gradual, uninterrupted process it has nonetheless been a fairly slow process, one of the main obstacles has been that most of the available technologies were not developed for use in cultural heritage but were imported from other fields of research. Adaptation to conservation needs has meant new studies, controlled experimentation and necessary modifications [Varoli - Piazza, 2007]. During the 1990s, laser used in art conservation became a well-known alternative for structural and analytical as well as laser cleaning procedures. There was also success in numerous other laser diagnostic applications in the field, such as laser spectroscopic techniques for accurate compositional definition [Castillejo 2003].

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 a micro-plasma produced by focusing a high-power laser on or in a material [Giakoumaki 2008]. The LIBS technique was found to be a capable method to analyze solid samples, to determine their elemental composition and provide their lateral and in-depth analysis. This proved the capacities of LIBS as fast, universal, versatile and multi elemental technique for analysis of ceramics as complex materials and multilayered samples, it is practically non-destructive as well as rapid elemental analysis technique with the critical advantage of being applicable in situ. LIBS, is able to detect all elements and has the ability to provide simultaneous multi-element detection capability with low absolute detection limits. Simple and rapid or real time analysis, the ablation and excitation processes are carried out in a single step; little-to-no sample preparation, which results in increased throughput and reduction of tedious and time-consuming sample digestion and preparation procedures [Mikoláš 2002].

This work is dealing with study of porcelain by Laser Induced breakdown spectroscopy, porcelain is a ceramic material made by heating raw materials, including clay in the form of kaolin in a kiln to temperatures between 1200 °C to 1400 °C. Kaolin is a group minerals are sheet silicates, and they belong to a group of clay minerals, with 1:1 stacking of the unit layer with a chemical composition of $Al_2Si_2O_5(OH)_4$ .The toughness, strength, and translucence of porcelain arise mainly from the formation of glass and Mullite $3Al_2O_8.2SiO_2$ crystals are derived from the solid-state decomposition of the clay component, and are endowed with excellent mechanical, creep, thermal and chemical properties .Within the fired body at these high temperatures the enamels are painted on to already fired porcelain glazes, then matured in an oxidized firing to about 700–800°C (low-fired). A number of coloring pigments used in the porcelain and they differ depending on the elements dissolved in the glaze or by inert pigment particles suspended in the glaze produce color .

Indeed in order to characterize the chemical composition isn't the most important information in material science, it is also the start point for further studies leading to complete and satisfactory results. The main research objectives are to identify the chemical composition of the porcelain pigments in Egypt, before studying the chemical composition by LIBS, the object were first studied by optical microscopy, to locate suitable points for the white paste, colored decorated pigments on exterior surface.

2. Materials

The samples are from Al Manial Museum - Egypt, the studies carried out on flakes of pigments fall down from the object during the transportation of the object during the conservation of the museum building. The studied object is quite modern comparing to ancient Egyptian civilization, however, it is a unique object with its decorations , there is few objects like this in Egyptian museums , second, this type of materials didn't studied before in archaeomteric way. The porcelain object refers to Mohamed Ali Dynasty 1805-1952 A.C, the glaze is opaque, the opacity of the glaze determined by the particles which spread through the glaze, therefore the light is absorbed by the particles, being scattered back before reaching the ceramic body, leading to the opaque glaze, the concentration of the absorbing or scattering particles in the glaze could determine the degree of opacification , upon this glaze was decorated with wide line of turquoise in the middle of the body, there are three birds (sparrow) on the upper part of the object , the bird were painted with red- brown head and yellow body. The gilding outlines the bird and also on the upper part of the piece, as well gilding lines around all the decorated parts of the piece. The object was covered with adhesive (shellac) as result to previous conservation, the adhesive spread on the surface, fig.1.

