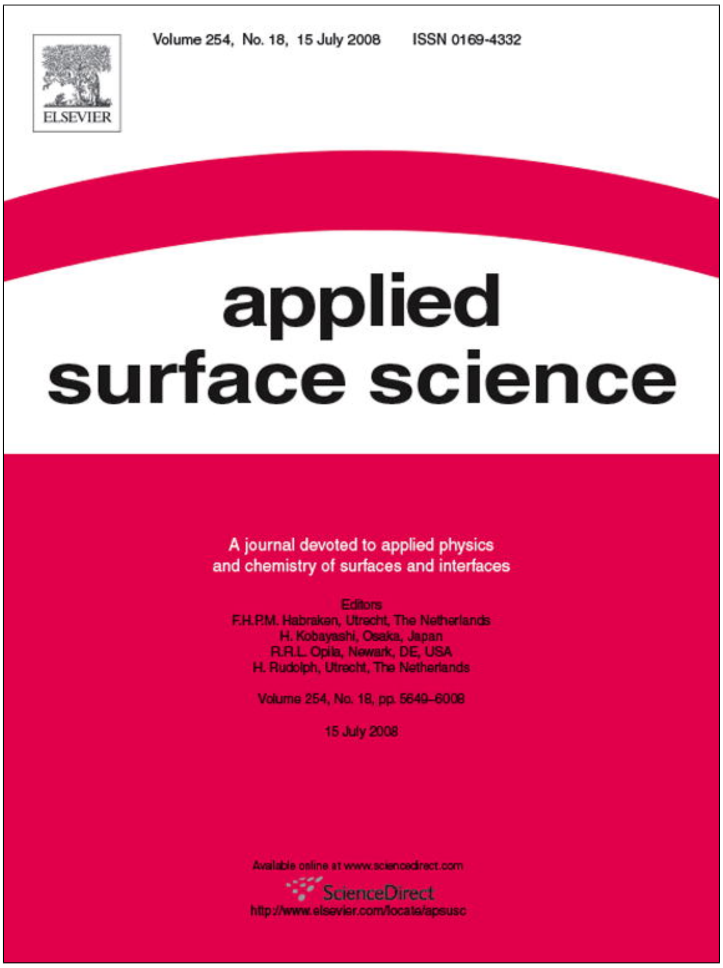
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Evaluating the use of laser radiation in cleaning of copper embroidery threads on archaeological Egyptian textiles

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ABSTRACT

Cleaning of copper embroidery threads on archaeological textiles is still a complicated conservation process, as most textile conservators believe that the advantages of using traditional cleaning techniques are less than their disadvantages. In this study, the uses of laser cleaning method and two modified recipes of wet cleaning methods were evaluated for cleaning of the corroded archaeological Egyptian copper embroidery threads on an archaeological Egyptian textile fabric. Some corroded copper thread samples were cleaned using modified recipes of wet cleaning method; other corroded copper thread samples were cleaned with Q-switched Nd:YAG laser radiation of wavelength 532 nm. All tested metal thread samples before and after cleaning were investigated using a light microscope and a scanning electron microscope with an energy dispersive X-ray analysis unit. Also the laser-induced breakdown spectroscopy (LIBS) technique was used for the elemental analysis of laser-cleaned samples to follow up the laser cleaning procedure. The results show that laser cleaning is the most effective method among all tested methods in the cleaning of corroded copper threads. It can be used safely in removing the corrosion products without any damage to both metal strips and fibrous core. The tested laser cleaning technique has solved the problems caused by other traditional cleaning techniques that are commonly used in the cleaning of metal threads on museum textiles.

1. Introduction

A dirty textile embroidered with metal threads can cause visual offence. Dirt can also act as a catalyst for deterioration [1]. After the excavation the corrosion of archaeological metals continues and can even accelerate [2]. Cleaning is one of the most important stages in the conservation processes of historical textiles [3–8]. Since the benefits of cleaning usually outweigh the drawbacks are advantage is that it often greatly alters the appearance of the fabrics, revealing textiles disfigured by soiling. Another is that it can enhance the long-term preservation of textiles by removing soiling that enhances the deterioration of textile objects [1,3,9].

