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Technical Analysis, Laser Cleaning and Numismatic Study of Tarnished Abbasid Silver Dirham from the 4th C A.H. (10th A.D)

دراسة وتحليل وتنظيف بأشعة الليزر لدرهم فضي عباسي من القرن الرابع الهجري (العاشر ميلادي)

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Abstract:

This work approaches the Islamic coinage as a rich resource for understanding the Islamic metallurgy. Interdisciplinary scientific research of Islamic coin, using numismatic and multi-analytical studies, provided complementary data to overcome the limitations of the current numismatic research by conservators, curators, and scholars in the Arab region. The chemical analysis of the coin alloy using XRF, EDS, LIPS, and XRD showed the presence of silver-Copper alloy, and the corrosion products. Moreover, the use of Nd: YAG ns laser cleaning (1064 nm) for removal of the tarnish and corrosion layers for conservation and aesthetics purposes was assessed using scanning electron microscope couples Energy Dispersive X-Ray Spectrometer (SEM-EDS), Laser Induced Plasma Spectroscopy (LIPS), and X-ray Florescence spectrometer (XRF).

The sensitive surface of the Islamic silver coin was treated safely using ns laser (1064nm) with fluences of 0.5-0.6 J/cm2 without inducing thermal side effects or chemical damage while a slight surface contrast loss was detected. Following the

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laser cleaning, the numismatic analysis of the selected coin's features showed that the coin was minted in the Abbasid period in Kofa (Iraq) dated to the Abbasid Caliph Al-Mustakfî billâh (333-334 A.H.; 944-946 A.D.).

Keywords: Numismatic, silver, Abbasid Dirham, laser cleaning, LIPS, corrosion.

الملخص:

يدرس هذا البحث العملات الإسلامية كمصدر غني لفهم علم المعادن الإسلامي، يقدم البحث العلمي دراسة متعددة التخصصات للعملة الإسلامية، باستخدام الدراسات النقدية والتحليلات الطيفية المتعددة لتوفير بيانات تكميلية للتغلب على قيود البحث الحالي في علم العملات من قبل القائمين على الترميم وأمناء المتاحف والعلماء في المنطقة العربية، أظهر التحليل الكيميائي لسبائك العملة باستخدام XRF و EDS و LIPS و XRD وجود سبائك الفضة والنحاس ومركبات الصدأ، علاوة على ذلك، تم تقييم استخدام التنظيف بالليزر Nd: YAG ns (١٠٦٤ نانومتر) لإزالة البقع والتآكل لأغراض الحفظ والجمال باستخدام أزواج المجهر الإلكتروني الماسح للأشعة السينية المشتتة للطاقة (SEM-EDS)، البلازما المستحدثة بالليزر التحليل الطيفي (LIPS) ، ومقياس الطيف الضوئي للأشعة السينية (XRF). تمت معالجة السطح الحساس للعملة الفضية الإسلامية بأمان باستخدام الليزر (1064nm) ns بمؤثرات ٠,٥-٠,٦ / J cm2دون إحداث آثار جانبية حرارية أو أضرار كيميائية بينما تم الكشف عن فقدان طفيف في التباين السطحي. بعد التنظيف بالليزر، أظهر التحليل النقدي لخصائص العملة المختارة أن العملة قد ضُربت في العصر العباسي في الكوفة (العراق) مؤرخة بفترة الخليفة العباسي المستكفي بالله (٣٣٣-٣٣٤هـ/ ٩٤٤-٩٤٦ م).

الكلمات المفتاحية: مسكوكات، فضة، درهم عباسي، صدأ، تحليل بالليزر.

1. Introduction

The Islamic numismatic collections in museums and private collections are source of significant historical information of Islamic documentary heritage which need to be documented, preserved, and interpreted to visitors and scholars[1]. In addition, the Islamic coinage is very rich resource for understanding the Islamic metallurgy and political and economic history across the Islamic eras and geographical territories. The Islamic coins are characterized by its distinctive shape, design, and inscription. The Umayyads (661-750 A.D/ 41-132A.H.) established a standard for all-epigraphic dirham (a quarter-dinar) where the dirhams were written mainly in an Arabic Kufic script ignoring the figural compositions inherited from Byzantium and Sasanian civilizations. likewise, the Abbasids (750-1517 A.D/ 132-

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750 A.H.), for example, dropped Qur'anic verses (sura) from the center of their coins and replaced it with the phrase "Muhammad rasul Allah". However, Islamic numismatists define the coin obverse as the side with the affirmation of God's unity (shahada). Previous studies of Islamic coinage and minting centers[1], proved that the Islamic dinars-made of gold, dirhams-made of silver and fals-made of copper were started to be struck in 76 A.H[2].