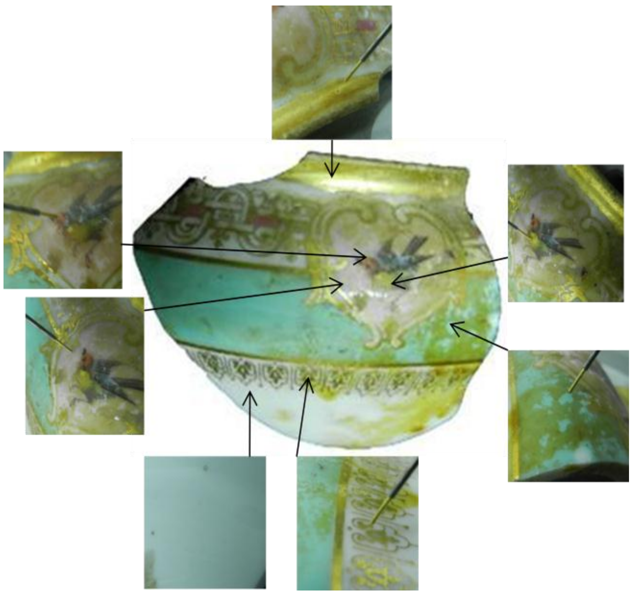

Fig.1 shows the studied sample and analysis points.

3. Experimental set-up

Laser Induced Breakdown Spectroscopy was developed in last decades as one of the very efficient method for material qualitative characterization. One of the most important advantages is the simplicity of the technique and the possibility of fast collection of the data. The set-up is transportable [Simileanu 2008] and in some situation even portable [Simileanu 2011] and most recently it is tested as remote controlled method of investigation and diagnosis [Angheluta 2011].

The method's fast acquisition of data permits the analysis of a relatively large number of objects in a short time. The present paper exploits this aspect because the archaeological excavations ask a large number of investigations over a huge number of artifacts and samples. LIBS is a very suitable method for the necessary fast and simple screening. LIBS is not strictly a non-destructive technique, but it is a very small consumer of material, and time is acting over a very limited area of interaction of the laser pulse with the sample surface.

The experimental set-up includes a Q-switched Nd:YAG laser for induced plasma formation to the artwork's surface, and an optical path for the capture of the plasma emission and analysis/interpretation of the spectral data. The wavelength of the laser used to determine plasma formation on the irradiated material surface is 1064 nm. The emission is collected by an optical objective and transferred to the spectrograph through the optical fibers. The used spectrograph (ANDOR) is based on Echelle gratings, which coupled to two-dimensional CCD type detectors provide wide spectral coverage simultaneously with excellent spectral resolution. A convergent lens of appropriate focal length (60 cm) focuses the laser beam on the investigated surface. The values of the laser pulse energy is adjustable in the range of 10-300 mJ, which translate to energy density values on the sample surface in the range of 20 – 600 mJ/cm^2 .Fig.2 .

The collection of the emitted radiation is done by using an optical collector placed near the plasma plume. Lens systems lead to improved collection efficiency and the transmission through optical fibers assures high flexibility and compact design of the system.

