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EVALUATING THE USE OF LASER IN ANALYSIS AND CLEANING OF THE ISLAMIC MARINE ARCHAEOLOGICAL COINS EXCAVATED FROM THE RED SEA

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Abstract

This study aims to evaluate the use of laser in cleaning and LIBS analysis of the Islamic Marine Archaeological coins excavated from under the Red Sea water. Laser tests using a Q-switched Nd:YAG laser at 1064 nm were performed on 2 different types of corroded coins. For evaluating the usefulness of the suggested setup protocol of laser used in this study, the coins taken into study were investigated, before and after the laser cleaning, with Scanning Electron Microscope with attached energy-dispersive x-ray analyzer (SEM-EDX). The results show that the number of shots of LIBS is a very important task while acquiring LIBS spectra. The first shot is very useful for investigating the corrosion layer. The fourth and the fifth shot are useful for investigating the core of the coins with a medium layer of corrosion. The second shot is the best for the coins covered with very thin layers of tarnish. This study confirms that the fifth shot (20 pulses) is the best condition to clean the coin with a medium layer of corrosion, while the second shot (2 pulses) is the best condition to clean the coin with a very thin layer of corrosion.

Keywords: *Marine archaeological coins; Laser cleaning; Nd:YAG laser; LIBS; SEM-EDX.*

Introduction

Saudi Arabia is located in the center of the ancient world, and it is usually considered as the sacred land of Muslims. Due to that, there is a high probability of excavating many different types of coins in archaeological sites. These coins may be dated back to different periods of history. Archaeological coins are important findings during archaeological excavations that provide the archaeologists with more information that is usually revealed by written documents that come in forms of effigies, short inscriptions, and useful symbols [1]. Coins can provide us with valuable information about the various aspects of ancient civilizations that used them.

Archaeological coins are subjected to various corrosion processes resulting in different corrosion products that gradually alter their aspect, shape, nature, and resistance [2-3]. The most typical type of deterioration seen in metal artifacts is the result of chemical changes rather than physical damage. Most metals except gold are not particularly stable [4]. The state of excavated archaeological coins, the corrosion products, and thickness of their layers on the archaeological coins depend on many factors such as the chemical composition of the coins and the environmental condition that surrounded the coins in their archaeological sites. There are many

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studies that have been done to investigate, understand, and analyze the corrosion products found on metals [5-16].

Silver objects consist of alloys with other metals, partly to make the alloy harder and to reduce the amount of silver used. These alloys, often containing copper as a major alloying element and lead and gold as impurities, can either be cast directly or cold–worked into the final form. In general, the most commonly employed alloys used to produce objects are: the so called "sterling silver" (92.5% Ag, 7.5% Cu), "coin silver" (90% Ag, 10% Cu), and eutectic or brazing alloy (71.9% Ag, 28.1% Cu). Since most "silver" objects are made from silver–copper alloys, it is important to know the structural characteristics of this type of alloy [17]. Silver corrosion processes vary according to the original composition of the silver alloy and the conditions to which it has been subjected. Therefore, the corrosion behavior of silver is a function of the surrounding environmental conditions. Silver is normally a malleable, ductile, and easily fabricated metal. However, some archaeological silver objects can be brittle, as a long-term consequence of corrosion and micro-structural changes [18].

Silver objects can be damaged by a saltwater environment. Thick encrustations form around the metal and objects undergo considerable attack by sulfate reducing bacteria. Accordingly, the most commonly encountered corrosion products on silver and silver alloys in a marine environment are silver sulfide and silver chloride. Both compounds are stable mineral forms and do not take part in any further corrosive action with the remaining silver. Therefore, like lead, silver corrosion products need to be removed only for aesthetic reasons and to reveal details hidden by the corrosion layers. Base silver alloys with copper, however, differ because copper corrodes preferentially and forms cuprous chloride, which continues to corrode the copper component of the silver alloy. Metal artifacts recovered from archaeological sites, especially marine sites, are very unstable and must be treated to prevent irreversible deterioration [19-20]. The reason to treat silver is to remove disfiguring corrosion layers to reveal details, for aesthetic reasons, to reduce mineral products back to a metallic state, and to remove the chlorides from the copper component of base silver alloys. Prior to the conservation treatment, the marine encrustations should be removed mechanically or, in some cases, by immersion in 10-30% formic acid solution [21]. The choice of cleaning method for a particular object has to be assessed by conservators in terms of risk and benefit to the object, as no method currently in use is 100% successful. Chemical cleaning methods are not easily controlled and can be unpredictable, usually resulting in the loss of the original surface. Air abrasive, whilst useful, is often dificult to control and can produce a matt surface. Mechanical cleaning can take a long time and damage can occur either through breakage due to pressure applied to the object or scratching of the surface [22].