These coins were characterized by their low relief where the script and layout are the dominant elements with no concern on producing deep relief of humans or animals' depictions with relatively thin flans. The Islamic coins normally bear Arabic inscriptions of the names of caliphs and where the coin was struck in the minting centers which were distributed in different Islamic territories such as Damascus, Baghdad (Madînat as-salâm), Kufa, Isfahan. Rayy, Bukhara, Nishapur and Balkh[3]. Interdisciplinary scientific research of the Islamic coins using multi-analytical analytical techniques can provide complementary data for the research activities of the curators, conservators, numismatists, and scientists, and overcome the limitations of the current numismatic research in the Arab region[4].

Local numismatists focus mainly on the study of the decorative and inscriptional content disregarding the study of the coins alloy, microstructure and degradation which could provide integration with the historical studies. Interdisciplinary teams in the Egyptian and Arab museums should work together to preserve, authenticate, and interpret the historical values of the numismatic collections to visitors. Therefore, preservation of the numismatic collections requires characterization of the metal alloys, tracing the provenance of the metal and ore sources, and understanding the deterioration mechanisms, and providing well assessed conservation treatments. Precious and sophisticated metalworks were created for different purposes (such as jewelry, armor, and coins) through the Islamic

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civilizations using gold, copper, iron, lead, tin zinc and silver-based alloys and various production methods[1]. However, the study of Islamic metalworks has received a little emphasis by heritage scientists and art historians[2].

Islamic metalsmiths commonly used brass alloy through the cementation production process for producing metal products[3], silver-copper alloy (Ag-Cu) was mainly used for fabrication of early Islamic silver dirhams. Furthermore, the silversmithing was intensively used by Islamic craftsmen to product different types of artworks such as ornaments, jewelry, and household items using beaten metal industry[4]. The chemical compositions of the archaeological Ag-based alloys in the Mediterranean civilizations are mainly consist of Ag, Cu, and other elements such as Pb[5]. However, the chemical analysis of Islamic silver-based alloy of some early Abbasid coins (769-812 A.D/152-196 A.H.) showed the high presence of silver (Ag), with other elements such as copper (Cu), lead (Pb), and other impurities like P, Zn, Al, Mg and Si) using the cupellation process for silver alloying[6]. Different corrosion products (including copper and silver chlorides) on silver coins may grow on the surface during the burial, exhibition and storage times causing a serious damage.

Formation of thin or thick black tarnish (Ag_2S) on silver coins is a common deterioration aspect when the coins stored or exposed to an oxidative humid polluted environment, mainly rich of hydrogen sulfide (H_2S) or carbonyl sulfide (OCS)[7]. Moreover, due to the weathering agents and the presence of copper in the silver allow, different corrosion products could be formed on the silver coins such as Covellite (CuS), Brochantite ($CuSO_4.3Cu(OH)_2$), Chlorargyrite (AgCl), and Cuprite in reddish

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color where the coin's aesthetic, eligibility are altered[1]. Different cleaning methods have been tested for cleaning tarnished and corroded silver[2]. Mechanical, chemical, and electrochemical cleaning methods showed moderate and inhomogeneous cleaning effectiveness and aggressiveness on silver objects with need of special set up[3]. Laser, comparing to other traditional techniques, could be more controllable, non-contact, very selective and self-limiting cleaning technique, when optimized can provide a satisfactory cleaning of the archaeological delicate and sensitive silver surfaces without involvement of mechanical actions[4]. It was demonstrated that silver exhibit low absorptivity in the range of nm where the Nd: YAG 1064nm and 532 nm wavelengths were successfully exploited in laser cleaning experiments of pure and alloyed metal and silver artefacts comparing to other cleaning methods[5].

The paper aims to assess the potential of Nd: YAG nanoseconds laser cleaning using the fundamental wavelength (1064 nm) for removal of the tarnish and corrosion layers for conservation, aesthetics and improving the text readability. Moreover, the aim of the proposed study is to integrate both chemical analysis and numismatic information towards the characterization of corroded Islamic silver coin from the Abbasid period. Scanning Electron Microscope coupled with Energy Dispersive X-

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Ray Spectrometer (SEM-EDS), Laser Induced Plasma Spectroscopy (LIPS), X-ray Florescence Spectrometer (XRF), X-Ray Diffraction (XRD) analysis were applied for the characterization of coin alloy, soiling products, and assessment of laser treatment.

