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Investigation of Historical Egyptian Textile using Laser-Induced Breakdown Spectroscopy (LIBS) - a case study

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ABSTRACT

This paper evaluates the use of Laser Induced Breakdown Spectroscopy (LIBS) for the analysis of Egyptian historical textiles. The chemical information provided by LIBS, as well as the detrimental effects of laser-induced damages were studied as a function of laser energy and the number of laser pulses used for analysis. The main elements in the metal fibers were Cu, Au, Ag, Cr, Mn, Zn and Ca. The results obtained through LIBS were confirmed by Scanning Electron Microscopy coupled to Energy-dispersive X-ray spectroscopy (SEM-EDX). The damage of the metal threads after LIBS application was monitored by SEM and Optical Microscopy. The textile samples used were obtained from the museum of the Faculty of Applied Arts, Helwan University, Egypt.

Keywords: Textiles, Metal fiber, Historical, LIBS, SEM-EDX, Elementals.

1. Introduction

Textiles are a part of our daily life now as much as they were in the past. From very early times, textiles created by humans have been used in clothing, not only for warm, but also as a means of demonstrating social status and signifying personal individuality. Decorative metals have been incorporated into textiles for thousands of years (Balazsy and Eastop, 1998; Hache et al, 2000). Embroideries were one of the most sumptuous kinds of textiles produced in sixteenth- century Europe, and among these costly goods, gold embroideries were the most precious. Metal threads deteriorate over time and corrode due to chemical attack by different corrosive factors such as high and fluctuating relative humidity, air pollutants and elevated temperatures (Balazsy and Eastop, 1998; Boeck et al, 1987; Landi, 1992).

The comprehensive study of archaeological or historical artifacts and works of art, that are essential components of our history and cultural heritage, often requires an in-depth knowledge of their macroscopic and microscopic structure. This can best be achieved by means of various physical and chemical analysis techniques (Beilby, 1992).

Laser-Induced Breakdown Spectroscopy (LIBS) is a rapid elemental analysis technique, attracting the attention of the archaeologist and conservators. A typical LIBS system includes a laser, focusing optics to concentrate the laser intensity onto the sample and create plasma, collection optics coupled to a spectrometer (and detector) to collect the plasma emission and record spectra. This apparatus is generally easy to use, so operating a LIBS system doesn’t require much specialized personnel training. The main advantage in LIBS is the fact that the sampling and excitation steps can be done with only one laser pulse, making easier the analysis of the sample compared to other techniques. It is a rapid analysis technique that solid samples can be analyzed directly with little preparation before analysis, so LIBS shortens the full analysis cycle compared to most other analysis techniques and can even be used in situ. This latter ability is a distinct advantage over other comparable techniques for identifying atomic content. Indeed, in the recent literature, several examples of the use of LIBS in the analysis of pigments in easel paintings, icons, and wood polychromes have been reported, demonstrating the prospects of the technique for becoming a useful analytical tool in art and archaeology (Anglos et al, 1997; Melessanaki et al, 2002; Brysbaert et al, 2006; Burgio et al, 2000; Galbacs et al, 2011).

The current research project focuses on the use of LIBS in the field of historical textiles conservation, especially the; investigation of metal threads embedded in antique samples. The chemical information was studied as a function of laser energy and irradiation regime and the number of laser shots used for the analysis. In parallel, the laser induced damages during the analysis was measured.

2. Experimental

2.1. Experimental approach

A Q-switched Nd:YAG laser (Brilliant, Quantel) operating at its second harmonic wavelength (532 nm) at 10 Hz repetition rate with a 5 ns pulse duration FWHM was used in this study. The light emitted from the plasma plume was collimated by a lens (25 mm diameter with focal length 38 mm) and then focused into a UV transmitting optical fiber by a second lens (25 mm in diameter with focal length 60mm). The spectrometer (Acton 2300i Acton 2300i, Princeton Instruments) was equipped with an ICCD camera (PI-MAX2, Princeton Instruments) providing a pixel resolution up to 0.04 nm/pixel. 25 spectra (each covering a spectral range of approximately 15 nm) were taken and spliced into final spectrum extending the spectral analysis from 300 nm to 650 nm. Each individual spectrum was the result of 5 laser shots. Single shot spectra were also used to study the sample damages. Ten locations were analyzed as a representative population of the sample. All the experiments were performed at atmospheric pressure in air.