The application of laser technology in the conservation process of archaeological metals has led us to define its benefits, especially in the cleaning process compared to the traditional techniques. Laser treatment vaporizes the active chlorides on the surface, avoiding possible damages derived from traditional cleaning techniques: Scratches and marks from mechanical treatments. Immersion in chemical substances often leaves remains, very difficult to remove [23]. Laser offers many advantages over traditional methods. Laser cleaning is a selective, non-contact method that leads to a better preservation of the surface [24-25].

Many researches have been done to investigate the use of lasers in investigating and cleaning different materials [26-35]. However, very few applied studies in using the laser in investigating and cleaning metal artifacts have been reported. The present work aims to evaluate and determine the most suitable setup protocol of laser such as condition, pulses and shots for successful cleaning and LIBS analysis of the Islamic Marine Archaeological coins (Shoiba Hoard Coins) excavated from under Red Sea water archaeological site, Shoiba Port, Near Jeddah, Saudi Arabia.

Experimental

Ancient Coins

Two selected coins were chosen for this study as examples for coins excavated from archaeological marine excavation site. The selected coins are 2 various examples for Islamic marine archaeological coins (called Shoiba Hoard Coins) excavated from under the Red Sea water archaeological site, Shoiba Port, Near Jeddah, Saudi Arabia. It is a treasure that contains thousands of silver coins (called Rasols coins) dating back to the seventh century.

Description of the studied coins

The studied coin A was found covered with a medium layer of corrosion products (in different colors: black, light blue, and blue-green) resulted from the degradation that occurred during its long-term undersea stay. Its aspect was so distorted that no details of the original surface could be retrieved (see Fig. 1A). The studied coin B in figure 1B was found covered with a very thin black layer of corrosion products resulted from the degradation that occurred during its long-term undersea stay. The corrosion layer was very thin and partially covered the surface details, such as inscriptions, marks, and stamps.

Fig. 1. Photos show the condition of the selected studied marine archaeological coins:
A - a coin covered with medium corrosion layer; B - a coin with a thin layer of corrosion;

In a previous study that have done by Abdel-Kareem et al (in press) using XRD on coins from this treasure, it was confirmed that these coins are made from an alloy made from silver (Ag), and copper (Cu). They confirmed that the corrosion products identified on the coins contained various types of copper and silver corrosion products. The identified corrosion products are Chlorargyrite AgCl which is in white color, Acanthite Ag_2S which is in black color, Brochantite $CuSO_4$ which is in black color, and Covellite CuS which is in black to grey color. The identified corrosion products consisted mainly of copper (II) carbonates $[Cu_2CO_3(OH)_2]$ Malachite in green color, Copper(II) oxide (CuO), Tenorite in a black corrosion layer, Paratacamite $[Cu_2(OH)_3Cl]$, Nantokite CuCl in green color, Copper oxide (Cu_2O), Cuprite in reddish color, Atacamite $[Cu_2(OH)_3Cl]$, Azurite $[2CuCO_3{\cdot}Cu(OH)_2]$ Silver(I) Chloride, Metallic Copper (Cu) and Metallic Silver (Ag) [36].

