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EVALUATING LASER CLEANING OF CORRODED ARCHAEOLOGICAL SILVER COINS

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ABSTRACT

The present work aims at evaluating the use of laser in cleaning and analysis of archaeological corroded silver coins. The selected corroded silver coins used in this study have been excavated from burial soil in Najran excavation site where there were more than 2500 rare coins dating back to pre-Islamic eras.. Laser cleaning tests were performed on 2 different types of corroded coins using a Q-switched Nd: YAG laser at 1064 nm. LIBS diagnostics was used to monitor the laser ablation process during the removal of different kinds of corrosion products with the aim of stopping the process once the cleaned surface is reached. XRD analysis was done to characterize the corrosion crust on the coin surface. For evaluating the usefulness of using laser in this study for analytical and cleaning of the selected corroded coins, the same coins were investigated, before and after laser cleaning, with (SEM - EDX). The results showed that for analysis of the corrosion products on the crust on the surface of coin, the best LIBS spectra have been obtained after the first laser shot. The number of laser shots needed for surface cleaning depends essentially on the corrosion layer thickness. Only 5 laser shots were needed for the removal of thin corrosion layers while for thick layers 15 laser shots were used. Laser is successful, effective and safer cleaning technique for removing corrosion products of the studied archaeological coins.

KEYWORDS: Laser cleaning, Nd: YAG laser, corroded archaeological silver coins, corrosion products, XRD, SEM-EDX, LIBS

1. INTRODUCTION

Archaeological coins are important excavations findings that provide the archaeologists with more information that is usually revealed by written documents appearing in form of effigies, short inscriptions and useful symbols. Coins are particular and important findings during archaeological investigations as source of documentation, understanding and knowledge of mankind evolution (Reale, et al, 2012). Archaeological coins are subjected to various corrosion processes resulting in different corrosion crust products that gradually alter their aspect, shape, nature and resistance (Al-Zahrani and Ghoniem, 2012, Ioanid, et al, 2011). The status of the excavated archaeological coins, the corrosion products and thickness of their layers depend on many factors such as the chemical composition of the coins, the environmental conditions in the archaeological sites. There are many studies that have been done for investigating, understanding feature and analysis of corrosion products on metals and explaining the mechanisms of the corrosions on the metals (Jegdic, et al. 2012, He, et al, 2011, Ghoniem, 2011, Mousser, 2011, Rodrigues, et al, 2011, Sandu, et al, 2008, Beck, et al, 2008, Ingo, et al, 2006, Nord, et al, 2005, Sandu, et al, 2005, Ingo, et al, 2004, Ullén, et al, 2004, Tronner, et al, 1995). There is no doubt that coins pose challenges to conservators, archaeologists and historians. From an archaeological perspective, the study of coinage reveals important information related to dating, social structure, economy and politics (Kotoula and Kyranoudi, 2013). From the conservators' perspective, all conservation processes should be done to reveal the surface morphology of coins to be legible, identified and dated, must be safe on coins and preserve them for the next generations.

Cleaning is usually the first step of many processes in conservation work. It is one of the most difficult operations undertaken when conserving metal artifacts (Novakovic, et al, 2013, Khedr, et al, 2011, Abdel-Kareem and Harith, 2008, Koh, and Sarady, 2003, Hamilton, 1999). Any cleaning process must be carried out with great respect and consideration of the original object's form, function and material. For this reason efforts should be done to find and develop new techniques and methods which are more suitable for cleaning of corroded archaeological silver coins. Laser cleaning is now becoming an accepted and important technique in conservation (Khedr, et al, 2011). Laser is effective and safer cleaning technique for archaeological artifacts. Laser offers many advantages more than traditional methods. Laser cleaning is a selective, non-contact method that leads to acceptable preservation for the surface of conserved objects (Koh, and Sarady, 2003, Lee, et al, 2003, Lee, 1999, Cooper, 1998). The other methods can damage the surface of the coin. For example the mechanical cleaning to complete reveal the surface of the decoration on the coin, the surface of coin will be damaged. Also the chemical cleaning react with the coin and deteriorate it.