Cleaning is usually the first step of many processes in a conservation work. It is also one of the most difficult operations undertaken when preserving metal artefacts [2]. For that a clean object is preferable to a dirty one. It must be realized, however, that cleaning is one of the most irreversible of all conservation processes [1]. The cleaning of metal threads on archaeological textiles is a delicate task. The methods used should take into consideration the type of object, the composition of materials and the state of conservation. Each case should be evaluated individually. Cleaning metal threads in historical textile objects is considered a difficult task because materials and methods suitable for used in cleaning metal threads may be harmful to core yarns, ground fabric, or to needlework pads. So the conservator should compromise and select cleaning materials and methods that respect and preserve all component materials of an object. So assessing the possible advantages and disadvantages of any cleaning treatment is an important task in the cleaning process of metal threads in historical textile [10].

A wide variety of mechanical and chemical treatments have been used in the past to clean metal threads on historical textiles [5,8,11–13]. Now it is recommended to avoid using mechanical cleaning methods for cleaning metal embroidery threads. This is due to the disadvantage results of using these methods. The traditional mechanical cleaning methods can remove the noble patina and a coating layer on the surface of a cleaned metal [1,14]. There are various materials and methods commonly used in chemical cleaning of metal embroidery threads [5,8,11–16]. Most of the chemical treatments commonly used in the past for cleaning metal threads are incompatible for both metals and organic fibers core [14]. During any chemical treatment for cleaning metal threads, it is almost impossible for cleaning solutions to avoid contact with fibers. So treatment involving liquid agents, aqueous

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or non-aqueous, could produce irreversible changes to the organic fibrous core inside metal threads [12]. However, wet cleaning processes still are used in removing corrosion layers from metal threads. In most cases, some detergents and chemicals have to be added to water to enhance the ability of wet cleaning to remove corrosion stains. Some examples of commonly added materials are non-ionic detergents plus sequestering agents such as the sodium salt of ethylene diamine tetraacetic acid [10].

Techniques and methods used in cleaning metal embroidery threads on historical textiles are developing all the time to find more suitable and efficient methods to clean these metal threads without causing damage to them. In recent years, a number of new methods for cleaning metal threads have been used [2,14,17–20]. Laser has been considered to be a promising cleaning technique for artwork conservation due to the fact that laser is highly controllable and a monochromatic energy source which can remove the surface contaminants precisely and selectively [7,18,20]. The advantage of pulsed laser cleaning is to remove the surface contamination layer by layer [14]. Laser cleaning is an effective cleaning technique of metal artefacts since it provides a high degree of control that allows fragile objects with a considerable amount of surface detail to be effectively and safely cleaned. High control permits the preservation of objects with surface details, such as relief, original tool markings, and surface patina. The use of this technique requires skilful conservators in order to achieve the most satisfactory results [19]. This study aims to evaluate using the laser cleaning technique compared with the modified wet cleaning technique for cleaning dirty and corroded metal embroidery threads on archaeological Egyptian textiles without any damage to the underlying organic fibers. In this study, the used wet cleaning technique was adapted and modified to avoid or, at least, to reduce the contact of cleaning solutions with organic fibers in the core of tested metal threads and in the textile fabric itself.

2. Experimental

2.1. Samples

An archaeological corroded copper embroidery thread samples on a textile piece obtained from an archaeological Egyptian wooden coffin in Tanta Museum, Egypt, were used (see Fig. 1).

2.2. Cleaning Methods

Two recipes of wet cleaning method and laser cleaning method have been tested and evaluated for the cleaning of tested corroded

Fig. 1. The tested archaeological Egyptian corroded copper threads.

copper thread samples. Upon the literature review the chosen tested methods are considered the most appropriate methods used in cleaning of metal embroidery threads on museum textiles [5,10]. The used methods were selected based on the nature of materials composed of tested metal threads. As Landi 1998 confirmed, all chemicals used in cleaning metal threads should be prevented from penetrating the fabric in the surrounding areas as much as possible [1]. So this study has selected methods that may achieve this fact. Chemicals that have used in this study were distilled water, synperonic N, IMS, and EDTA, all of which are not harmful to both copper threads and cotton fiber core [5]. Although many authors have confirmed that formic acid is useful and effective in cleaning copper threads it did not use in this study because the harmful effect on cotton fiber core. As it is known well that cotton fibers deteriorate from acids [3].

