

# Laser Cleaning of Textile Artifacts with Metal Threads: Process Parameter Optimization

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This paper presents the results of the laser cleaning effects on textile samples with corroded metallic threads. In many museum collections, there are textile exhibits like uniforms, national costumes, flags and home textile, embroidered with metallic threads. Corrosion of metal threads is one of the most common problems that damage embroidered items. In the practice, the application of conventional cleaning methods rarely gives the expected results, and the implementation of laser technology was the next step for corrosion products cleaning. The Nd:YAG laser was used to clean the corrosion of embroidered items from a museum study collection. The effects on the laser irradiated zones were investigated by optical and SEM microscopy and the EDX analysis. The laser irradiation process parameters of the metal threads corrosion

*Key words:* textile, textile material, uniform, metal thread, corrosion, corrosion cleaning, laser application.

## Introduction

THE use of embroidery to decorate clothes is a very old technique. The earliest samples of handmade embroidery are available from ancient times. Each country portrayed its own distinctive style in designs based on its culture, history and traditions [1-3].

Embroidered clothing was considered a symbol of wealth and a social status. It was used mainly in the clothing of the royalty and aristocracy, in church vestments and on military uniforms and other regalia. Luxury threads for this purpose were produced as a combination of precious metals and organic fibers. There are many types of metal threads: metal strips, wires, strip wound around a silk yarn and others [2, 4].

Machine embroidery brought new varieties of yarn like rayon, apart from cotton and wool. Computers brought in embroidery software with digitized patterns to finish the texture and designs in the clothing. Even though technology has made embroidery work easy, there has not been much change in materials or techniques in the history of embroidery.

National, ethnographic and military museums have rich collections of uniforms, national costumes, flags, banners and home textiles [4]. Environment influences induce structural damage, modification of materials, corrosion and agglomeration of pollutants and microorganisms on the cultural heritage artifacts, stored in museum depots or exhibited in galleries. Cleaning methods can be classified into four types: electrolytic reduction, electrochemical stripping, chemical stripping and mechanical stripping.

Corrosion of metal threads is one of the most common problems that inflict damage on embroidered items. Metal surfaces gradually become less shiny. They tarnish during time, which is often manifested as a dull, gray or black film or coating over metal [1-3, 5]. Conservators have to understand the methods of material cleaning and how different methods can affect materials differently. They also follow the principle of minimum intervention on artifacts. Chemical or electrolytic techniques can be used for corrosion cleaning, but the immersion process may damage fibers and dissolve any dye. A lot of techniques and methods in conservation are being developed in search for more suitable and efficient ways to treat materials with metal threads [1, 3, 5-7].

Protection and preservation of cultural heritage are based on the application of new technologies, methods and materials in diagnostic and conservation processes of museum items [3, 6].

The study of the laser radiation impact on the surface of different materials is important in cultural heritage preservation, in diagnostics and cleaning—of artwork surfaces by the laser ablation process, in the compositional analysis via laser induced breakdown spectroscopy - LIBS, in laser induced fluorescence - LIF, in Raman spectroscopy, or in many other diagnostic methods [6, 7]. These studies are also important in laser scanning instruments for cultural heritage documentation of complex objects, holography for damage assessment [7] and the diagnosis of environmental influences, optical coherence tomography, as well as a series of non-destructive analytical and diagnostic

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applications. In recent years, laser has been considered to be a promising cleaning technique for textile artwork conservation due to the fact that laser is highly controllable and can remove the surface contaminants precisely and selectively [6-14]. First of all, it was necessary to establish the safety conditions to avoid textile fiber damage. Several combinations of energy density (fluence) and number of pulses have been used: each one can give a particular result that could be sometimes associated with some degree of damage on cultural heritage items.

Conservation of cultural heritage requires the elimination of existing deterioration and the prevention of future one as efficiently as possible. Metallic threads for embroidery on textiles are copper or zinc, silver or gold plated, either alone or combined. The thickness of the precious metal is a few microns. Metal tapes wrapped around silk or cotton are white or yellow. The substrate of embroidered items is very often homemade cotton, flax, hemp, wool or mixed - colored materials [15-17].

Since historical artifacts exhibit a wide range of material varieties, shapes, surface textures and production techniques, applicability of any conservation method should be carefully evaluated and tested for each type. The immersion process that takes place in chemical or electrolytic corrosion cleaning techniques may damage fibers and dissolve any dye [3, 5, 6] while mechanical cleaning removes the plating. The study of the laser radiation impacts on the surface of embodied items is significant in terms of lasers application in diagnostic, cleaning, and other conservation methods. The application of lasers in conservation has a lot of advantages and disadvantages [6, 7]. Most metals absorb the light strongly at ultraviolet wavelengths, relative to infrared. Therefore, laser irradiation might lead to the heating of metal threads, which can be a problem when artifacts are made of textile and metal [15-21].