2. Materials & Methods:

2.1 Object:

Silver coin, from of private collection of the Numismatic Research Center at the Fayoum University in Egypt was selected for this study. The coin is dark and has uniform thin tarnished and corrosion layers, and soiling particles between the inscriptions where cleaning is necessary to improve the coin readability and stop further degradation (see fig. 1. a, b). The coin has no missing parts with a thickness of ˜ 0.89 mm, a weight of ˜ 3.68 g and diameter of ˜ 25.5–25.8 mm. The SEM investigation showed brittle surface with pitting and cracking by corrosion products (see fig. 1.c).

2. 2 Analytical Methods:

2.2.1 Microscopy

The surface morphology, technical analysis and assessment of laser cleaning tests of the coin were investigated using stereo microscope ZEISS (Stemi 2000-C, Germany), Scanning Electron Microscope coupled with Energy Dispersive X-Ray spectrometer (ESEM-EDS Quanta-200 FEI) in secondary electron (SE) and backscattered electron (BSE) modes with an acceleration voltage range from 25 to 30kV, low vacuum pressure (0.50–0.70torr) and working distance of 10mm. SEM Benchtop microscope Joel JCM-6000 was also used for assessment of coins conditions.

2.2.2 Laser Induced Plasma Spectroscopy (LIPS):

The portable LIPS apparatus[1] has been used consisting of a compact Q-switched Nd: YAG laser (1064 nm, 7-ns pulse duration, 0–20-Hz pulse repetition rate) as the excitation source. The laser emits an almost top-hat, low-divergence beam (0.8 mrad, using a graded reflectivity mirror), with a spot diameter of 2.5 mm and a maximum energy of 50 mJ /pulse (Ultra 50 CFR, BigSky). Such a laser source allows a sufficiently high intensity to be achieved using common planoconvex lenses. Here, it is about

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100 GW/cm2 using a focusing length of 60 mm. Under this condition, the laser spot on the sample has a diameter of about 120 µm and a corresponding maximum intensity of about 63 GW/cm2. Quantitative analyses of the main elements of the alloy and corrosion layers before and after laser cleaning were derived through the examination of the depth profiles (100 laser pulses; ablation rate ~1µm/pulse). The estimation of the top-layer depth from the measured depth-profile is not trivial due to the instrument response function, determining the measurement depth resolution[1].

2.2.3 X-Ray Fluorescence (XRF) spectrometry

The employed XRF Spectrometer (ELIO, XGLab srl, Italy) used to analyze the silver alloy and assessis based on a 25 mm2 active area Silicon Drift Detector and on a 50kV-4W X-ray tube generator, which employs a Rh anode. The excitation X-ray beam is collimated to a ~ 1.2 mm spot diameter on the sample surface. The typical energy resolution of the spectrometer is below 135 eV. The XRF head has been mounted on a stable tripod equipped with a lateral side arm (60 cm long). For all measurements, the following experimental conditions have been used: working distance ~ 1.4 cm, tube voltage = 40 kV, tube anode current = 40 µA, acquisition time = 40 s.

2.2.4 X-Ray Diffraction (XRD) spectrometry

In situ XRD analysis of the coin surface was performed using XRD spectrometer (XRD-6100, Shimadzu, Japan), at 40Kv, current 30.0 (mA), scan range 5.000-80.000, scan speed 12.0000 (deg/min) in continuous scan mode and multi-functional auto-search/match quantitation software using the base standard absorption correction method[2].

2.3 Laser Cleaning Tests

An optical fiber-couple long Q-Switched Nd: YAG laser with 120ns pulse duration and the fundamental wavelength 1064 nm was used to perform the laser ablation tests. The laser is equipped with a single-lens handpiece of homogenized laser beam distribution to allow a fine control of the laser spot diameter (Ø 1.6 mm) with a minimal overlapping. In all the cases a pulse repetition frequency of 2 Hz was operated with a wet irradiation condition using distilled water (which brushed once over the surface) to reduce

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the thermal effect of accumulated heat of laser irradiation. The pulse energy ranged from 5-50mJ which allowed a sufficiently wide variation of the operative fluences. Energy meter and neutral density filters were used to finely set the fluence. The laser fluence threshold (the lowest fluence at which ablative texturing of the unwanted layers was observable under the microscopes) for safe removal of the encrustation was determined through optical microscope and SEM observations, which were also exploited for measuring the alteration threshold of the silver substrate.