2.2.1. Wet cleaning method

Applying the wet cleaning method, we used the poultice technique to prevent, or at least to reduce the penetration of the chemical into both the organic fiber core and the ground fabric carrying metal threads. A poultice is an absorbent material applied to a surface to draw stains and dirt from the surfaces. Two types of poultices were tested in this study.

2.2.1.1.Poultice A. Poultice pulp paper that contains an emulsion consisting of IMS (10 cm^3/L) and a non-ionic detergent (Synperonic N) (1 g/L).

2.2.1.2.Poultice B. Poultice pulp paper impregnated with an emulsion consisting of IMS (10 cm^3/L), EDTA (2%) and a non-ionic detergent (Synperonic N) (1 g/L).

2.2.1.3.Application of tested poultices. The wetted poultice used and coated the corroded metal thread sample. After an hour poultice was removed and the metal thread sample was rinsed with a gentle sponge immersed in distilled water. The applied poultice was repeated three times to achieve a good result. Finally, the cleaned metal threads were rinsed well with a gentle sponge immersed in distilled water. Then the metal threads were dried with acid-free tissue paper.

2.2.2. Laser cleaning technique

Cleaning of the copper thread samples is performed using a Q-switched Nd:YAG laser (Brio, Quantel, France) operating with its second harmonic generator (SHG) module to provide laser pulses of wavelength 532 nm, energy 50 mJ/pulse and maximum repetition rate of 20 Hz. The fluence of the unfocused beam used for cleaning was 0.25 J/cm^2. The laser fluence was chosen in order not to damage the threads due to that the literature review confirmed that the 532 laser radiation and energy fluences <1 J/cm^2 is less destructive for cellulose [21]. Our results showed that the tested threads are cotton (cellulose fibers).

2.3. Investigation methods

Conservation of metal threads on archaeological textiles (composite materials) should be based on a thorough and deep understanding of the nature of the object and its deterioration mechanisms. Identification of the nature of component materials is an essential initial step for the successful chooses of an effective conservation treatment. Only non-destructive methods should be used [10]. All samples were investigated visually, with optical microscopy and a scanning electron microscope with EDX before and after cleaning with tested methods. Used investigation methods are effective and commonly used in investigation of metal threads [10,22–25]. The scanning electron microscope (SEM) investigation was carried out for tested samples using SEM Model

Philips XL 30 attached with EDX Unit. SEM-EDX analysis was applied on samples to examine composition of samples before and after cleaning. The samples were mounted on carbon stubs using adhesive-coated carbon discs and were investigated directly without any surface coating.

The metal thread samples cleaned with laser technique were also investigated and analyzed before and after the cleaning with laser induced breakdown spectroscopy (LIBS) technique. The same laser has been used for the elemental analysis of the samples to follow up the cleaning procedure adopting (LIBS) technique. However, in case of LIBS the laser light pulses have been focused via a 120 cm focal length fused silica lens and the emitted light from the laser-induced plasma is collected and fed to the entrance of an optical fiber (600 μm, diameter) which is coupled to an echelle spectrometer (Mechelle 7500, Multichannel instruments, Sweden) provided with an ICCD camera (DiCAM-PRO-PCO computer optics, Germany) for detection of the dispersed light. The obtained atomic emission spectra are displayed on a PC where the analysis takes place with the LIBS^{++} software.