Many researches have done to investigate the use of lasers in cleaning of different materials (Abdel-Kareem, et al, 2011, Koh, 2006, Colao, et al, 2004, Degrigny, 2003, Hacke, et al, 2003, Ochocinska, 2003). However, very few applied studies have been reported on the use of laser in investigation and cleaning of corroded archaeological silver coins. The present work aims to investigate and evaluate the use of laser cleaning on the Najran hoard coins. It aims to detect the chemical composition of the crust, corrosion products and the coin substrate by LIBS as well as to monitor the effects of the laser treatment on the surface of coins. SEM and optical microscopy (OM) are used to provide morphological information about the surface and how the cleaning has been affected. LIBS and SEM-EDX have been used to characterize the elemental composition and combined with XRD to provide the mineral constituents.

2. EXPERIMENTAL

2.1 Corroded ancient coins

This study is carried out on selected corroded archaeological coins from the Najran treasure. This treasure was discovered from the archaeological site of Al-Okhdood in Najran city, Saudi Arabia. It was discovered in the sixth season of the project excavation works in the year 1436 H. / 2007 A.D. The major finding in this excavation was the current treasure. This treasure is the first ever discovered treasure in the Arabian Peninsula through the excavations. It dates back to the era before Islam. It dates back to the 1st century A.D. It is a pottery jar filled with silver-copper coins (see Fig. 1).The treasure was found during the excavation carried out under agriculture burial soil in the middle of a room in the castle building (Al-Zahrani, et al, 2012).

2.2 Description of the studied corroded coins

The studied coins were found covered with thick layers of corrosion products, resulted from the degradation of the coins that occurred during their long-term burial. Their aspects were so distorted that no detail of the original surface could be retrieved. The corrosion layer had a nearly composite structure, including metallic remains, mineralized, metallic, insoluble phases and products formed from the interaction between soil components and metal corrosion compounds and also soil particles. For evaluat-

ing the laser cleaning of coins of the Najran Treasure, the laser cleaning process was carried on 2 different coins. A coin without any treatment before the application of laser cleaning and the second coin was cleaned previously mechanically.

The selected corroded coin A (without mechanical cleaning) represented in Fig. 1C, is covered with heterogeneous thick layers of crust in different colors and corrosion products coexisted with soil particles. The other studied corroded coin B represented in Fig. 1D that previously has been cleaned mechanically in the conservation laboratory. The mechanical cleaning is done to remove the crusts and corrosions that are loosely attached with the surface of the coin. The mechanical cleaning was done using spatula carefully to avoid scratching the main surface of the coin. The coin became after the mechanical cleaning covered with a thin layer of corrosion products and the surface morphology of the coins start to appear.

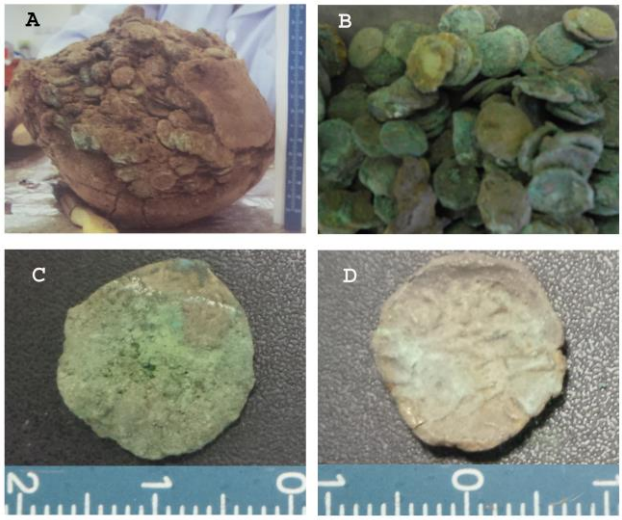

Figure 1: Pottery jar filled with corroded silver coins, A) Najran hoard coins excavated from the archaeological site of Okhdood, B) Magnified photo of the pottery jar in A), C) One of the selected corroded coin without any treatment. D) Another selected corroded coin after mechanical cleaning.

2.3 The experimental set-up used in investigation and cleaning of the selected corroded coins

A schematic detail of the experimental set-up used for analysis and cleaning of the selected corroded 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, 5 ns, 100 mJ). The laser pulse energy used for LIBS analysis was 35 mJ/pulse measured by a Joulmeter (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° with respect to the target surface. The plasma emission collected by the optical fiber was sent into an echelle spectrometer (Mechelle 7500, Multichannel Instruments, Stockholm, Sweden, with a focal length of 17 cm and f-number = 5.2, Wavelength range: 200-1000 nm.) 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 displayed and stored on a personal computer. The same PC was used to control the delay between the laser firing time and the spectra acquisition time, as well as the duration of the acquisition gate. The delay time was 1000 ns and the gate width was 2000ns during all experiments. The analysis of the emission spectra was accomplished using LIBS++ software.