2.2. Investigation methods

The morphology of the surface of metal threads was investigated before and after LIBS analysis. Furthermore elementals composition was confirmed of the metal fibers by Scanning Electron Microscope (SEM) with energy-dispersive X-ray analyzer (EDX) –ULTRA 55, ZEISS). The morphology of the surface of the metal fibers was investigated using an optical microscope (BX51, Olympus).

2.3. The Samples used in this study

Two samples were used in the present analysis. The first sample (sample # 1) was a small piece (around 2 x 2 cm) from the textile shown in cases no 121/5 in the museum of the Faculty of Applied Arts, Helwan University, Egypt. The full piece measures 86×86 cm. It contains many decorations such as plants (flowers and leafs) and animals (Flying birds). It also contains different types of fibers such as metal threads with a golden color and silk fibers that are red in color. See Fig. 1- A. The second sample (sample #2) is composed of metal threads from historical object in museum of the Faculty of Applied Art.as shown in Fig. 2-A. Piece is a curtain decorated with metal threads. The main color in object is a red color. The object is now in storage case in the museum.

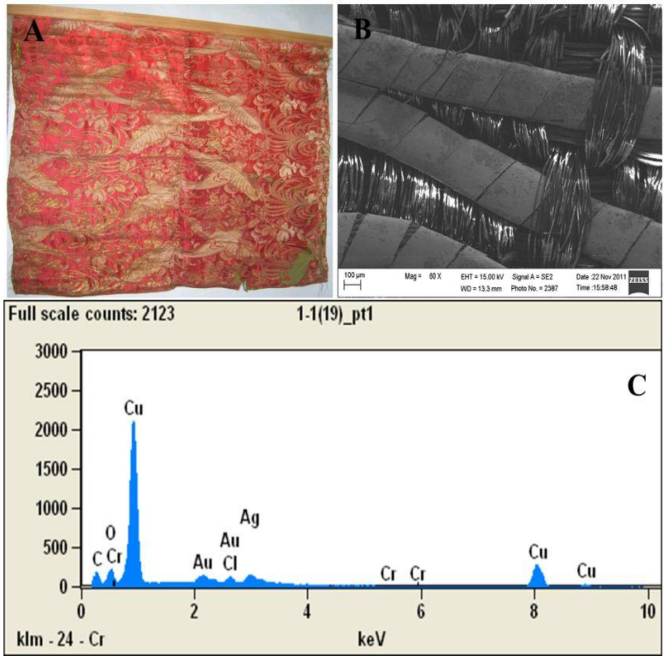

Fig (1) Photo of the first sample showing the colours, decorations, metal thread and silk fibres (A) SEM image of this sample, one can see metal threads included in the woven structure of the object (B) Elemental micro-analysis of this sample by using EDX (C)

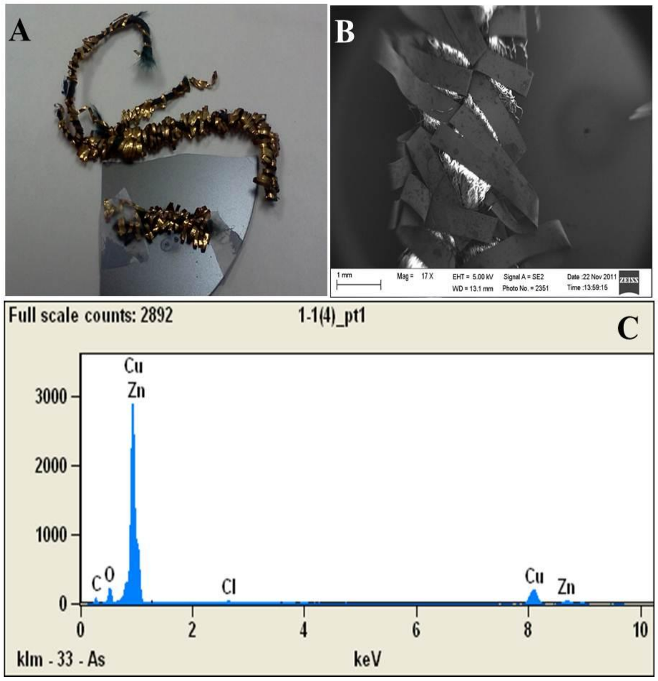

Fig (2) Photo of sample no#2 (A). SEM image of this sample, one can see metal threads included in the woven structure of the object (B) Elemental micro-analysis of this sample by using EDX (C).