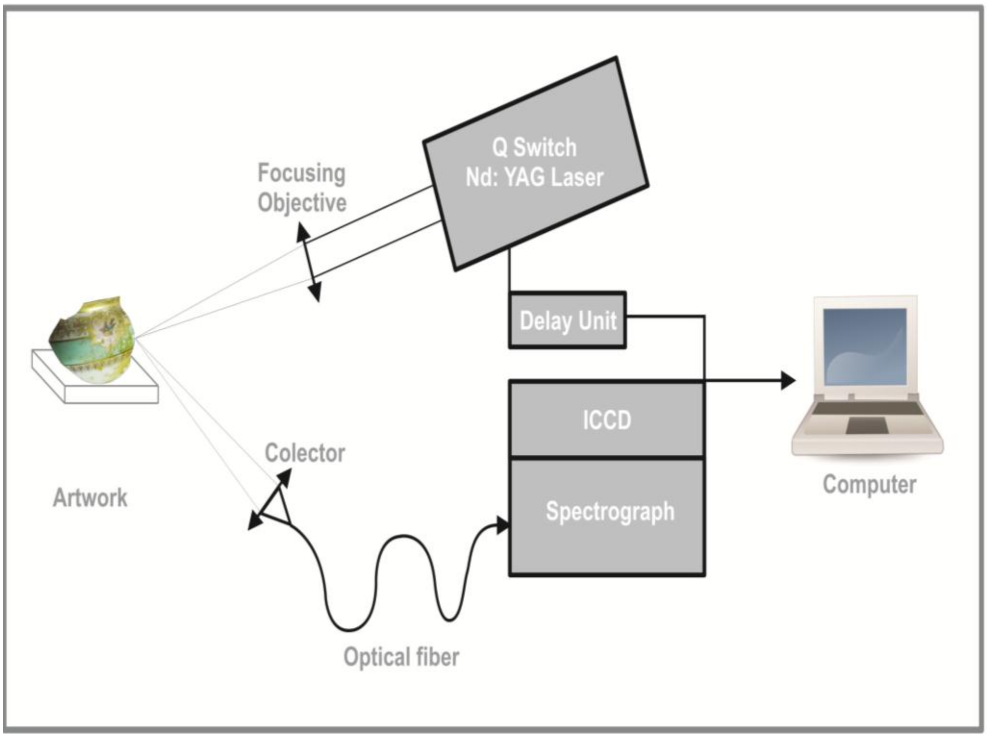

Fig.2. schematic diagram of LIBS.

3. Results and discussion

All examinations were performed on the polychrome surface, before investigation of the object by LIBS points selected on the surface by optical microscopy. Inserted spectra were selected for this article from a series of analysis in various points.

The opaque glaze (white): LIBS results of the opaque surface shows use of lead Pb mixed with alkaline – earth oxides such as Zinc Zn, Magnesium Mg and Calcium Ca as sources for fluxes. The LIBS analysis as well shows opacifiers used to have opaque glaze, from Tin Sn and Titanium Ti, beside these two elements LIBS find out addition of bone ash, which enhance the whiteness and thermal ability of the glaze [Karasu 2002]. The phosphate P obtained by calcinating bone up to approximately 1100°C and then cooling and milling. This material has important properties due to the unique cellular structure of bones that is preserved through calcinations, excellent non-wetting properties; it is chemically inert and free of organic matters and has very high heat transfer resistance. Bone ash has traditionally been added to porcelain to achieve a high degree of translucency. Up to 1-2% bone ash can be used in enamels for opacification (more will usually cause pinholes). In glazes, as with enamels, too much or too high a temperature will cause blistering [Pishch 1997]. Beside opacification materials and fluxes materials, there are oxides identified by LIBS such as Fe, Mn, and Ni, which found as impurities in the clay, Fig.3.

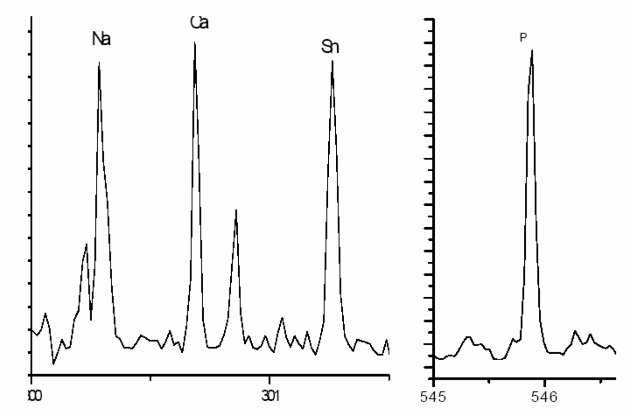

Fig.3 LIBS spectra of opaque glaze compositions.

The gilding: the analysis of gilding decorations includes the analysis of the surface characteristics on the upper part and the body decorations, many spots were investigated and from the optical microscope the gilding classified into two categories depending on the texture of substrate glaze, the first is a wide line on the nozzle of the jar, it characterized by rough texture substrate and deteriorated, second is more smooth and in good condition. The LIBS on both categories shows similar chemical composition, but there are more elements appeared in the first category such as Antimony Sb, Calcium Ca and Zinc Zn and Titanium Ti. This aspect because of the cracks and pores in the gilding as result to the preparation of substrate and the function of the jar, the laser beam penetrate to the substrate glaze, and laser beam can cause abrasion of thin painting to form the plasma.