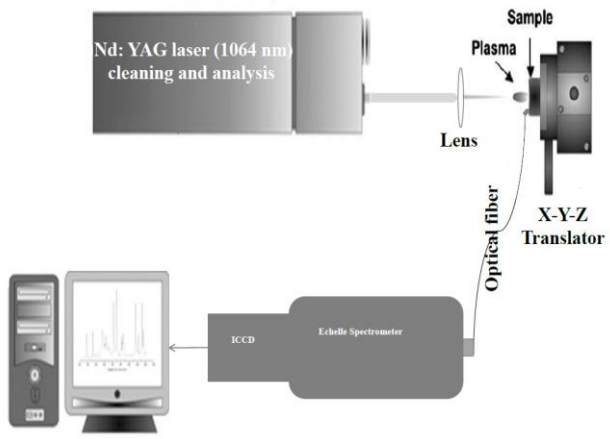

Figure 2: The experimental set-up used in LIBS and cleaning of the selected corroded coins

For establishing the cleaning of the selected corroded coins, the same setup shown in figure 2, has been used. The equipment that used to achieve laser cleaning in figure 2, were a Q-switched ns Nd: YAG laser at 1064 nm, the stage for controlling the sample motion and the Plano-convex lens (10 cm). The sample was not in the focus, but was at a distance of 16 cm, i.e. the lens to sample distance was more than 6 cm from the focal point (F=10 cm) (defocused setting). The cleaning has been performed with laser fluence values of 1.6 J/cm^2.The photos of cleaning have been obtained by optical microscopy (Olympus Model BH2-UMA) at magnification of 100X. The position of both coin A and coin B that have cleaned by different pulses were shown in Fig.3.

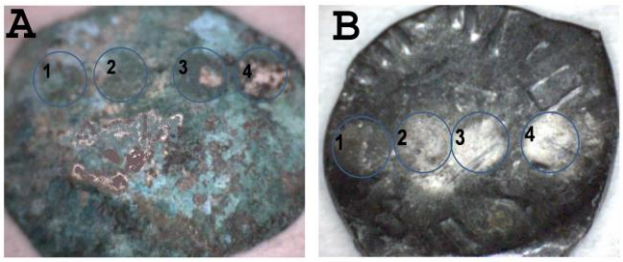

Figure 3: Process of laser cleaning of the studied corroded coins A) The corroded coin without any treatment before laser cleaning (1:1pulse, 2: 5 pulses, 3:15 pulses, 4:30 pulses), B) The corroded coin after mechanical cleaning (1: 1 pulse, 2: 5pulses, 3: 10 pulses, 4: 20 pulses).

For evaluating the analytical methods and conservation status of the selected coins, Scanning Electron Microscope with Energy dispersive X-ray Analysis has been used (Model JEOL JSM-6510LV, voltage 30 kV, magnification 10 X up to 4000X). It was used to examine the surface morphology of each type of the selected coins. SEM with 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 et al, (2008).

3. RESULTS AND DISCUSSION

3.1 The effect of laser on coin A

3.1.1 Visual and microscopic examination results

The results of visual observation and the microscopic examination showed that the coin A before the laser cleaning was badly deteriorated and an extensive corrosion layer impeded the tested coin surface (see figure 1). The surface of the tested coin characterized with a rough corrosive surface with cracks and pits. It is clear that there are various types of corrosion products in different colors: dark green, light green, greenish blue and metallic gray blackish surface covered with soil residues. The investigation of the layer of crust and corrosion products by XRD showed that it contains various types of copper and silver corrosion products mixed with soil residues such as calcite ($CaCO_3$) (see figure 4). The identified corrosion products consist 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 [$Cu_2(OH)_3Cl$], copper oxide (Cu_2O) cuprite in reddish color, chrysocolla ($CuSiO_3 \cdot H_2O$), atacamite [$Cu_2(OH)_3Cl$], Silver (I) Chloride, and traces of metallic silver (Ag). This results are in agreement with the results obtained by Al-Zahrani and Ghoniem, 2012, who identified the most of the corrosion products on the coins that they studied from this treasure. The current study suggest that it is probably that the corrosion products on the coins may be formed because the treasure was embedded in agriculture burial soil. The effect of the laser cleaning process on the surface of coin A in Fig. 5, show that the surface of the coin (cleaned surface) was observed at 15 pulses, and the spot removed completely by increasing the number of pulses (see Fig. 5).