The experimental set-up used in investigating and cleaning of coin samples

A schematic detail of the experimental set-up used for analyzing and cleaning the coins is shown in figure 2. Briefly, the analytical LIBS technique consists of a Q-switched Nd: YAG laser ((BRIO, Quantel, France) operating at its fundamental wavelength (1064 nm, 5ns, 100mJ). The laser pulse energy used for LIBS analysis was 35mJ/pulse measured by a joule-meter (SCIENTECH, model AC5001, USA energy meter). The laser beam was focused on the target using a plano-convex lens of 10-cm focal length. The target was mounted on an X-Y-Z micrometric translation stage. The plasma optical emission was collected by a quartz optical

fiber with a diameter of 1.5mm. The direction of observation was fixed at an angle of 45^o with respect to the target surface. The plasma emission collected by the optical fiber was sent into an Echelle spectrometer and Mechelle software (Mechelle 7500, Multichannel Instruments, Stockholm, Sweden, with a focal length of 17cm and f-number = 5.2, Wavelength range: 200-1000nm.) coupled with an intensified CCD (ICCD camera, DiCAM – PRO, PCO-Computer Optics, Germany) for dispersion and detection of the spectral emission of the plasma. The obtained LIBS spectra then was displayed and stored on a personal computer. The same PC was used to control the delay between the laser firing time and the spectral acquisition time, as well as the duration of the acquisition gate. The delay time was 1000ns and the gate width was 2000ns for the entire duration of the experiment. The analysis of the emission spectra was accomplished using LIBS++ software.

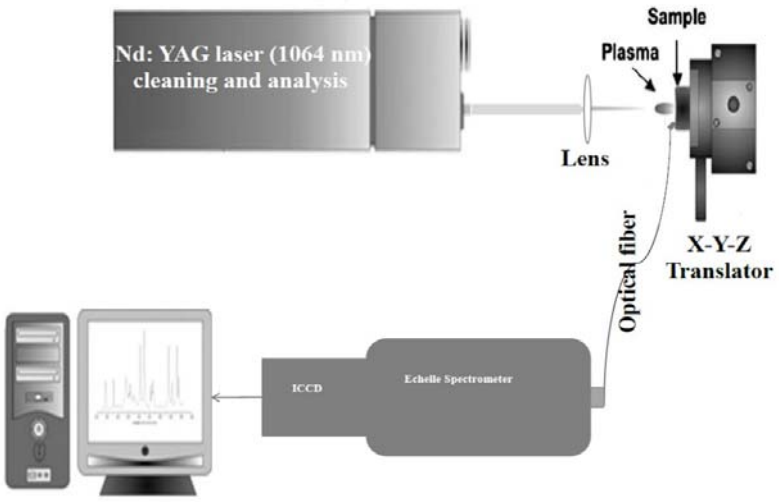

Fig. 2. The experimental set-up used in cleaning of coin samples

For establishing the cleaning of the coins, the setup shown in Fig. 2 has been used. The equipment that was used to achieve laser cleaning was a Q-switched ns Nd: YAG laser at 1064nm, the stage for controlling the sample motion and the plano-convex lens (10cm). The lens was not in the focus, but was at a distance of 16cm, i.e. the lens to sample distance was more than 6cm from the focal point (F = 10cm) (defocusing lens). The cleaning process has been evaluated with laser fluency values, at 1.6J/cm^2. The process of laser cleaning of the studied coins was shown in figure 3. The photos of the cleaning process have been obtained by optical microscopy (Olympus Model BH2-UMA) at a magnification of 100X.

For evaluating the usefulness of the suggested setup protocol used in this study, for analyzing and cleaning the selected coins, the same coins taken into study were investigated, before and after the cleaning, with a Scanning Electron Microscope (SEM) with attached energy-dispersive X-ray analyzer (EDX) that was commonly used in investigating the ancient coins. Scanning Electron Microscope (SEM) Model Quanta 200 with EDX was applied to examine the surface morphology of each type of metal threads with accelerating voltage of 30KV, at a magnification of 10X up to 4000X. SEM Energy dispersive X-ray analysis (EDX) was used to chemically analyze the corrosion layer of the two coins and the uncontaminated spots on their surfaces. The samples were prepared and investigated according to the protocol used by Abdel-Kareem [37].