Fig. 2. An image of the corroded copper threads using the reflected optical microscope. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3. Results and discussion

3.1. Diagnostic investigation prior to cleaning

The results of optical microscope investigation show that the tested metal threads made from solid metal strips wound around a fiber core in a 'S' twist (from right to left) (see Fig. 2). The microscopic examination showed that tested metal threads are badly deteriorated and an extensive corrosion layer impeded the tested metal threads surface. It is clear that there are various types

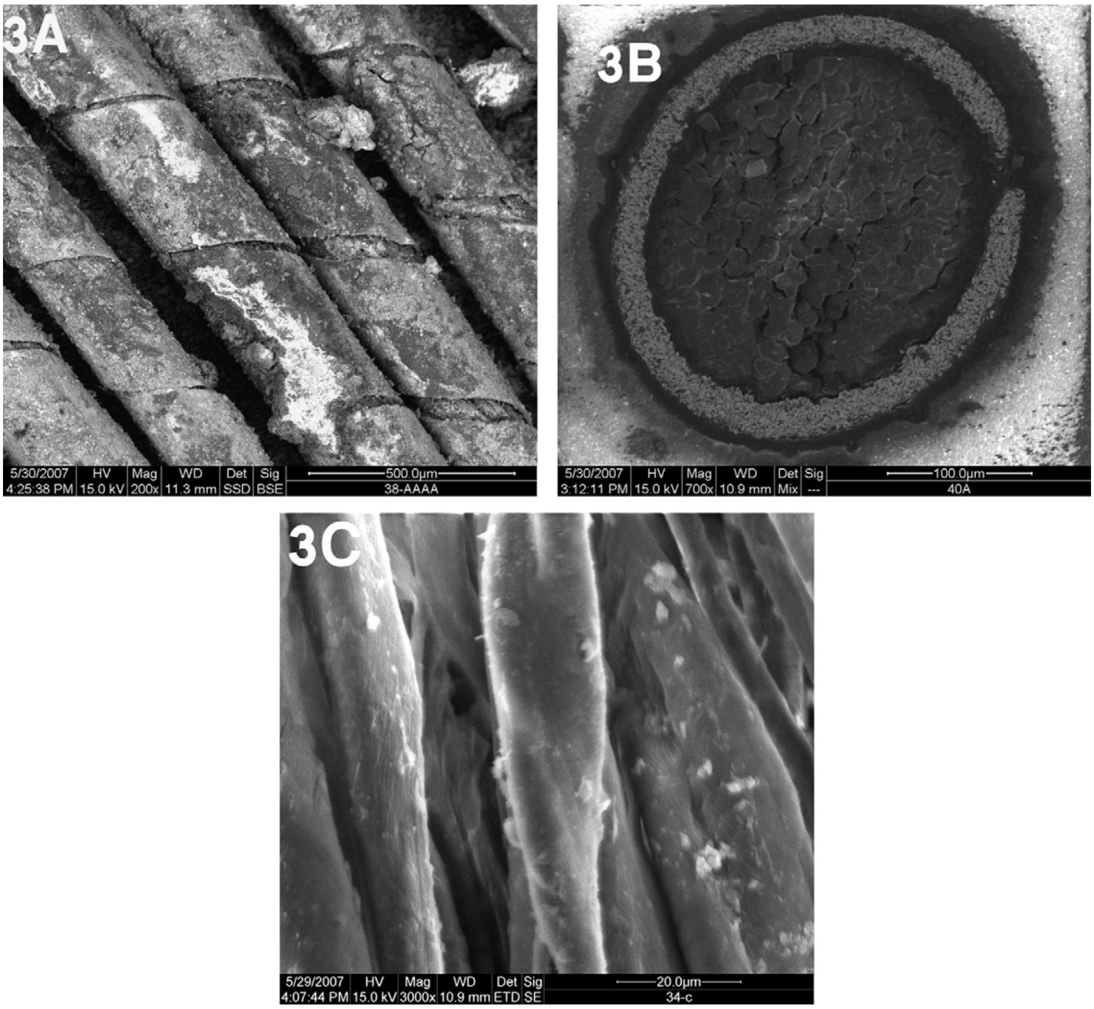

Fig. 3. SEM images of the tested copper threads before the cleaning treatments (A) the surface of copper threads, (B) the cross-section of the copper thread and (C) the cotton fiber core.