3. Results and discussion

3.1. Investigation by SEM-EDX

The investigation of the metal thread surface using Scanning Electron Microscopy (SEM) shows that all the metal thread is the typical structure of historical metal threads, which consists of metal strips wound around a fibrous core of cotton fiber. The twisting direction of the strip wound around the fiber core is anticlockwise, that is a ‘Z’ twist. Furthermore, SEM images show that there is a slight corrosion layer on the surface of the metal strips as shown in Fig. 1-B and Fig. 2-B. Four different positions from the metals threads were investigated by using EDX in order to study the reproducibility of the results. Fig. 1-C shows the results of EDX analysis of the tested metal thread sample. The results show that the metal threads in sample one were manufactured from different type of elements such as copper (Cu), silver (Ag) and gold (Au). The results show that the main components of the sample are copper (Cu) average 73%, silver (Ag) average 8%, gold (Au) average 5% and (Cl) average 2%. Also results show Carbon (C) and Oxygen (O). The EDX results of sample #2 are shown in Figure. 2- C the main components of the samples are copper (Cu) with average around 65% and Zinc (Zn) with average around 25% (Cl) average 1.5%. Also results show Carbon (C) and Oxygen (O). The EDX results of different positions of metal threads show that the sample is heterogeneous, the different ratios for the concentrations of the main elements are found, different studies were found the same results of the ancient metal threads and metal decorations (Karatzani, 2008; Rezic et al, 2010; Nord et al, 2000; Enguita et al, 2002; Hacke et al, 2004).

3.2. Investigation by LIBS

A summary of the LIBS spectra from the metal threads analyzed are shown in Fig.3 while Table 1 displays the emission lines used for identifying elements in LIBS spectra and obtained from the NIST atomic database. The results from LIBS spectra of sample # 1 are in agreement with the results obtained by EDX analysis. The LIBS spectra show that the main elements of the metal thread are Copper (Cu), Silver (Ag), Gold (Au). In addition some elements such as Aluminum (Al), Magnesium (Mg), Calcium (Ca), and Sodium (Na) were also found in the metal threads of sample # 1. The study suggests that the metal threads are Cu-Ag-Au alloy, while other elements (Al, Mg, Ca, and Na) are probably corrosion and contemned components due to sample handling and interaction with environment. These elements are actually highly concentrated in soils and a surface contamination of the textile sample, including the metal threads, is probable. On the other hand, LIBS Spectra of sample #2 also is agreement with the obtained results of the same metal threads by EDX. The main elements of this second samples were Copper and Zinc. There were other elements such as Calcium (Ca) and Sodium (Na), these results were in good agreement with that obtained by different studies (Giakoumaki et al, 2007; Melessanaki et al, 2002; Osticioli et al, 2009)

By this finding, it is clear that all the tested samples are covered with layer of corrosion and dirt products. These results are agreement and confirmed by investigation of test samples by using SEM. The contamination elements are probably from corrosion products, dust and dirt on the surface of metal threads. This finding refers to the museum environments (the higher pollution and the incorrect conditions surrounding the object) and uncontrolled display and storage of these objects. Investigation of metal threads by LIBS show very important results that the contamination elements are more in the first shot while the main component elements are high in the second up to the fifth shots. This confirms that these elements come from contaminants in that they are primarily on the surface of the samples.