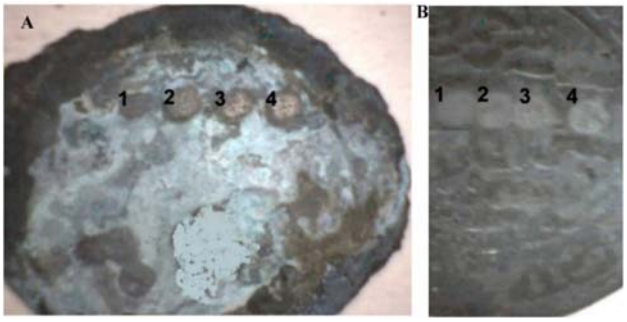

Fig. 3. The process of laser cleaning of the studied coins

Results and Discussion

Coin A (covered with medium corrosion layer)

Visual and microscopic examination

The superficial corrosion layer on coin A was treated with the tested laser radiation until the main surface of the coin was revealed. The results of visual observation of figures 1 and 3 and the microscopic examination of figure 4 showed that coin A before the laser cleaning was badly deteriorated and an extensive corrosion layer impeded the tested coin surface. The surface of the tested coin was characterized with a sticky corrosive surface with cracks and pits. It was clear that there were various types of corrosion in different colors: black, light blue and blue-green surface covered with marine residues. The results of the tested coin after the laser cleaning showed that the main surface of the silver coin (cleaned surface of the coin) was observed at the fifth shot (20 pulses)

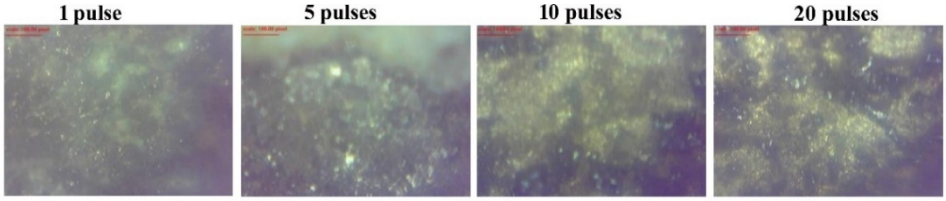

Fig. 4. The effect of cleaning conditions (using defocusing 16cm lens) at a focal length = 10cm) on the surface of Coin A

LIBS analysis

The results of LIBS analysis for the chemical composition of the tested coin A are shown in figure 5. These data represent the total elements identified from all LIBS spectra collected by shots from one to fifth which are used for acquiring the LIBS spectra. These data gave us information on the effect of the cleaning conditions (using defocusing 16cm lens, at a focal length=10cm) on the surface of Coin A.

It is noticed from the collected LIBS spectra, that the percent of these elements in LIBS spectra varies according to the number of LIBS shots used for acquiring the LIBS spectra. The results show that the contamination elements, such as Ca and Cu were more in the first shot (1 pulse) while the main substrate of the coin (silver Ag) had a low percentage. After increasing the shots it was noticed that the contamination elements such as Ca and Cu decreased and disappeared while the main component elements (Ag) increased. The results of LIBS spectra for the coin A (figure 5) indicate the presence of Ca and Cu as major elements in the corrosion compounds of corrosion layer, while the spectrum of the fresh surface indicates that the coin was made from silver Ag.