Table 1
The EDX spot analysis of the chemical composition (wt%) of the corroded surface and the cross-section of the tested metal thread samples

Elements	Corroded surface area	Cross-section
C	18	8
O	38	4
Cu	27	86
Mg	1	–
Al	2	–
Si	3	–
Au	1	1
S	2	–
Cl	3	–
Ag	2	1
Ca	2	–
Fe	1	–

Table 2
The EDX spot analysis of the chemical composition (wt%) of the metal thread surface before and after the cleaning with poultice A

Elements	Before cleaning	After cleaning
C	18	10
O	37	16
Cu	27	49
Mg	1	–
Al	2	–
Si	4	–
Au	1	11
S	2	–
Cl	3	–
Ag	1	14
Ca	3	–
Fe	1	–

of corrosion in different colors: red, blue, green and black colors. These colors result from the corrosion layers that may contain various types of copper corrosion products such as copper oxide (Cu_2O) in reddish color, copper (II) oxide, (CuO) in a black corrosion layer, copper (II) carbonates [$CuCO_3{\cdot}Cu(OH)_2$] malachite in green color, and [$2CuCO_3{\cdot}Cu(OH)_2$] azurite in blue color and copper (I) chloride [CuCl] and green colored basic copper (II) salts [$CuSO_4{\cdot}Cu(OH)_2$]. These colors are mixed on the surface of tested metal threads. These identified corrosion products are commonly identified on archaeological copper objects [5].

The results of the morphological examination of tested metal threads by the scanning electron microscope (SEM) confirm that all tested metal thread samples were made of solid metal strips wound around a fibrous core in a 'S' twist (see Fig. 3). The results show that the strips were cut from a thin metal foil. The effect of the cutting tool on the edges of the metal strips can be detected. The results show that the metal threads are very weakened, too dirty, very corroded and damaged. It is clear that there is a thick layer of corrosion products covering the metal threads. The fibrous core is identified as cotton fibers (see Fig. 3C).

The results of EDX spot analysis of different areas of tested metal thread show that the whole surface is covered with various copper corrosion products (see Table 1). Many types of contamination elements were identified on the surface. These identified elements are the main components that composed most corrosion products that are commonly present on copper. It is noticed that the percentage of contamination elements C, O, Si, Mg, Ca and Cl are too high. The results show that the percentage of elements composed of C, O, Mg, Al, Si, S, Cl, Ca and Fe are about 75%, while the percentage of copper is about 25% only. The results of the EDX analysis of a cross-section of the tested metal threads indicate that the main components of the tested metal thread are about 85% copper (Cu). In comparing the results in both the surface and the cross-section it was found that both Au and Ag are more common in the surface. This leads to the conclusion that gold and silver were used as coating materials on the copper surface. These results confirm that the coating layer on the surface may be composed of copper, gold, and silver.

However, the severity of the corrosion products in metal thread samples is indicative of the inappropriate environmental conditions that these metal threads have been preserved in either before their discovery or in the display case where this wooden coffin is exhibited in Tanta Museum. The obtained results show that most identified dirt and corrosion may have resulted from environmental condition in the burial site. The results show that the metal threads are coated with soot and organic constituents as well as salts and mineral particles. All the previous contaminations may have resulted from the very poor burial condition. These metal thread samples were obtained from an archaeological wooden coffin discovered in the Delta region in Egypt. The environmental conditions of the delta region are characterized by high humidity and a wet soil containing soluble salts. The corrosion on the tested copper threads may be due to the wooden coffin since previous studies have reported that bronze and copper corroded when stored in wood [26].