The thin gilding has rather high and variable gold Au content, most due to the dissolution of gold from the gilding into the Mercury Hg. Artificial gold pigment is known as mosaic gold, it was manufactured to resemble mineral gold; LIBS present in gilding decoration other elements compositions of substrate opaque glaze such as Al, Pb Sn ,Al, Fe and Pb. Fig. 4.

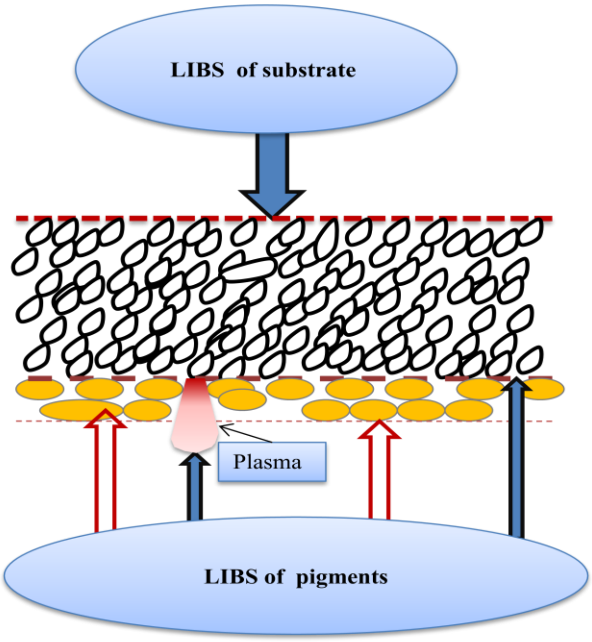

Fig.4 penetrate of laser beam to substrate glaze.

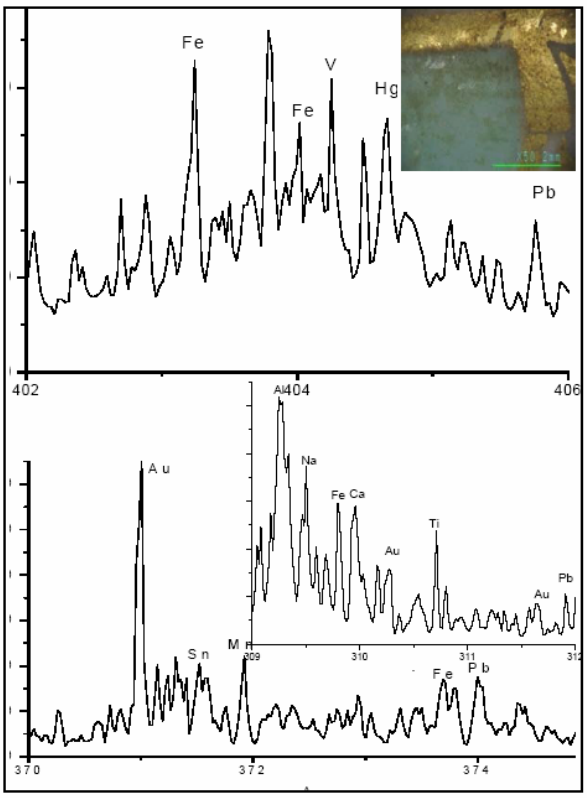

Fig.5 LIBS emission spectra of gilding compositions.

Smooth surfaces of porcelain improved for bonding by roughening with abrasives such as medium-grit emery paper. Abrasion always followed by degreasing to remove contaminants and loose particles, Fig. 5.