A special attention has been paid to control the operation conditions that enable the safe application of laser cleaning procedures on cultural heritage objects and save working conditions for conservators. Very often the contaminants are not uniformly distributed on the artifact surface and the surface of embroidery is irregular. If the same laser irradiation parameters are applied over the whole surface during the artifact cleaning, some textile areas may suffer damage, while metal threads can still have residual corrosion products or contamination.

### Laser - material interaction

The interaction of laser beams with materials is a complex phenomenon that depends on many factors [8-10, 21]. Laser ablation is a process consisting of optical, photo thermal, photo acoustic and photo mechanical phenomena, which depend on the parameters of the laser beam and materials. The energy density of the laser beam (fluence), the time of irradiation or pulse length, the wavelength, and the energy distribution within the beam are related to laser characteristics. The reflection and absorption coefficients, surface shape, homogeneity, temperature coefficient, melting point, and boiling point are related to the material of the object.

The application of laser in cleaning the corrosion layers on metallic threads is a complex phenomenon with non-linear occurrences and induced laser plasma, the explanation of which requires the knowledge of the characteristics of laser lights and materials. Different

parameters were analyzed to study laser effect on cleaning. The laser beam fluence is very important. High values may cause the metal to melt or lead to the formation of craters and because of that it is very important to use the proper fluence [7, 9-11, 21]. Better cleaning results may be obtained with a low fluence and high repetition rates. Spraying the surface with water before cleaning can optimize the cleaning process.

Absorption, reflection, refraction, transmission, and scattering take place when the laser beam is incident on the irradiated sample. The major part of the energy is absorbed and this absorption depends on the wavelength and spectral absorptivity characteristics of the material.



**Figure 1.** Uniform, epaulettes and a belt from the Military Museum in Belgrade with metal threads [4]

The laser absorbed energy converted into heat. When the surface sample temperature reaches the melting point, material removal occurs by melting. When the surface temperature further increases and reaches the vaporization point of the material, material removal takes place by evaporation instead of melting. The surface temperature is variable during laser irradiation. It depends on variations in thermal conductivity and specific heat, as a function of temperature. The main processes are mathematically described in open literature [11-13, 21].

### Experiment

The tested, embroidered sample was taken from the museum study collection. The metal embroidery is made on velvet. The metal threads are a combination of metals ribbons (copper silver plated) and organic fibers (cotton). The dimensions of the sample are 3 x 7 cm. In atmospheric conditions, silver can be transformed into two compounds, i.e.  $\text{Ag}_2\text{O}$  and  $\text{Ag}_2\text{S}$ . It is possible to differentiate between the products by color, i.e.  $\text{Ag}_2\text{O}$  is formed by a thin white layer and  $\text{Ag}_2\text{S}$  is black depending on the degree of corrosion. The threads and fabrics of the sample are all in a relatively good condition since the corrosion process is at its beginning.

The experiment was carried out using a commercial Nd:YAG laser, Thunder Art Laser, produced by Quanta System. The laser impacts on the sample were performed under normal atmospheric conditions. A laser operates in the Q-switch mode, with the three-wavelength, 1064 nm,

532 nm and 355 nm. The pulse duration is <8 ns. The repetition rate is 20 Hz, with a beam diameter of 10mm. The energy of the laser beam can be as follows: for 1064 nm maximum energy is 1000 mJ for 532 nm and 550 mJ for the smallest wavelength 200 mJ. It has a movable, articulated arm, through which the laser beam is directed with 7 mirrors and can approach the sample at different angles and at different distances. Some initial tests with the lasers were needed to find the optimum energy density.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) were performed for microstructural and microchemical characterization. The sample surface was monitored by an optical USB microscope, too. The SEM (JEOL JSM-6610LV) was connected with an INCA350 energy-dispersion spectroscope (EDX). Prior to the examination, the specimen surface should not be sputtered with gold. The EDX is used for the analysis of the metal thread composition and for determining the changes in the material composition of the irradiated zones and the ablated material.