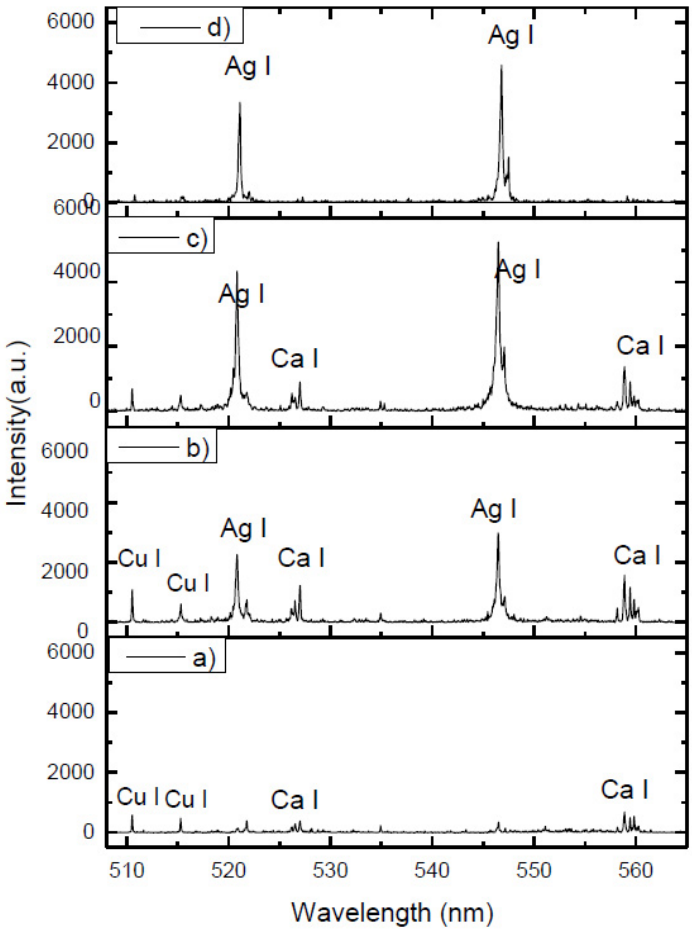

Fig. 5. Evolution of LIBS spectra with the number of pulses of coin A by depth profiling on crust for different spectral lines compared with the: a) 1st shot; b) 3rd shot; c) 4th shot; d) cleaned surface

The results in figure 5 show that the fifth shot (20 pulses) has the best condition to clean the coin A. The results show that all contaminated elements were removed and evaporated and only the silver, the main component of the coin is presented. From the obtained results it is clear that the number of shots of LIBS is a very important task while acquiring LIBS spectra. By comparing all the collected data and analyzing the corrosion products and contamination elements on the surface of coin, it is noticed that the first shot is the best condition for acquiring the LIBS spectra. This result confirms that the first shot is very useful for investigating the corrosion layer. The results show that the best shot for investigating the component of the core metal of the coin or the main composition of the coin depends on the thickness of the crusts and the corrosion layers on the surface of the coin. In our case, with a medium layer of corrosion, the fifth shot is the best condition for acquiring the LIBS spectra.

SEM morphological examination

Results of SEM morphological examination for coin A before and after laser cleaning are presented in figure 6. The results of SEM investigation of the coin A before the laser cleaning showed that the coin was covered with a layer of corrosion products mixed with marine deposits that disfigured it, hid its surface, figures and inscriptions and made it ugly. This composite layer can be seen clearly under SEM investigation (Fig. 6A). The results of SEM investigation of the coin A after laser cleaning by the fifth shot (Fig. 6B) showed that the

corrosion layer was removed from the surface of the coin. The surface of the coin becomes clear and the silver grains become clear and homogenous.

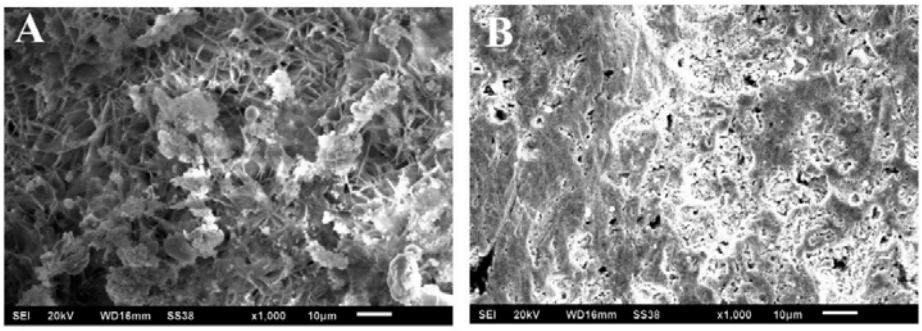

Fig. 6. SEM images of the coin A before and after the laser cleaning:
A - before the laser cleaning; B - after the laser cleaning

SEM-EDX analysis

The results of EDX analysis of coin A before and after the laser cleaning are shown in figure 7. The results of the EDX analysis for the corrosion layer of the coin A before laser cleaning (see Fig. 7A, B) indicate that the contamination elements such as Cu, O, C, Al, S, and Fe are identified. The results show the presence of Cu, O and C as major elements while Al, Fe, S, and as minor elements. These results confirm that the corrosion layer consists mainly from copper corrosion products. The results show that the main components of coin are silver (Ag) and copper (Cu).