The red pigments: the red pigments used in various selected points on the surface of the glaze, rose as back ground of the bird, and some parts of the sparrow body and other oblongs with the gilding decorations. The LIBS analysis for the red pigments presented glaze compositions and fluxes oxides (Si, Al, Pb, Na, Mg,) as result of laser penetration. LIBS analysis shows the red pigments sources in the studied porcelain from the Cadmium Cd, Mercury Hg, Sulphide S, they called cadmium cinnabar, and they are produced by initially co-precipitating Cadmium Cd and mercury sulfides HgS in solution. The mixture is then calcined in an inert atmosphere, a process that converts the cubic crystal structure to a hexagonal one. [Eastaugh 2004]. The Cadmium oxide by itself does not produce color in a glaze, but when used in combination with selenium it gives red. LIBS analysis shows Selenium Se with Cadmium mixture first commercialized at 1910 A.C. Vanadium V also considered as source for red pigments in porcelains and in ancient civilizations, Its color in generally weak, but can be strengthened when fritted with Tin and Zirconia. Chrome-tin pinks are stronger if some tin oxide opacifier is used. Titania-based pigments used in enamels require Titania opacifiers [Eppler 2000]. The difference in rose back ground of the bird is it has more whiting elemnts such as Antimony Sb, and calcium Ca, and the intensity of red color peak is less than in the sparrow head. In all teseted points gold Au found as traces , but the authors are not sure, if the Au found as impureties in the red pigment or intended added to the mixture ,more researches need to be done in the future up on trace elements Fig.6.

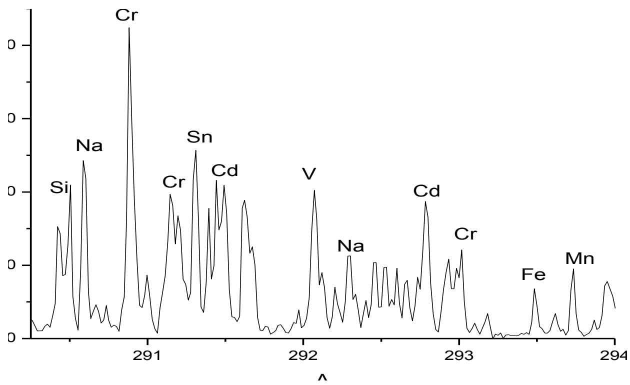

Fig.6. LIBS graph of read pigments.

The turquoise: Up on the body characterized as turquoise green, the analysis results by LIBS shows the following elements Cr, Al, Co which forming a chromium aluminum and cobalt oxide, the color is made by calcining a mixture of Cobalt $CoCO_3$ carbonate aluminum hydrate and chrome oxide, Cobalt is a powerful colorant and as little as 0.02% CoO produces a noticeable tint in a transparent glaze. Copper Cu one of the strongest coloring elements**,** was one of the earliest colorants of glaze in early Egyptian faience. Copper compounds are very soluble in all type of glaze and frit. Copper Cu is an active flux in glaze which reduces the firing range of any composition to which it is added.

The Sparrow body lemon yellow to greenish color, the LIBS identifies the opacifiers Sn and Ti, as mentioned before for the result of laser beam penetration. Strontium Sr, chrome Cr , Strontium yellow ($SrCrO_4$) identified as source of the yellow pigments, in addition to Pb and Sb forming Lead antimonate yellow which is also known as Naples yellow, the composition of the principal form of lead antimony oxide given as $Pb_2Sb_2O_7$,Yellow of Antimony holds the middle place between chrome yellow and Naples yellow.

4. Conclusions

LIBS used in analysis in different fields and especially in archaeology. The results presented in this paper demonstrate the advantages of LIBS analysis in obtaining elemental analysis information about the materials used for decorating the porcelain in Egypt. One of the important aspects of LIBS is the speed of analysis, that allow quick examination of large number of samples in situ, this is the first archaeometric study on porcelain Egypt .The obtained results from LIBS analysis for porcelain from Egypt, it shows using mixture of pigments for paint, From the microscopic studies shows the preparation of the surface before gilding to give better adhesion. One of the most interest results in this paper is red pigments that used for some part in the bird and different places on the surface show Cadmium and Cd and selenium Se, didn't used before 1910 which indication to dating of the object for the first half of 20^{th} century . The results show that LIBS is very valuable methods not only as archaeomtric tool but also as it helps in dating of the studied jar. More researches are required to apply on huge number of porcelain in Egypt for study of more pigments and study of trace elements.

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