The results show that there are calcium in all the tested samples this is probably due to result of environmental pollution deposits and corrosion. This hypothesis is confirmed by the presence in the spectrum of the CN group molecular band at 382–388 nm, the carbon coming from the sample and nitrogen from the atmosphere, these results are similar to the results of [16]. They indicate that LIBS analysis can quickly provide qualitative information on the elementals content of metal threads and aid their characterization. The compromise between the sensitivity of LIBS and the microscopic damage caused by laser ablation was studied by varying the number of accumulated laser shots (5,10,80) as well as the energy of the laser pulses (10, 20, 30 mJ).

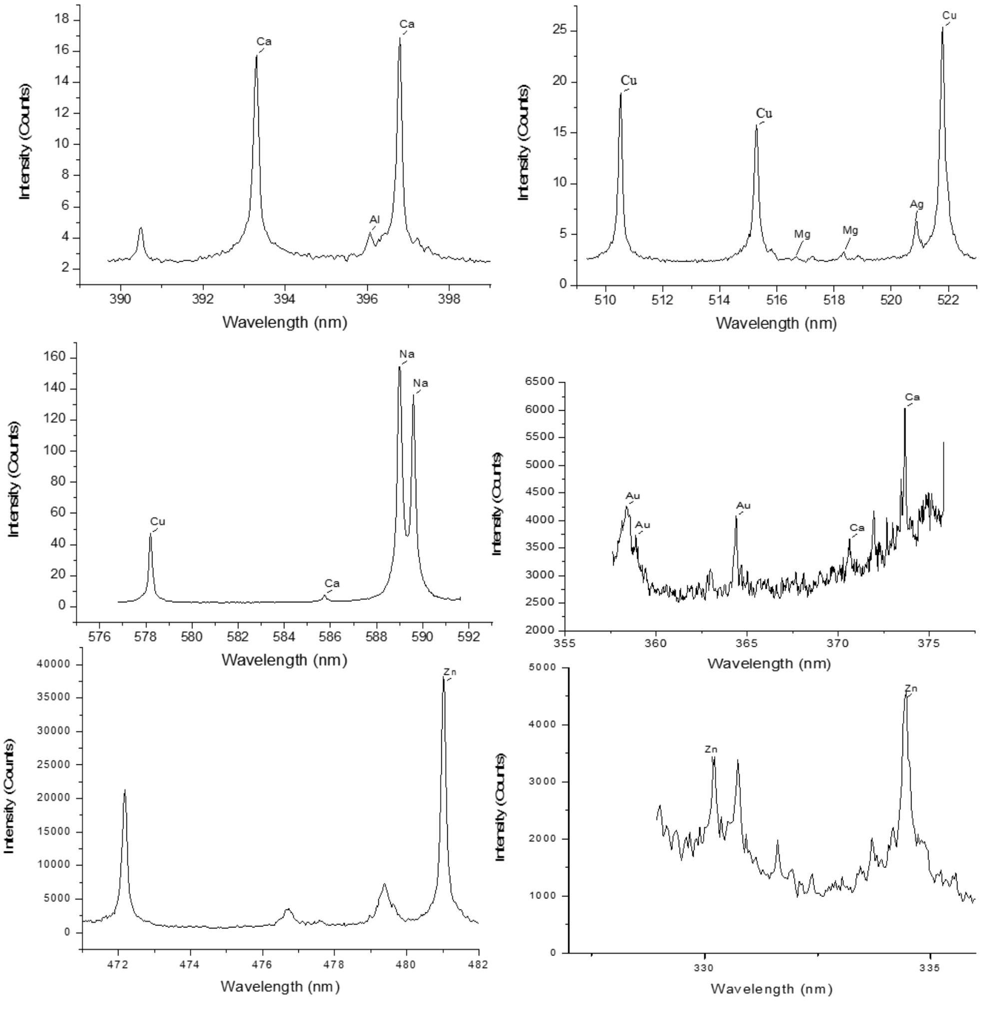

Fig (3) shows LIBS spectra of different elements were detected such as Cu, Ag, Au, Zn, Al, Mg, Ca, and Na in two samples.