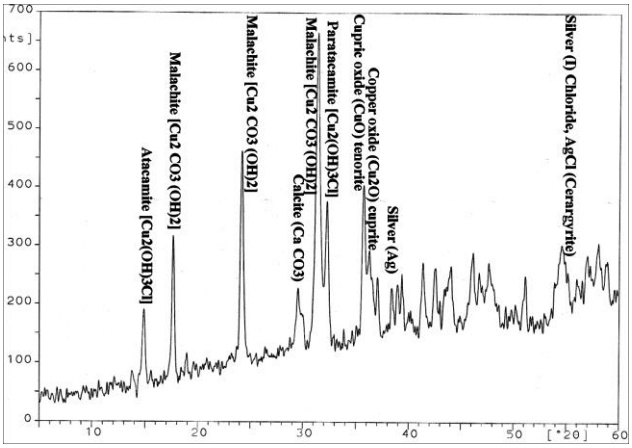

Figure 4: Example of the X-ray patterns of the corrosion products on the studied coins before any treatment

Figure 5: The effect of cleaning conditions (using defocusing 16-cm lens) the focal length=10cm) on the surface of coin A.

3.1.2 LIBS analysis results

The results of LIBS analysis for the chemical composition of the tested coin A are shown in figure 6. The emission spectra have been obtained for consecutive pulses and therefore provide an in-depth profile of existing elements. Depth profiling gives us indication about the appearance of the original elements of the coin when the crust layer is removed. It was clear that from the first pulse (figure 6a) the contaminated corrosion layer contains Ca, and Mg which may be come from the reaction between the coin and the soil around the pottery jar. Ca may be come from calcite ($CaCO_3$) observed in XRD results. At the 3rd pulse (figure 6b) the substrate is observed by detecting its characterizing elements such as Cu and Ag, while the emission lines of Ca and Mg approximately disappear. The elemental lines intensity of Cu and Ag is increasing at the 4th pulse (figure 6c) approximately with the same amount. By comparing the spectra of successive pulses with that of the coin surface after cleaning, it was found that the intensity of the emitting lines of Cu is decreasing and that of Ag lines is still high (figure 6d). We conclude from LIBS results; the pres-

ence of Cu lines along the successive pulses gives us probability that it was added to the main component which is silver during manufacturing of coin. Also the presence of copper in the first pulse in high percentage, indicates that these elements moved to the surface of the coin and chemical reaction between them and the surrounding environment occurred. This is emphasized by the minerals observed on XRD results mentioned above.

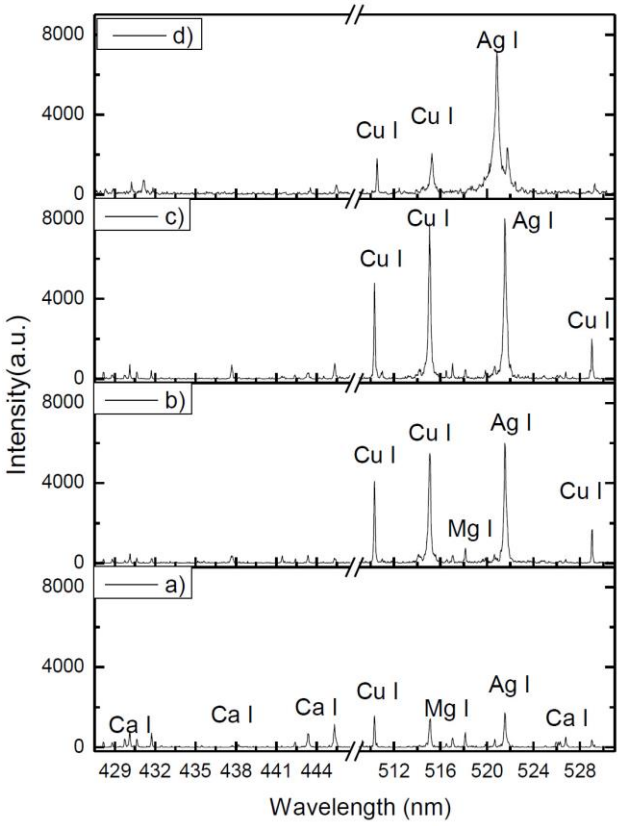

Figure 6: Evolution of LIBS spectra with the number of pulses of coin A by depth profiling: a) 1st pulse, b) 3rd pulse, c) 4th pulse, on crust and corrosion layer for different spectral lines compared with the cleaned surface (d).