## Results and discussion

Cleaning by laser has shown different effects on the

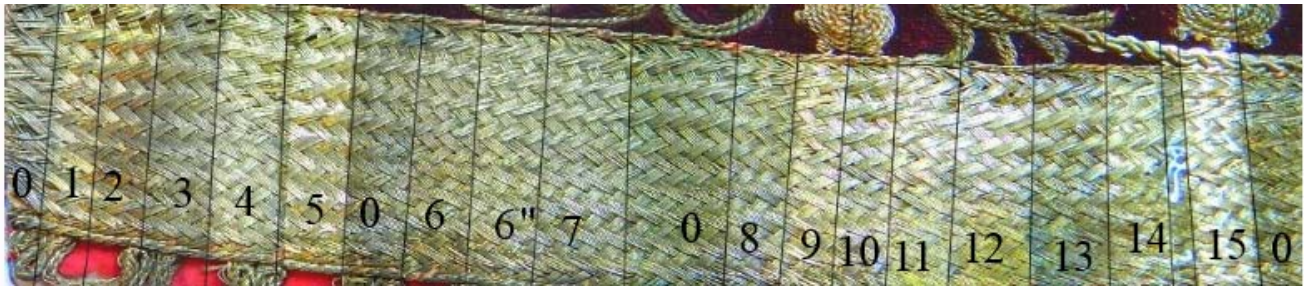


Figure 2. The irradiated zones on the embroidered sample

Figures 4-9 and Tables 2-4 show the SEM and EDX results for laser cleaning of metal threads. The analysis of the tested samples shows that the applied laser fluencies have resulted in very efficient surface cleaning of corrosion products and other depositions. The spectra were recorded in the different points of areas irradiated with three wavelengths (Table 1). There are significant changes in cleaning with increasing laser beam power (zones 1-3). All results in Table 2 are given in weight %.

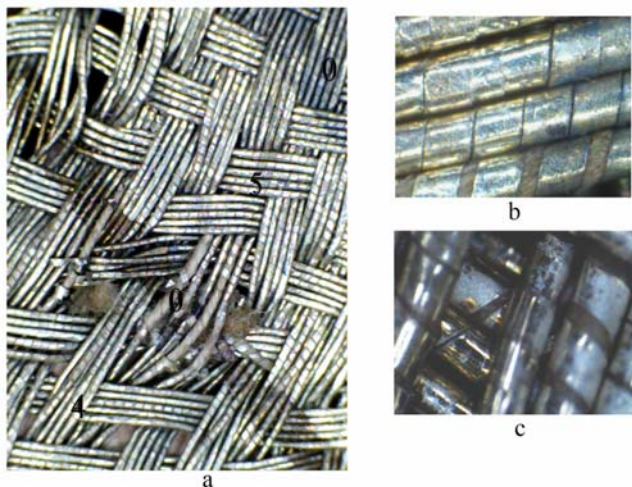


Figure 3. Zones a-4, 0 and 5, zoomed images of b-zone 5 and c- zone number 0

In some SEM images (4a, 5a and 6a), dark areas (the layers of dirt) that are not removed can be seen. The EDS

surfaces of the tested samples. The Nd:YAG laser has some difficulties in removing organic materials since they absorb poorly at shorter wavelengths. The use of pulsed near infrared and green Nd:YAG lasers for cleaning corroded metals is limited by the risk of surface melting and blackening due to thermal and photochemical changes. This process is very sensitive and correct operating parameters and care by the operator are required.

This paper presents only the results related to the cleaning of metal threads. The laser effects on the textile parts under metal threads or on the organic fibers inside threads require a special attention and analysis. The main aim of laser cleaning is to clean without any damage to the textile.

Fig.2 is a photo of the whole tested sample, after laser irradiation. Fig.3 shows the photos of the irradiated zones on the embroidered sample, recorded by an optical USB microscope (x20 for 3a and x200 for 3b and 3c). Visual inspection shows that the effects of laser corrosion cleaning depend on the laser wavelength and energy. The energy density, fluencies of the laser beam, the wavelength, and the number of pulses applied on the marked zones are presented in Table 1.

spectra (Table 2) confirm that their composition consists of Al, Ca, Na, Mg, S, K, P, Cl, O which are the result of corrosion products and the impact of the environment. The textile surface and metal threads are contaminated with salts and other pollutants that comprise these elements. The same elements are detected in untreated zones 0, 6, 8 and 10 (Table 1 and Table 2)