The results of the EDX analysis for the fresh surface of the coin A after laser cleaning by the fifth shot (see Fig. 8C and D) indicate that the contamination elements such as Cu, O, C, Al, S, and Fe were removed. The main component of the main surface of the coin is Silver (Ag). The percent of the silver after the laser cleaning is around 80% while before the laser cleaning was around 2%.

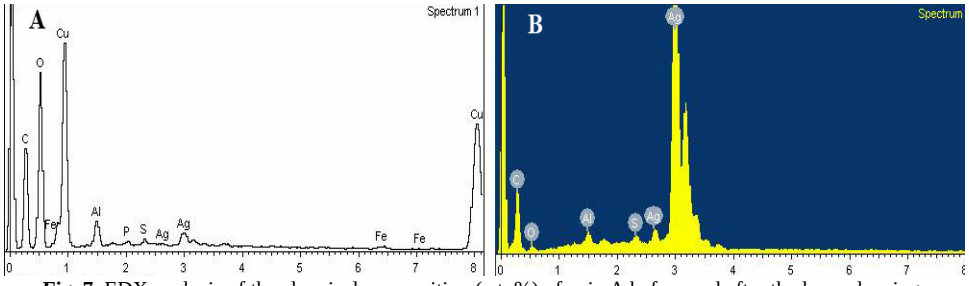

Fig. 7. EDX analysis of the chemical composition (wt. %) of coin A before and after the laser cleaning:
A - before the laser cleaning; B - after the laser cleaning

Coin B (covered with too thin layer of corrosion)

Visual and microscopic examination results

The results of visual observation (Figs. 1 and 3) and the microscopic examination (Fig. 8) showed that the coin B was covered with a very thin corrosion layer that partially covered the surface details, such as inscriptions, marks, and stamps. By observing the effect of laser cleaning on the surface of coin B while and after applying the laser cleaning process, it was noticed that the surface of the coin (cleaned surface) was observed at the forth shot (10 pulses) (see Fig. 8).

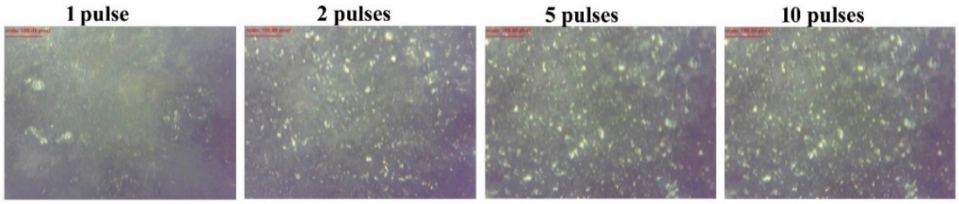

Fig. 8. The effect of cleaning conditions (using defocusing 16-cm lens) at a focal length = 10cm) on the surface of coin B

LIBS analysis results

The thin layer of corrosion products on coin B was treated with the tested laser radiation until the fresh surface of the coin was revealed. The results of LIBS analysis for the chemical composition of the tested coin B are shown in figure 9.