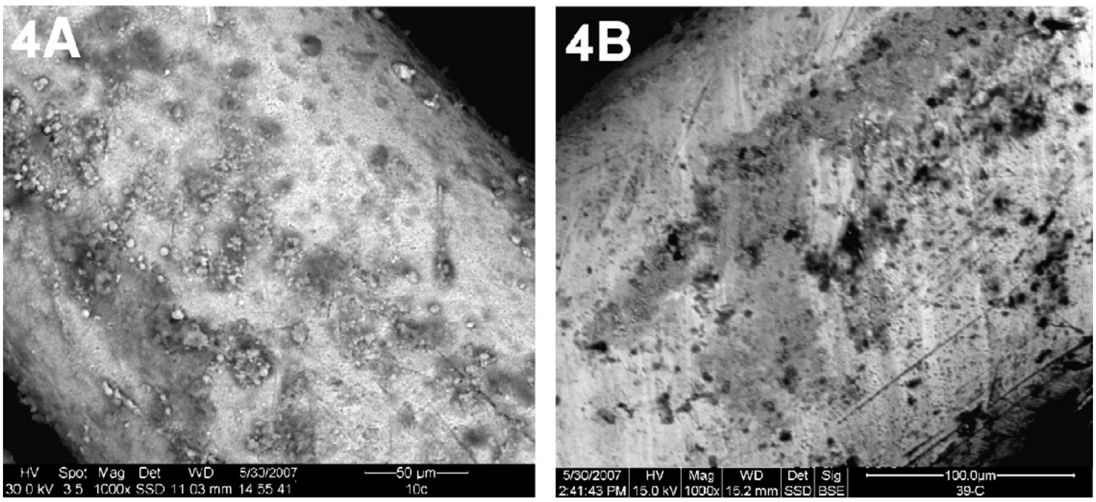

Fig. 4. SEM images of the tested metal thread before and after the cleaning with poultice A: (A) before the treatment and (B) after the treatment.

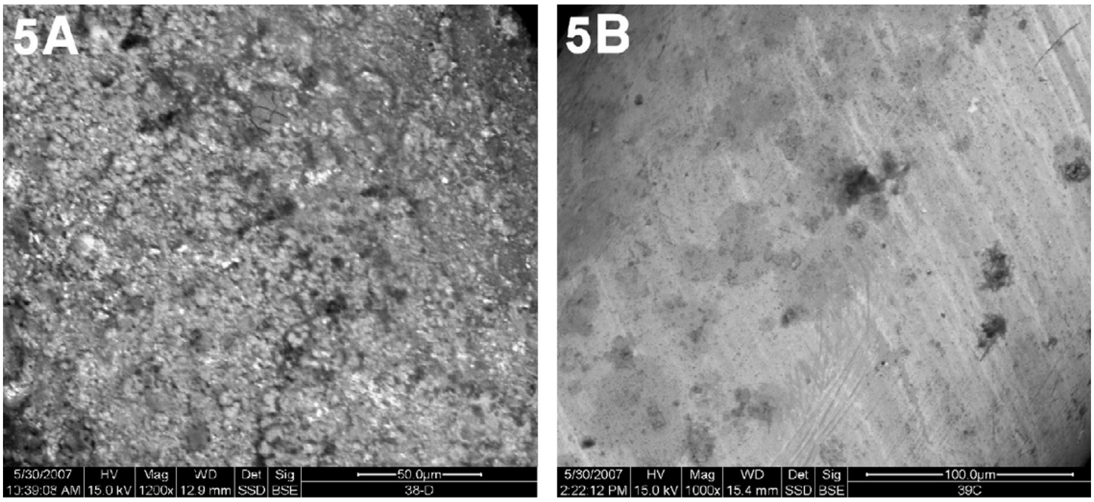

Fig. 5. SEM images of the tested metal thread before and after the cleaning with poultice B: (A) before the treatment and (B) after the treatment.

3.2. Diagnostic investigation after cleaning

The results of SEM investigation of metal threads after cleaning with poultice A, show that there is no evident improvement on the surface of the treated metal threads since there is no evidence of change in the surface (see Fig. 4). Additionally, the results of the EDX analysis of the metal threads after cleaning with poultice A, show that there is little reduction in contamination elements on the surface of treated metal threads (see Table 2). This may be due to the fact that synperonic N removes dirt from the metal thread surface but cannot remove the other corrosion products, as it is known that dirt can be removed from textiles using wet cleaning with any surfactant detergents [1].