Table 1. Experimental conditions of laser irradiation

| Zone           | Fluence [mJ/cm <sup>2</sup> ] | Wave length [nm] | Time of irradiation [s] | Comments |
|----------------|-------------------------------|------------------|-------------------------|----------|
| 0              | 0                             | 0                | 0                       | 0        |
| 1              | 390                           | 1064             | 2                       | dry      |
| 2              | 300                           | 1064             | 2                       | dry      |
| 3              | 150                           | 532              | 2                       | dry      |
| 4              | 180                           | 532              | 2                       | dry      |
| 5              | 220                           | 532              | 2                       | dry      |
| 6              | 110                           | 355              | 2                       | dry      |
| 6 <sup>2</sup> | 110                           | 355              | 4                       | dry      |
| 7              | 350                           | 355              | 2                       | dry      |
| 8              | 300                           | 1064             | 2                       | wet      |
| 9              | 390                           | 1064             | 2                       | wet      |
| 10             | 330                           | 1064             | 2                       | wet      |
| 11             | 120                           | 532              | 2                       | wet      |
| 12             | 150                           | 532              | 2                       | wet      |
| 13             | 229                           | 532              | 2                       | wet      |
| 14             | 110                           | 355              | 2                       | wet      |
| 15             | 550                           | 355              | 2                       | wet      |

The EDX spectra recorded in the holes of the metal thread surface show that the base metal of threads is copper, with a thin layer of silver (Fig.7a). The presence of sulfur is also registered by these EDX spectra. It is known that silver

combined with sulfur forms silver sulfide as a black layer. Silver can be returned to its former luster by removing the silver sulfide coating from the surface. The total cleaning effects may be obtained by longer irradiation time rather than by high laser fluence.

Different kinds of damage may be visually observed on the sample surface after laser irradiation: darkening, yellowing, burning, and hole making. The laser irradiation with intensity sufficient for cleaning may produce the

alteration in the color of the silver surface that could be attributed to the inducing of oxide and sulphide films during the irradiation. The results are strictly dependent on the choice of severity of irradiation (energy density) and its duration (number of pulses) (Fig.2). Fig.6a, recorded in zone 3, cleaned by the wave length of 532 nm, has the areas with more than 98 % of Ag (Fig.6c). It is the evidence that the best results in the elimination of depositions are obtained by using a laser light of the wavelength of 532 nm.

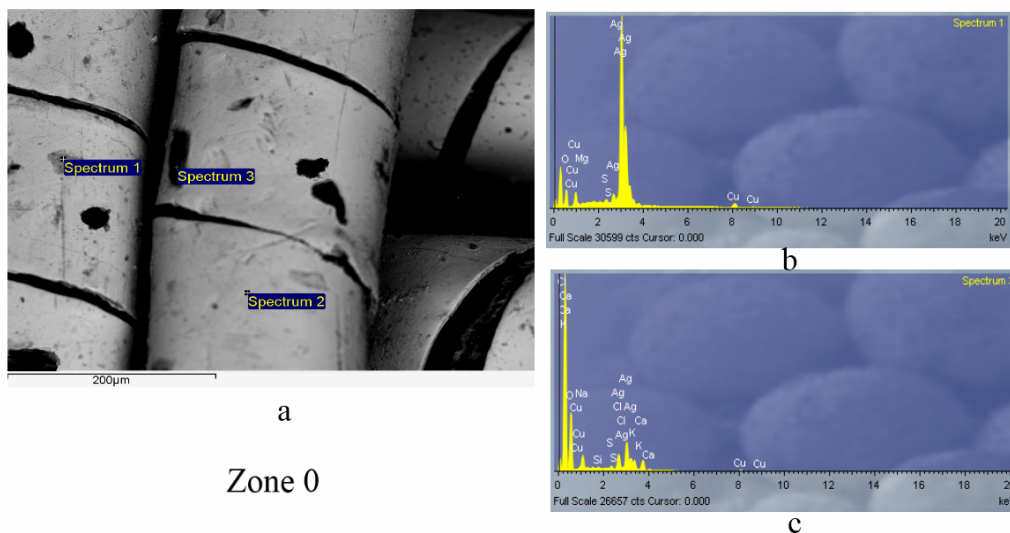


Figure 4. SEM (a) and the EDX spectra of zone 0 (b, c)

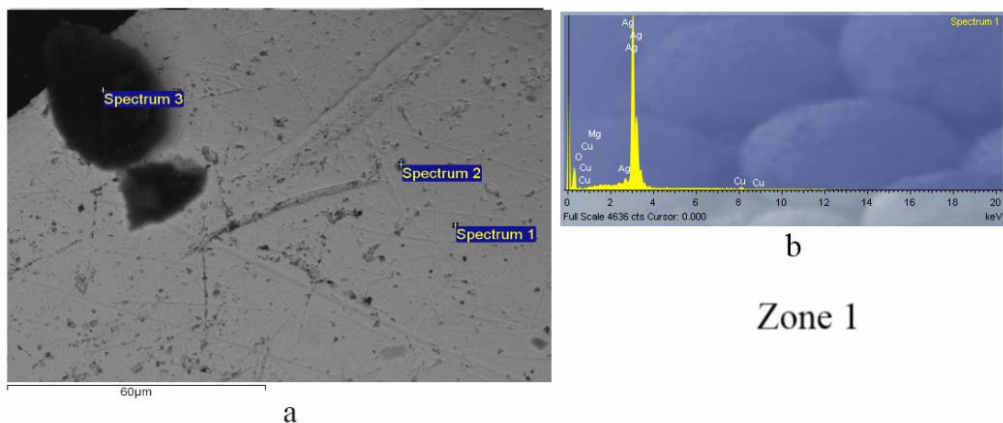


Figure 5. SEM (a) and the EDX spectra of zone 1(b)