Elements	Wavelength (nm)				
Cu	327.310	402.259	406.240	510.542	515.292
	521.795	529.226	555.474	570.018	578.192
Ag	327.973	338.218	520.892	546.557	547.167
Au	358.412	364.396	583.730	627.583	
Al	266.039	308.215	309.271	394.391	396.152
Mg	516.673	518.318			
Na	568.247	568.824	588.994	589.578	
Ca	396.805	422.623	442.503	443.401	445.402
	452.702	457.792	458.058	458.489	487.731
	504.138	526.245	526.519	526.997	534.911
	551.284	558.181	558.871	559.428	559.827
	585.733	610.296	612.243	616.224	643.932
	645.001	646.267	647.170	649.426	
Zn	330.214	334.425	472.231	481.056	492.461

Table.1. Emission lines used for identifying elements in LIBS spectra obtained from the NIST atomic database

3.3. Evaluation of the sample damage produced by LIBS

This study presents clear statements of the effect of different LIBS shots with different pules energy on the metal threads. The metals threads were exposed to 1, 5, 10, 20, 30, 40, 50 and 80 laser shots at a single location on the sample with laser pulse energies set at 5, 10, 20, and 30 mJ. The Fig. 4 shows the effect of different shots at different laser energies on metal threads. Fig (4 -A) show the metal threads damage by effect of 40 shots with 5 mJ application while Fig (4 -B) shows the metal threads damage by effect of 50 shots with 5 mJ application. The reported damages have a characteristic size much smaller than 100 µm (the typical diameter of a hair) and are consequently not visible to the naked eye. Moreover, no damages were observed by using 1, 5, 10 and 20 laser shots with 5 mJ laser energy. Fig (4 -C) shows the metal threads damage by effect of 40 shots with 10 mJ application while Fig (4 -D) show the metal threads damage by effect of 50 shots with 10 mJ application. The damage size according to SEM images was close to 100 µm . With 1, 5, 10 shots, damage were not visible. The damage sizes observed by using 20, 30 laser shots were much smaller than 100 µm . Fig (4 -E) shows the metal threads damage by effect of 40 shots with 20 mJ application while Fig (4 -F) shows the metal threads damage by effect of 50 shots with 20 mJ application. It is noticed that the metal threads were cut by using 40 and 50 shin both cases. There is a slight damage, i.e. smaller than 100 µm by using 20 and 30 shots while no damage are noticed by using 1 and 5 shots.

Finally, Fig (4 -G) shows the metal threads damage by effect of 50 shots with 30 mJ application while Fig (4 -H) show the metal threads damage by effect of 80 shots with 30 mJ application. With 1 and 5 shots at 30 mJ there was no clear visual damage observed only some corrosion and dirt was removed from the surface of metal threads by the laser pulses. LIBS application by using 10 and 20 shots at 30 mJ caused a light damage (i.e. smaller than 100 µm) on metal threads. But again, the damages obtained by LIBS application 50 and 80 shots at 30 mJ, were still close to 100 µm diameter and thus invisible to the naked eye. LIBS analysis leads to removal of material from the surface of metal threads but the damage is minimal (micrometer- size) and any damage to the sample surface is practically invisible to the naked eye. Thus LIBS can be regarded as almost nondestructive. These features make LIBS quite competitive compared with other techniques commonly used in archaeological science for obtaining elemental analysis information. According to our results, LIBS for the analysis metal threads has key features which make it an attractive analytical technique by its simple implementation, the speed of analysis, the simple preparation of samples and the ability to achieve high spatial resolution nearly non-invasively. SEM images show that the tested samples are metal strip wounded around the fibrous core.