The results of the SEM investigation of metal threads after cleaning with poultice B show that there is an evident improvement in the surface of treated metal threads as there is no change in the surface (see Fig. 5). Also the results of the EDX analysis of the metal threads after cleaning with poultice B show that there is an obvious reduction in contamination elements on the surface of treated metal threads (see Table 3). These results are in agreement with results obtained with other researchers who confirm that EDTA is effective in removing the corrosion stains from textiles [5,12].

The results of visual and optical microscopic investigation of metal threads after laser cleaning show that there is an obvious improvement of the appearance of the surface of treated metal threads after laser cleaning. Most of the corrosion products characterized with green, grey and blue colors were removed from the surface of the treated metal threads. They became smooth and appeared in a reddish-yellow color that characterizes the copper metal (see Fig. 6).

The results of the SEM investigation of metal threads after laser cleaning show that there is an obvious improvement in the appearance of the surface of tested metal threads after laser cleaning (see Fig. 7). The results show that the tarnish and corrosion product layers on the surface were removed successfully without any apparent damage such as surface melting. Also, it was found from the magnification proved that the underlying cotton is still good, is not burnt and fibers are in good condition too. These results are in agreement with results in the literatures [18,21].

The results of the EDX analysis of the metal threads after laser cleaning show that there is a noticeable reduction in contamination elements on the metal surface after laser cleaning (see Table 4). The results show that the wt% of copper (Cu) has increased to become about 66; the wt% of both silver (Ag) and gold (Au) became 16 and 11, respectively. These results confirm that a high percent of corrosion products layers were removed well from the surface of metal threads after laser cleaning.

The results of the LIBS analysis of metal threads before and after laser cleaning confirm the results obtained by the EDX analysis

Table 3
The EDX spot analysis of the chemical composition (wt%) of the metal thread surface before and after the cleaning with poultice B

Elements	Before cleaning	After cleaning
C	21	4
O	35	8
Cu	26	60
Mg	1	–
Al	1	–
Si	2	–
Au	2	15
S	2	–
Cl	4	–
Ag	3	13
Ca	2	–
Fe	1	–

Fig. 6. An optical microscopy image shows the surface appearance of the tested metal threads after the laser cleaning. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

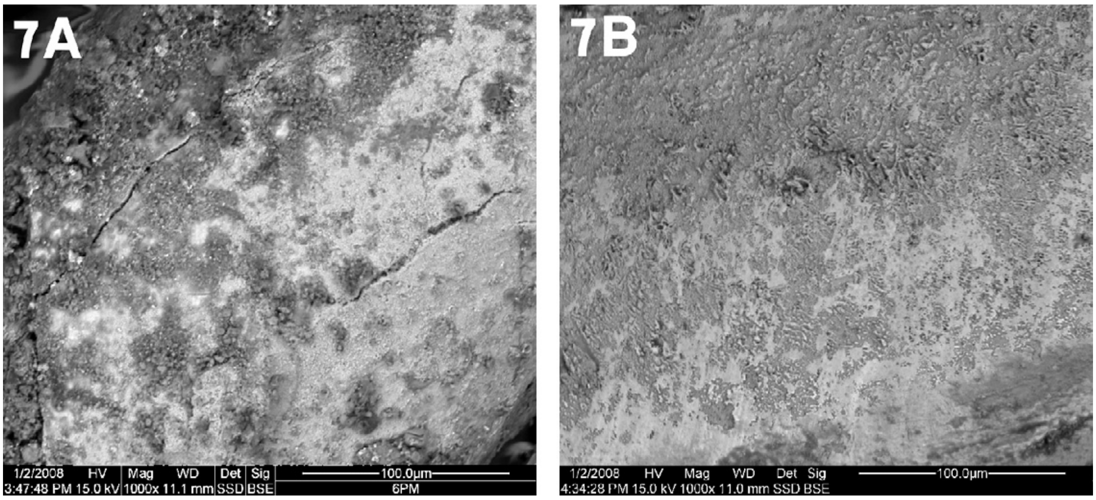

Fig. 7. SEM images of the tested metal thread before and after the cleaning with the laser technique, photo A before the treatment, photo B after the treatment.