Better sulfur (S) cleaning is obtained with the wavelength of 1064 nm than with the second (532 nm) and third harmonic (355 nm). The best laser wavelength for Cl

cleaning is 532 nm. Oxides are removed by the second harmonic. All registered spectra in zones cleaned by 355 nm wavelength show the lowest percentage of oxygen.

Table 2. EDX analysis for zones 0, 1 and 2

| Spectrum   | O     | Na   | Mg   | Al   | Si   | P | S    | Cl   | K    | Ca   | Fe | Cu   | Ag    | Zn | N    |
|------------|-------|------|------|------|------|---|------|------|------|------|----|------|-------|----|------|
| Zone 0     |       |      |      |      |      |   |      |      |      |      |    |      |       |    |      |
| Spectrum 3 | 57.58 | 6.73 | 0.42 |      | 0.31 |   | 0.64 | 4.30 | 2.08 | 4.37 |    | 1.26 | 22.31 |    |      |
| Zone 1     |       |      |      |      |      |   |      |      |      |      |    |      |       |    |      |
| Spectrum 1 | 3.35  |      | 0.48 |      |      |   |      |      |      |      |    | 1.86 | 94.31 |    |      |
| Spectrum 3 | 30.67 | 1.66 | 0.45 | 0.43 |      |   | 0.62 | 2.70 | 1.64 | 1.26 |    |      | 60.57 |    |      |
| Zone 2     |       |      |      |      |      |   |      |      |      |      |    |      |       |    |      |
| Spectrum 1 | 8.10  |      |      |      | 0.36 |   |      |      |      |      |    | 2.13 | 89.41 |    |      |
| Spectrum 2 | 24.04 | 1.88 |      |      |      |   | 0.32 | 1.32 |      |      |    |      | 64.15 |    | 8.29 |

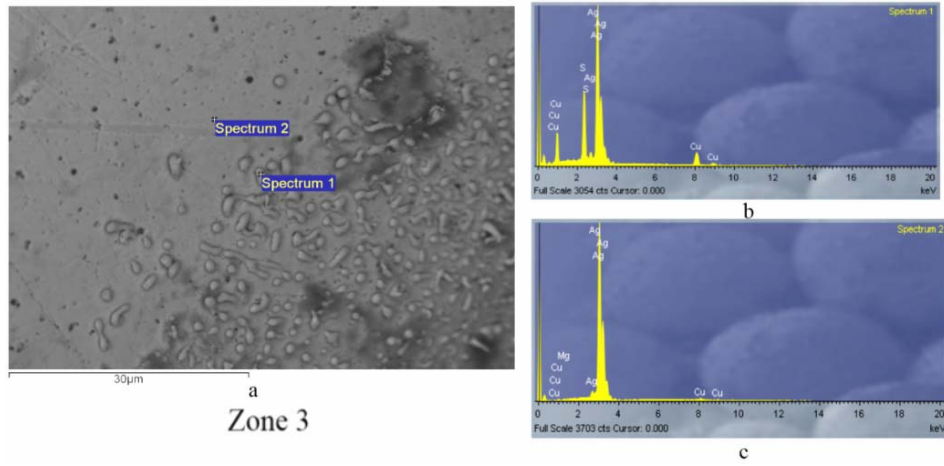


Figure 6. SEM (a) and the EDX spectra of zone 3 (b, c)