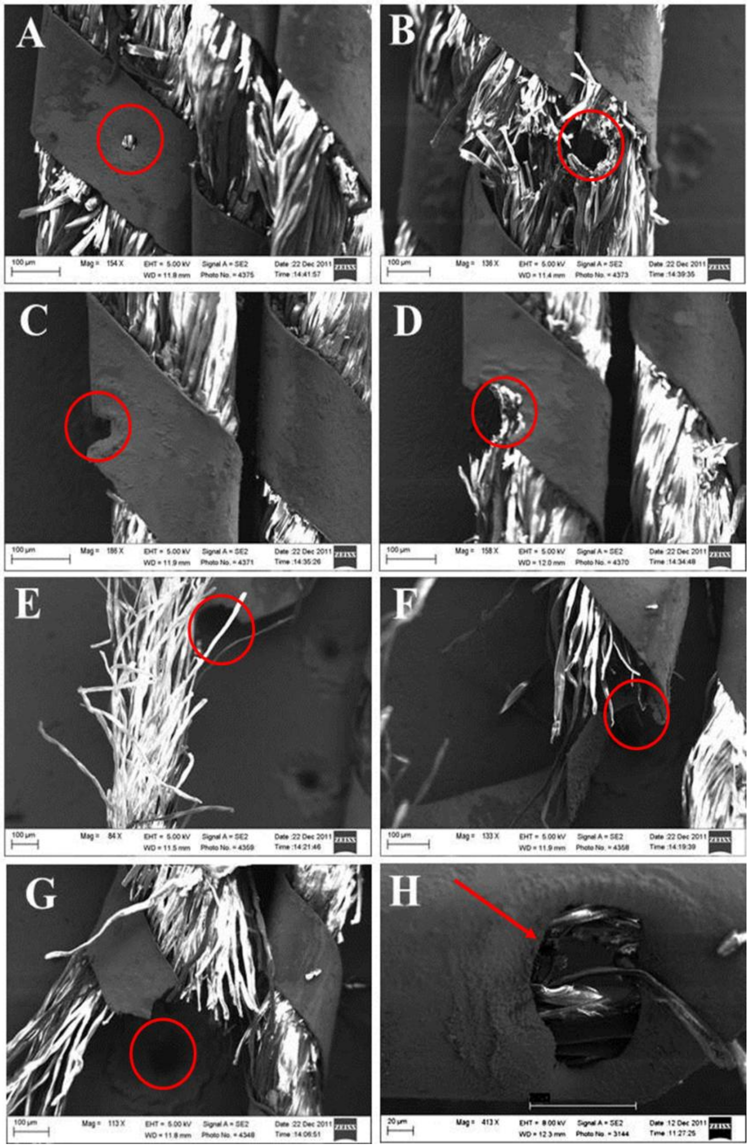

Fig.4. Images obtained with a scanning electron microscope (SEM) of the metal threads during LIBS analysis at 532 nm with : (A) 40 laser shots / 5 mJ, (B) 50 laser shots / 5 mJ, (C) 40 laser shots / 10 mJ, (D) 50 laser shots / 10 mJ, (E) 40 laser shots / 20 mJ, (F) 50 laser shots / 20 mJ, (G) 40laser shots / 30 mJ and (H) 80 laser shots / 30 mJ. Sample damage caused by laser shots is indicated by red circles or arrow.

Also the SEM results show that the metal thread could be penetrated by large number of laser pulses. This study also focuses on the relationship between the effect of laser shots and induced damage on metal threads. In other words, how many of shots are required in order to penetrate the metal threads. Fig. 5- A Shows the cross section diagram of the metal threads, one can the morphological structure of the metal threads from the outside to the inside, show slight corrosion layer (black) then the main metal strips (2) and then the fibrous core (1). While Fig 5-B shows image obtained on a scanning electron microscope (SEM) of the metal threads during LIBS analysis with 80 laser pulse at 532 nm with 30 mJ. This damage of sample surface is typically 100 Om diameter and thus invisible to the naked eyes. The first spectrum (first laser shot) displayed in Fig. 5.C shows the corrosion and dirt which be distinguished in the surface layer of metal threads. Therefore, it was found that the concentration of copper as one main element in metal thread composition was decreased after two laser shots as shown in Fig. 5 D. The concentration of copper was found to stay high from 2 to 20 laser shots. After 26 laser shots (Fig. 5.E) the LIBS signal of copper was clearly decreased and this was confirmed after 29 laser shots (Fig. 5.F). This result can be interpreted in two directions. This first one is that while the laser is drilling the material, the LIBS signal decreases, even if there is no change in the in-depth structure of the ablated material. The second one is that, due to the specific in-depth characteristics of the fiber, the LIBS signal related to copper naturally vanishes when the laser drilling is reaching the fibrous core of the sample. This second scenario was confirmed by the SEM image displayed in Fig 5.B on which one can see the textile fibers shining inside the damage.