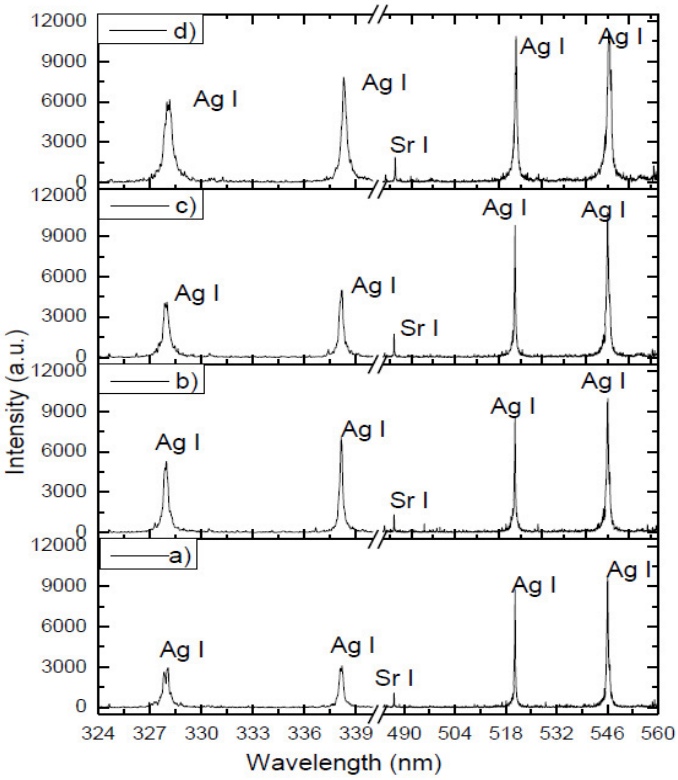

Fig. 9. Evolution of LIBS spectra with the number of pulses of sample 14 by depth profiling on crust for different spectral lines compared with the: a) 1st shot; b) 2nd shot; c) 3rd shot; d) cleaned surface

These data represent the total elements identified from all LIBS spectra collected by shots from one to forth, which are used for acquiring the LIBS spectra. These data give us information about the effect of cleaning conditions (using defocusing 16cm lens) at a focal length = 10cm) on the surface of the coin B. It is noticed from the collected LIBS spectra, that the percent of these elements in LIBS spectra varies according to the number of LIBS shots used for acquiring the LIBS spectra. The results show that contamination elements such as Sr are present in the first shot (1 pulse). From the second shot, it was noticed that the percent of

silver (Ag) became increased in a significant manner. This means that the contamination layer (corrosion products) was a very thin layer.

The results in figure 9 show that the second shot (2 pulses) is the best condition to clean coin B. The results show that all contaminated elements were removed and evaporated while only the silver remained presented. From the obtained results, it is clear that the number of shots of LIBS is a very important task while acquiring LIBS spectra. By comparing all the collected data, and by analyzing the contamination elements on the surface of coin B, it was noticed that the first shot is the best condition for acquiring the LIBS spectra. This result confirms that the first shot is very useful for investigating the corrosion layer. The results show that the best shot for investigating the component of the core metal of the coin or the main composition of the coin depends on the thickness of the corrosion layers on the surface of the coin. In our case, with a very thin layer of corrosion, the second shot is the best condition for acquiring the LIBS spectra.

SEM morphological examination

Results of SEM morphological examination for coin B before and after laser cleaning are presented in figure 10. The results of SEM investigation of coin B before the laser cleaning showed that the coin was covered with a thin layer of corrosion. The figures and the inscriptions on the coin surface appeared, but not clearly, because a very thin layer of corrosion covered them. This composite layer could be seen clearly under SEM investigation (Fig. 10A). The results of SEM investigation of the coin B after laser cleaning by the second shot (Fig. 10B) showed that the corrosion layer was removed from the surface of the coin. The surface of the coin became clear and the silver grains also became clear and homogenous. However, the results showed that the surface of coin B after the laser cleaning became cleaner than the surface of coin A after the laser cleaning.