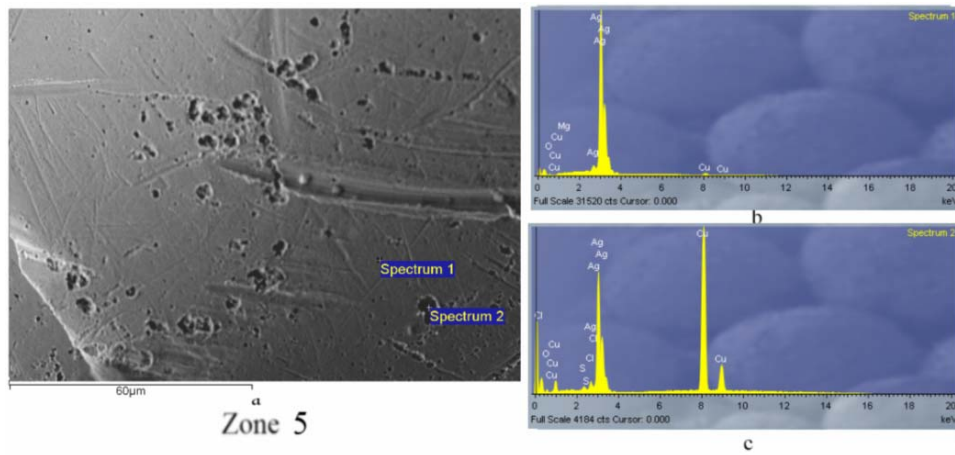


Figure 7. SEM (a) and the EDX spectra of zone 5 (b, c)

Table 3. EDX analysis for zones 3,4 and 5

| Spectrum   | O     | Na   | Mg   | Al | Si    | P | S     | Cl   | K | Ca | Fe | Cu    | Ag    | Zn | N |
|------------|-------|------|------|----|-------|---|-------|------|---|----|----|-------|-------|----|---|
| Zone 3     |       |      |      |    |       |   |       |      |   |    |    |       |       |    |   |
| Spectrum 1 |       |      |      |    | 11.51 |   |       |      |   |    |    | 13.92 | 74.57 |    |   |
| Spectrum 2 |       |      | 0.41 |    |       |   |       |      |   |    |    | 1.55  | 98.04 |    |   |
| Zone 4     |       |      |      |    |       |   |       |      |   |    |    |       |       |    |   |
| Spectrum 1 |       |      |      |    |       |   | 13.36 |      |   |    |    | 15.03 | 71.61 |    |   |
| Spectrum 2 | 12.33 | 1.53 | 0.46 |    |       |   | 0.56  | 2.05 |   |    |    |       | 83.07 |    |   |
| Spectrum 3 | 4.25  |      |      |    |       |   |       |      |   |    |    | 1.85  | 93.90 |    |   |
| Zone 5     |       |      |      |    |       |   |       |      |   |    |    |       |       |    |   |
| Spectrum 1 |       |      | 0.38 |    |       |   | 0.38  |      |   |    |    | 2.32  | 96.92 |    |   |
| Spectrum 2 |       |      |      |    |       |   | 10.97 |      |   |    |    | 20.24 | 68.79 |    |   |

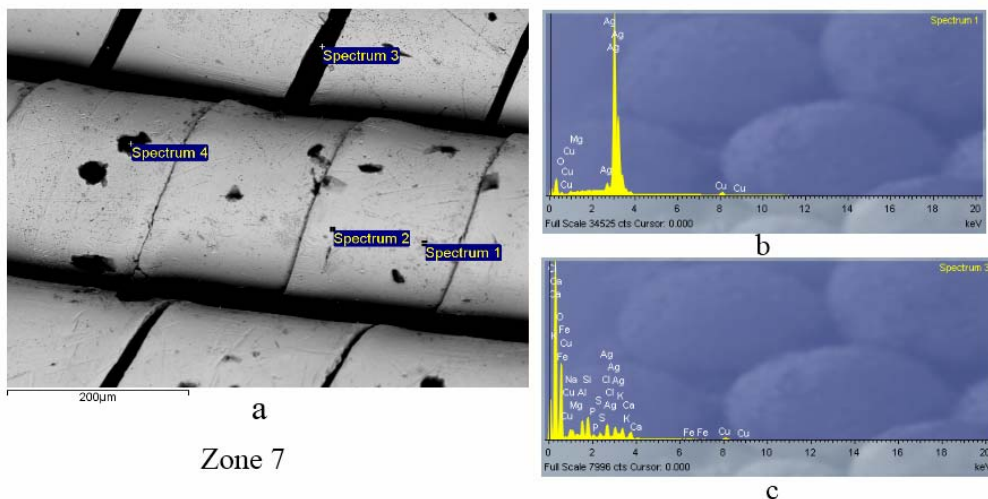


Figure 8. SEM (a) and the EDX spectra of zone 7 (b, c)