3.1.3. SEM-morphological examination results

Photos of SEM morphological examination for coin A before and after laser cleaning were presented in Fig. 7. The morphological structure of the coin A before laser cleaning show raw hard crust and corrosion layer which are colored by green-bluish due to the corrosion produced on its surface. This layer of corrosion products mixed with soil relics that covered its feature and leads it to become ugly as shown in figure 7A. After laser cleaning (15 pulses), the SEM photographing of the coin A (Fig. 7B) shows approximately homogenous surface composed from silver grains free from corrosion of large grains.

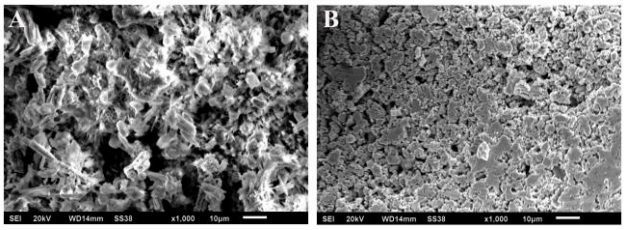

Figure 7: SEM images, A) photo before the laser cleaning, B) photo after the laser cleaning.

3.1.4 SEM-EDAX analysis results

The results of EDX analysis of coin A before and after the laser cleaning are shown in figure 8. The results of the EDX analysis for the corrosion layer of the coin A before laser cleaning (as shown in figure 8 A, B) indicate that the contamination elements such as O, C, Al, Si, S, Cl, K, Ca and Fe are detected. The results show the presence of Cu, O and C as major elements, while Al, Si, S, Cl, K, Ca and Fe as minor elements. These results confirm the results obtained by XRD that the corrosion layer consists of mainly of copper corrosion products.

The results of the EDX analysis for the fresh surface of the coin A after laser cleaning (15 pulses) (see figure 8 C, D) indicate that the main elements corrosion products such as Cu, O, C, Al, Si, S, Cl, K, Ca and Fe were removed. The main component of the fresh surface is mainly Silver (Ag) and the copper as minor element.

The comparison of EDX results before and after laser cleaning revealed that the essential element of coin A is the silver with concentration of 70%, while before the laser cleaning was about 3%. In addition to copper which is main element in the corrosion products in the crust was about 30%, while after laser cleaning its weight in the coin A by the EDX results becomes around 3%. The data obtained from EDX analysis of the coin A after the laser cleaning (Fig. 8C, D) is in agreement with LIBS results which revealed that the copper is found in the composition of the coin A after laser cleaning in low intensity, while the silver is found in high intensity (Fig. 6D). This confirms that the main component of the coin is mainly Silver (Ag) and the copper as minor element.

3.2 The effect of laser on coin B

3.2.1 Visual and microscopic examination results

The results of visual observation of coin B that is mechanically cleaned shown in figure 1D show smooth surface of thin layer of corrosion and the original surface of the coin was not observed. Fig. 3B and the optical microscopic photos (Fig. 9) showed that the spots and the corrosion layer on the surface of the coin after the laser cleaning were removed and the surface of coin became clear and the white shin-

ing color of silver is appeared. The silver is hardly observed at the 5th pulse and higher cleaning of corrosion was noticed at the 10th pulse. Damage has been observed at 20 pulses as shown in Fig. 3B and Fig. 9.