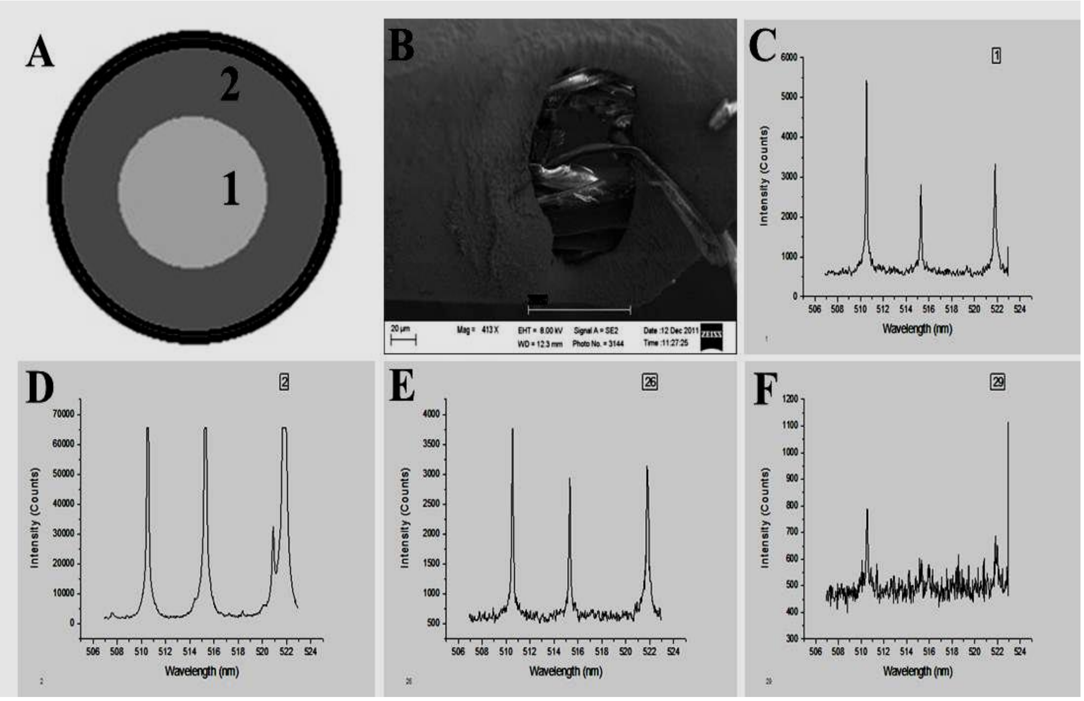

Fig.5. Shows the cross section diagram of the metal threads, it appears the fibrous core (1), metal strip (2) and corrosion layer (black) on metal surface (A), the laser-induced damage of the metal thread by using 80 laser shots / 30 mJ (B), the LIBS spectra obtained after 1 laser shot (C), 2 laser shots (D) 26 laser shots (E) and 29 laser shots (F)

4. Conclusion

Qualitative LIBS analysis was studied as the first step for rapid identification of the type of metal or alloy used in the making of the metal threads, enabling classification and screening of different metal threads. The LIBS analysis leads to removal of corrosion and dirt from the surface of metal threads. Any damage to the metal threads surface by using different pulses with high or low pulse value energy is blow 100 µm diameter and thus practically invisible to the naked eye. Thus LIBS can be regarded as an excellent non-destructive technique for the analysis of metal threads and is thus suitable for analysis and characterization of historical metallic threads. The main element in the tested samples is copper with other elements like silver, gold and zinc while other elements Al, Mg, Ca, and Na are due to corrosion and contamination of the samples. The number of laser shots is very important to achieve a relevant LIBS analysis. The first laser shot give access to the surface layer mostly related to contamination products and it is remarkable that laser cleaning is very efficient to further analyze the original material. Using LIBS could help conservators in choosing good and suitable materials and tools for conservation of archeological objects and in establishing an optimized conservation plan in order to preserve these objects.

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