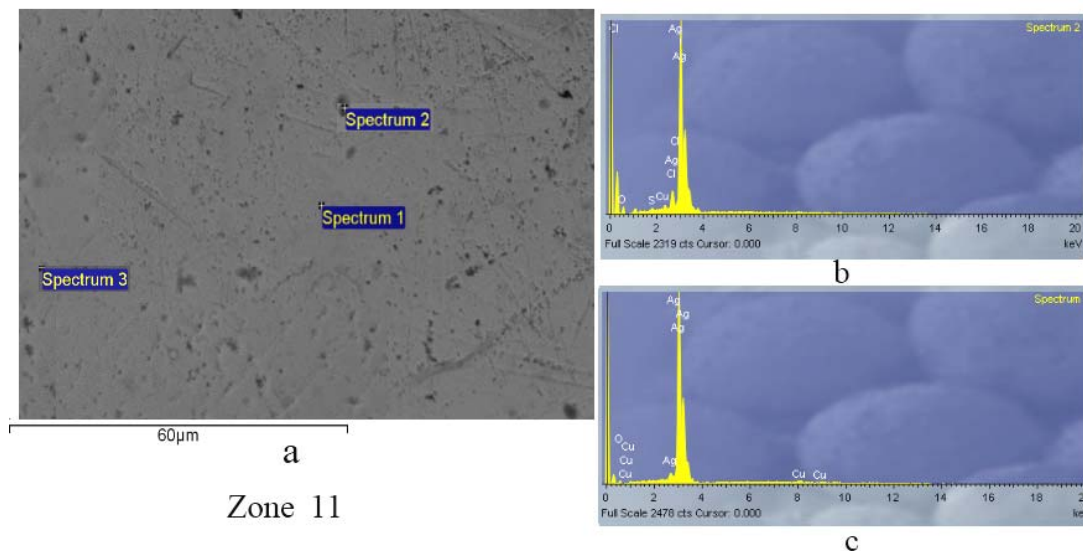


Figure 9. SEM (a) and the EDX spectra of zone 11 (b, c)

Table 4. EDX analysis for zones 7 and 11

| Spectrum   | O     | Na   | Mg   | Al   | Si   | P    | S    | Cl   | K    | Ca   | Fe   | Cu   | Ag    | Zn | N |
|------------|-------|------|------|------|------|------|------|------|------|------|------|------|-------|----|---|
| Zone 7     |       |      |      |      |      |      |      |      |      |      |      |      |       |    |   |
| Spectrum 1 | 6.05  |      | 0.37 |      |      |      |      |      |      |      |      | 3.14 | 90.43 |    |   |
| Spectrum 3 | 60.86 | 3.01 | 0.74 | 3.98 | 5.21 | 0.77 | 1.24 | 4.37 | 3.30 | 2.82 | 1.05 | 3.84 | 8.81  |    |   |
| Zone 11    |       |      |      |      |      |      |      |      |      |      |      |      |       |    |   |
| Spectrum 1 | 2.28  |      | 0.34 |      |      |      | 0.71 |      |      |      |      | 2.62 | 94.05 |    |   |
| Spectrum 2 | 3.25  |      |      |      |      |      |      |      |      |      |      | 1.85 | 94.90 |    |   |

As a result, the near infrared laser radiation of 1064 nm wavelength causes a large thermal effect both on silver and cotton, while the ultraviolet radiation of 355 nm has a small thermal effect on the surfaces and the radiation is more effective in removing silver tarnish successfully without damaging the underlying organic material.

In the case of the 1064 nm wavelength, the silver surface was changed and shows various colors such as orange, red, yellow and blue (Fig.1, zones 1, 2, 8, 9 and 10). This implies that the composition of the surface based on silver sulphides has been changed by laser-induced heat causing further surface degradation by thermal oxidation. At the 532 nm wavelength, similar phenomena appear, with the formation of surface whitening and the change of color is mostly to white- yellow (Fig.1, zones 4, 5, 11, 12). In the outer zones (Fig.1, zones 6,7,14 and 15), cleaned by a laser of 355 nm, there are no changes of color. This means that the thermal contribution or generation at the use of UV irradiation of 355 nm is too small to change the surface color. The similar results are presented in [14].

Spraying the surface with a very thin film of water before cleaning has been proposed in some papers [13]. Our tests show that this parameter has significant effects. The ablation rate of corrosion products could be increased. Zones 1 and 9 have been irradiated with the same laser fluence and wavelength, but the effects of cleaning are better in zone 9 than in zone 1. The thermal effects are less visible in zone 9. Zone 15 has been cleaned by 5 time higher energy in relation to zone 14. It is high and

unnecessary energy, since the goal of cleaning in the conservation process is to clean the artifact while preserving its original look.