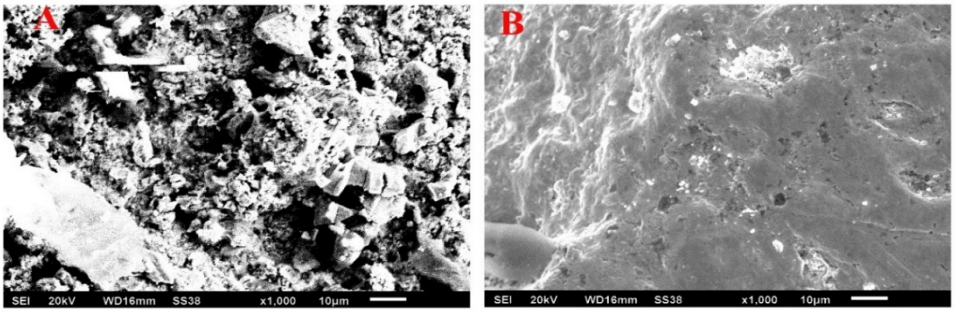

Fig. 10. SEM images of the coin B before and after the laser cleaning:
A - before the laser cleaning; B - after the laser cleaning

SEM-EDX analysis

The results of EDX analysis of coin B before and after the laser cleaning are shown in figure 11. The results of the EDX analysis for the corrosion layer of coin B before laser cleaning (see Fig. 11A) indicate that the contamination level of elements like S, C, O, and Al are too high. The results show that the silver is high (about 50%) compared to the same data for the corrosion layer on the surface of coin A (about 2%). These findings confirm our results obtained by visual observation, microscopic examination, and LIBS analysis, that coin B is covered with a very thin layer of the corrosion products.

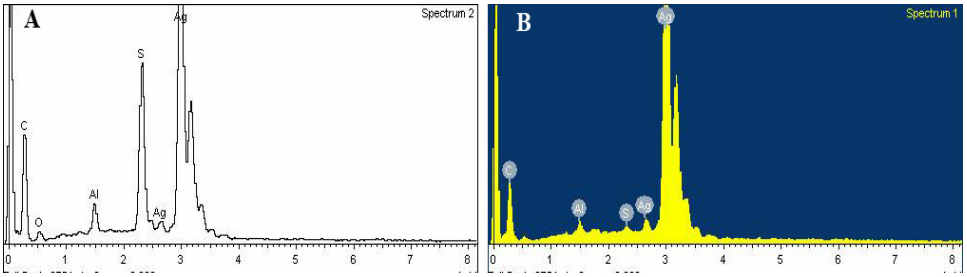

Fig. 11. EDX spectrum of the chemical composition (wt. %) of coin B before and after the laser cleaning: A - before the laser cleaning; B - after the laser cleaning

The results of the EDX analysis for the fresh surface of coin B after laser cleaning by the second shot (2 pulses) (see Fig. 11B) indicate that the contamination elements such as S, O, C, and Al were removed. The main component of the main surface of the coin is silver (Ag). The percent of the silver becomes about 85% while before the laser cleaning it was around 50%. The results show that the percent of the silver (about 85%) on coin B after laser cleaning (with the second shot, 2 pulses only) is higher than the percent of the silver (less than 80%) on coin A after laser cleaning (with the fifth shot, 20 pulses).

Conclusion

Q-switched Nd:YAG laser at 1064nm is very suitable technique for cleaning and investigating the ancient coins excavated from under Red Sea water archaeological site, Shoiba Port, Near Jeddah, Saudi Arabia. The results show that all contaminated elements were removed and evaporated from the tested coins after the laser cleaning.

The best condition for cleaning and revealing the surface of a silver coin that has a medium layer of corrosion is the fifth shot (20 pulses). While for cleaning and revealing the surface of a silver coin that has a very thin layer of corrosion, the second shot (2 pulses only) is considered as the best condition to clean that coin.

For using LIBS technique in analyzing ancient coins and evaluating the cleaning process, the number of shots of LIBS is a very important task while acquiring LIBS spectra. For the analysis of the corrosion products and other contamination elements on the surface of coin, the first shot is the best condition for acquiring the LIBS spectra. It means that the first shot is very useful for investigating the corrosion layer.

The best shot for investigating the component of the core metal of the coin or the main composition of the coin depends on the thickness of the corrosion layers on the surface of the coin. In case that the coin has a medium layer of crusts, the fourth and the fifth shot are the best conditions for acquiring the LIBS spectra, while for the coin that has a very thin layer of tarnish, the second shot is the best condition for acquiring the LIBS spectra.

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