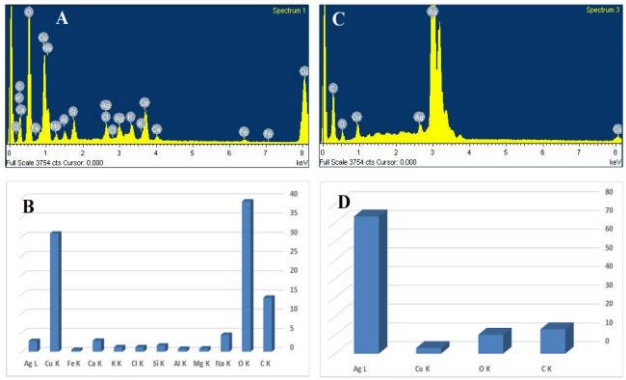

Figure 8: The EDX analysis of the coin A; A) the spectrum of EDX analysis before laser cleaning, B) Chart of the concentration (wt. %) of the detected elements in coin A before laser cleaning, C) The spectrum of EDX analysis after laser cleaning, D) Chart of the concentration (wt. %) of the detected elements in coin A after laser Cleaning.

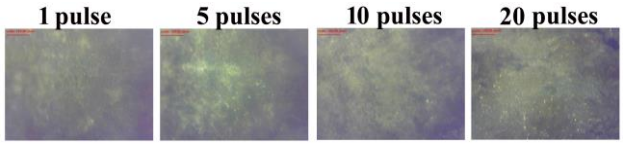

Figure 9: The effect of cleaning conditions (using defocusing 16-cm lens) the focal length = 10cm) on the surface of coin B.

3.2.2 LIBS analysis results

The results of LIBS analysis for the chemical composition of the tested coin B are shown in Fig. 10. By applying the depth profiling on the surface of coin B, the contaminated elements of corrosion layer disappeared and the silver was observed after 3 pulses. By comparing the spectra of the successive pulses with that of the cleaned surface, the contaminated elements of the corrosion layer disappeared completely and the silver lines are dominant. The results show that the copper was presented in the first and the 3rd shot but at the 5th shot the amount of Cu decreased and disappeared in the spectra of the cleaned surface. The results of LIBS spectra for the coin B (Fig. 10) revealed the presence of Ca, Mg and Cu as major elements in the corrosion compounds of corrosion layer. While the spectrum of the fresh surface shows the presence of silver.

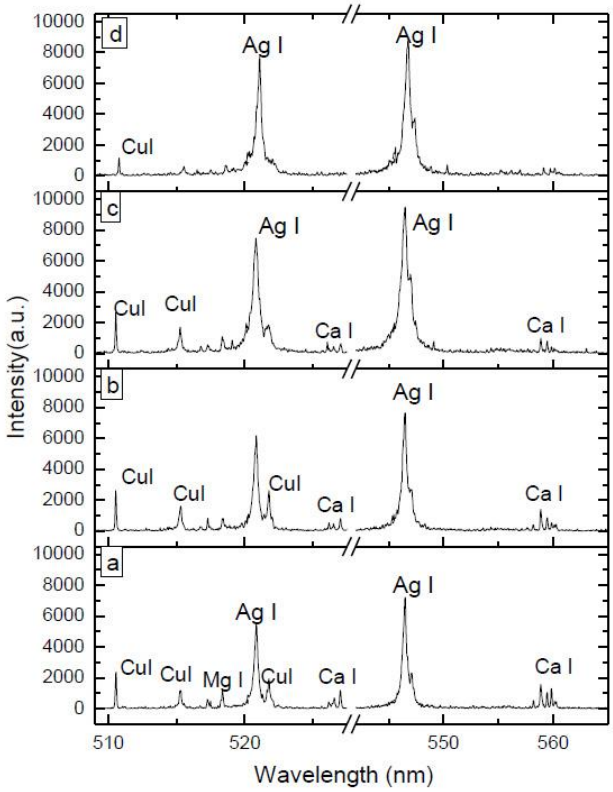

Figure10: Evolution of LIBS spectra with the number of pulses of coin B by depth profiling: a) 1st pulse, b) 3rd pulse, c) 5th pulse, on the corrosion layer for different spectral lines compared with the cleaned surface (d).

3.2.3 SEM morphological examination results

The morphological structure of coin B is shown in Fig. 11 that is photographed by SEM before and after laser cleaning. Due to the mechanical cleaning the crust becomes thin layer of corrosion with small sized grains (Fig. 11A). The white color of silver is noticed by laser cleaning in the second photo (Fig. 11B), and the characterizing feature of the surface appears to be more smooth and homogenous.