### Conclusion

The combined use of laser irradiation and a SEM analysis represents an interesting way to identify and study ancient textiles with silver threads. The obtained experimental results can be considered as a very important step in a study aiming at corrosion and dirt removal without impinging the original textiles and metal threads. Laser cleaning of metal threads is widely used for military uniforms and other regalia, but side effects that modify the appearance of materials are not yet eliminated. Our results confirm that, if lower laser fluence is applied for cleaning, less damage occurs, but sometimes the cleaning may completely modify the appearance of the material (the change of surface color in the heat-affected zone, in and around the laser-irradiated surface). Textile professionals and conservators must be included in laser cleaning processes, since they may give precise guidelines for future tests in the optimization of the cleaning parameters.

The results confirm that a shorter wavelength provides higher removal efficiency and lower threshold laser fluence for the removal of the surface corrosion and dirt layers. A shorter wavelength such as UV radiation (355 nm) is much more effective and efficient for cleaning silver threads since it does not provide any apparent damage both on cotton and inside metal threads.

The results of the tests show that the water sprayed surface of the sample can be well cleaned by much lower laser fluence. This is very important for successful and safe laser cleaning of ancient textiles with corroded silver threads.

Another important conclusion is related to the effect of the laser impact on the long term conservation of museum textile items such as collections of uniforms, national costumes, flags, banners and home textiles in national, ethnographic and military museums. Further tests have to be conducted to determine how reactive metal is after cleaning. If it does become more reactive, a cleaning process may not be advisable. In such a case, the artifacts have to be placed in a very pure environment.

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## Lasersko čišćenje tekstilnih eksponata sa korodiranim metalnim nitima: optimzacije parametara procesa

U radu su prikazani rezultati čišćenja korozije na tekstilnim eksponatima sa metalnim nitima pomoću lasera. U mnogim muzejskim zbirnama nalaze se eksponati kao što su uniforme, narodne nošnje, zastave i kućni tekstil, ukrašeni vezom metalnim nitima. Korozija metalnih niti je jedan od najvećih problema, koji oštećuje vezene eksponate. U praksi, veoma često, klasične metode ne daju očekivane rezultate i primena lasera je sledeći korak čišćenja korozionih produkata. Nd-YAG laser je korišćen za čišćenje korozije vezanih eksponata iz muzejske, studijske zbirke. Efekti u zonama ozračenim laserom su ispitivani optičkim mikroskopom, SEMom i EDX analizom. Određeni su izabrani parametri za uspešno i bezbedno čišćenje korozije na metalnim nitima.

*Ključne reči:* tekstil, tekstilni materijal, uniforma, metalna nit, korozija, čišćenje korozije, primena lasera.

## **Лазерные очистки коррозии экспонатов из текстиля с металлическими нитями: оптимизации параметров процесса**

В этой статье приведены результаты очистки коррозии на экспонатах из текстиля с металлическими нитями с помощью лазера. Во многих музейных коллекциях представлены экспонаты, такие как формы, народные костюмы, флаги и домашний текстиль, вышитые металлической нитью. Коррозия металлических нитей является одной из самых больших проблем, которая повреждает вышитые экспонаты. На практике, очень часто, классические методы не дают ожидаемых результатов и применение лазера является следующим шагом очистки следов коррозии. Nd-YAG лазер используется для очистки коррозии вышитых экспонатов из музейных исследовательских коллекций. Эффекты в областях облученных лазером были исследованы с помощью оптического микроскопа, SEM и EDX анализом. Некоторые параметры определяются и выбираются так, чтобы успешно и безопасно очистить металлические нити от коррозии.

*Ключевые слова:* текстиль, текстильные материалы, форма, металлическая нить, коррозия, очистки коррозии, применение лазера.

## **Nettoyage laser des objets exposés en textile aux fils métalliques corrosifs: optimisation des paramètres du processus**

Dans ce papier on a présenté les résultats du nettoyage de corrosion chez les objets exposés en textile aux fils métalliques réalisé au moyen du laser. Dans plusieurs collections de musée on trouve les objets tels que uniformes, costumes nationaux, drapeaux et textile de maison qui sont ornés de broderie faite en fils de métal. La corrosion des fils en métal est un des plus grands problèmes car elle endommage les objets exposés brodés. En pratique les méthodes classiques ne donnent pas souvent les résultats espérés et l'utilisation du laser est le pas suivant dans le nettoyage des produits de corrosion. Le laser Nd-YAG a été utilisé pour le nettoyage de corrosion sur les objets brodés appartenant à la collection d'étude de musée. Dans les zones irradiées par laser les effets ont été étudiés au moyen du microscope optique et en utilisant les analyses SEM et EDX. On a déterminé les paramètres choisis pour le nettoyage en sécurité et avec succès de la corrosion chez les fils en métal.

*Mots clés:* textile, matériau en textile, uniforme, fil métallique, corrosion, nettoyage de corrosion, application de laser.