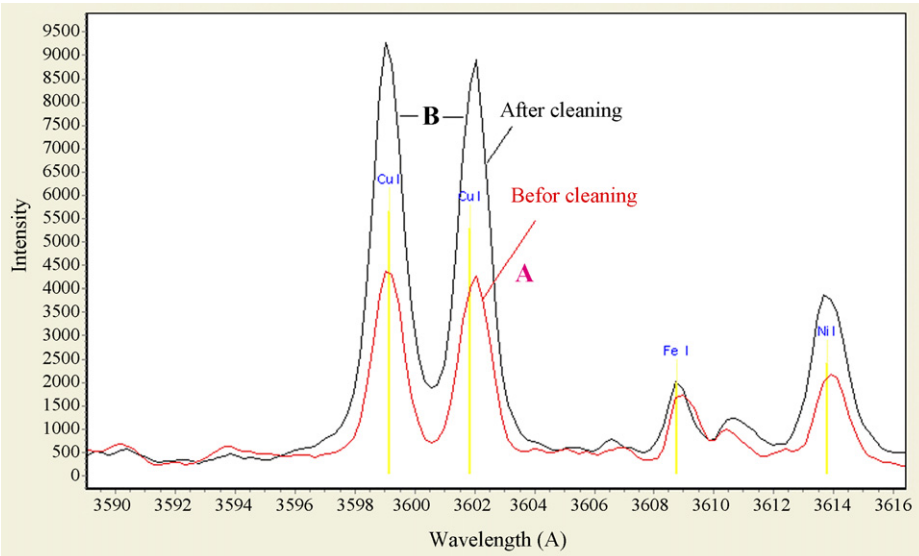

Fig. 8. A zoomed sections of the superimposed LIBS spectra before and after the laser cleaning of the metal thread surface. The curve (A), in red color, is before the cleaning. The curve (B), in black color, is after the cleaning. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

that laser cleaning improves the surface of metal threads after laser cleaning. The results show that there is a noticeable increase in the percentage of copper in the metal thread samples after laser cleaning (see Fig. 8).

By comparing all obtained results, it is noticed that laser cleaning is an effective method to clean archaeological copper metal threads. Laser cleaning is able to remove most of corrosion products that are commonly present on the surface of corroded archaeological metal copper threads. Also poultice B is able to remove corrosion products layers from corroded archaeological metal copper threads. But the effectiveness of poultice B in removing the corrosion products is less than the ability of laser cleaning. Results showed that the surface appearance of metal threads after laser cleaning is better than the appearance of the surface of metal threads after cleaning with poultice B. The results show that poultice A is not effective in the cleaning of archaeological metal copper threads, as there is no any obvious change in the surface of metal threads after cleaning with poultice A. There is sill a thick layer of corrosion products that cover the metal threads after cleaning with poultice A.

Table 4
The EDX spot analysis of the chemical composition (wt%) of the metal thread surface before and after the cleaning with laser

Elements	Before cleaning	After cleaning
C	24	3
O	40	3
Cu	19	66
Mg	1	–
Al	2	–
Si	4	–
Au	1	11
S	1	–
Cl	2	–
Ag	1	17
Ca	3	–
Fe	2	–

4. Conclusion

Laser cleaning is the most effective technique among all tested methods for cleaning corroded archaeological copper metal threads. It can be used safely in removing the corrosion products without any damage to both metal strips and the fibrous core. Laser cleaning techniques can solve the problems that can be caused by other traditional cleaning techniques that are commonly used in the cleaning of metal threads on museum textiles. Poultice B can also be used for removing corrosion products layers from corroded archaeological metal copper threads. But the ability of poultice B in removing the corrosion products is less than the ability of laser cleaning. Poultice A is not effective in the cleaning of archaeological metal copper threads. However, more studies should be done to investigate the long-term effect of laser cleaning on materials that are commonly composed of copper metal threads on archaeological textiles such as silk and linen fibres, dyes, painting, finishes, etc.

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