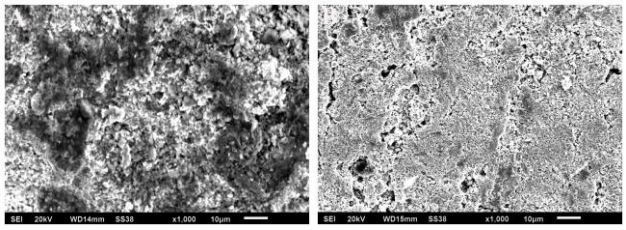

Figure 11: SEM images A) photo of surface coin mechanically cleaned but before the laser cleaning, B) photo after the laser cleaning.

3.2.4 SEM-EDX analysis results

The results of EDX analysis of coin B before and after the laser cleaning are shown in Fig. 12. The results of the EDX analysis for the corrosion layer (after mechanical cleaning) but before laser cleaning (as shown in Fig. 12 A and B) indicate that the concen-

tration of elements in the corrosion layer on the surface of coin B such as Cu, O, C, Al, Si, S, Cl, K, Ca and Fe are less than in with the same elements of the corrosion layer on the surface of coin A. The weight of the silver is higher than that of silver in coin A before cleaning. The results of the EDX analysis for the fresh surface of the coin B after laser cleaning (see Fig. 12 C and D) indicate that the main elements of the corrosion layer such as Cu, O, C, Al, Si, S, Cl, K, Ca and Fe were removed. The main component of the fresh surface is mainly Silver (Ag) and the copper as minor element. The weight of the silver as shown in figure 12D becomes about 80% after laser cleaning while before the laser cleaning is about 30% as seen in Fig.12B.

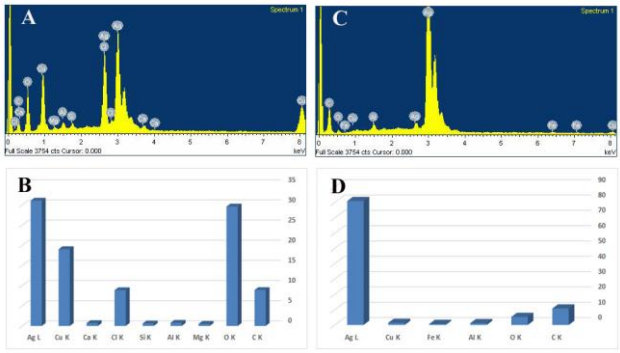

Figure 12: The EDX analysis of the coin B; A) the spectrum of EDX analysis before laser cleaning, B) Chart of the concentration (wt. %) of the detected elements in coin B before laser cleaning, C) The spectrum of EDX analysis after laser cleaning, D) Chart of the concentration (wt. %) of the detected elements in coin B after laser cleaning

The conclusion of these results were expected because of the effect of mechanical cleaning on coin B that remove some layers of corrosion before laser cleaning. In addition the processes of mechanical cleaning may also lead to the appearance of original surface of the coin in small parts that in turn leads to the presence of silver in the data before laser cleaning. These results confirm our results by optical microscopy examination and LIBS analysis that the mechanical cleaning remove a big part of the corrosion layer that cover the excavated coins. The coin became after the mechanical cleaning covered with a thin layer of corrosion products and the surface morphology of the coins start to appear.

4. CONCLUSION

Q-switched Nd:YAG laser at 1064 nm is very suitable technique for cleaning and investigation of ancient coins excavated from burial soil such as Najran excavation site. The results show that all elements of corrosion products that cover the tested coins were removed from the coins after the laser cleaning. This will preserve the coins against the deterioration as cleaning the coin avoid the reactivation of corrosion processes. 30 pulses are the best condition for cleaning and reveal of the surface of silver coin that has a thick layer of corrosion. While 10 pulses are the best condition for cleaning and reveal the surface of silver coins that have a thin layer of corrosion such as the coin cleaned mechanically. For using LIBS technique in analysis of ancient coins and evaluating the cleaning process, the number of shots of LIBS is very important task for acquiring LIBS spectra. For analysis of the corrosion products, crusts and other elements of the corrosion products on the surface of coin, the first shot is the best condition for acquiring the LIBS spectra of the crust. It means that the first shot is very useful for investigation the corrosion and dirt layer. The best shot for investigation 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 case that the coin has a thick layer of crusts, the fourth and the fifth shot are the best condition for acquiring the LIBS spectra. While for the coin that have a thin layer of tarnish, the second shot is the best condition for acquiring the LIBS spectra.

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