3. Results and Discussion

3.1 Technical Analysis and Laser cleaning:

The chemical analysis of the coin alloy using LIPS, XRF, EDS and XRD shows the presence of silver (Ag) as the main component (~94%) with substantial amount of copper (Cu, ~4%), with other impurities such as Pb, to make it harder and cost effective[1]. However, lead was normally found in a low concentration (2 wt%) in the Islamic metal alloys such as beaten brass and probably added foe economic reasons[2]. With LIPS analysis, a semi-quantitative evaluation of the bulk composition, in correspondence of the last fifty laser pulses, can be performed assuming a binary alloy (Ag-Cu) composition (neglecting other minor components) and using previously calculated LIPS calibration curves where the calculated copper concentration amounts to 4.4 (±0.4 wt%). The absence of lead in the chemical composition of the coin may indicate improvement of the production process and deliberate removal to avoid long-term embrittlement of the silver alloy[3].

The high content of silver and copper in the coin with the absence of gold could be an indicator of technological attempt during this Abbasid period to remove the gold from the silver alloy with better extraction quality of silver ores, or the use of difference silver ores of low gold content[4]. However, further analysis of Abbasid silver alloys is needed to track such hypnosis. ESEM-EDX, XRF and LIPS analysis evidenced that soiling and corrosion encrustations (fig.2.a) were mainly composed of Mg, Al, Si, Fe, Ca

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S, Cl, and Cu with respect to Ag peaks[1] (see fig. 2. b, c). These elements could be associated to earthy deposits from burial and Ag-Cu alloy corrosion products[2]. The presence of black tarnish layer on the coin may indicate the presence of silver sulfide (AgS) due to the reaction between the silver alloy and pollutants from the surrounding environment or the use of the coin. LIPS profile and XRF analysis reveal the presence of chlorine which may indicate the Cl rich burial or exhibition environments. The XRD analysis detected the crystalline compounds of atacamite (Cu_2Cl (OH)[3] and silver oxide (Ag_2O) (see fig.)[3]. The LIPS analysis confirms the presence of sequence of corrosion layers including the cuprite, atacamite and tenorite[4] (see fig.2.d).

For the coin conservation, readability, and aesthetic reasons, revealing details hidden by the encrustations layers is necessary. The laser cleaning of silver objects is a reliable technique which was standardized to minimize the risk of damaging the aesthetical appearance or chemical structure. However, the challenges of laser cleaning of silver include the preservation of the original surface and laser induced physic-chemical surface alterations. Following the characterization of the coin core and corrosion layers, laser irradiation at 1064 nm was conducted using a range of fluences to optimize the cleaning process using microscopic and spectroscopic analysis. Due to the expected high optical absorption of laser radiation by the black tarnish layers, and the high reflectance of the silver surface at 1064 nm comparing to the tarnish layers[5], and the relatively high alteration threshold of the latter favored by the present pulse duration (120ns) and repetition frequency of 2 Hz, satisfactory uncovering results were achieved within a rather wide operative fluence range[6]. Soiling was safely removed (fig. 3.b, c) with fluences of 0.6 J/cm2 and no surface micro-melting features were observed under ESEM examination. XRF analysis confirmed the effectiveness of the laser cleaning for the

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removal of the main elements constituting the soiling and corrosion layers which has an average thickness of 8μm. However, the shiny cleaned area showed a slight loss of surface contrast while the LIPS depth profiles acquired presenting an almost constant Cu/Ag ratio from surface to bulk (fig.2.b)[1].

The LIPS profiling shows the high level of Cu on the surface which act as a deoxidant and form copper oxides[2]. There is also a considerable value on the bulk is related to the formation of copper compounds such as cuprite (CuO) which is also responsible of the reddish appearance in some cleaned area (see fig.3a). As copper is more reactive with oxygen than silver[3], the cuprite thin layer is usually the first produced compound in Ag-Cu alloy oxidation phenomena and could be taken as an indicator of the effectiveness of the cleaning test (fig.4)[4]. Higher fluences, using pulse energy of over 35mJ, caused micro-melting of the silver coin surfaces due to the photo-thermal effects of laser radiation (fig. 3.d) as reported by previous studies[5]. Moreover, thorough inspections of the coin allowed to observe that the surface of the silver may be porous, and residues of material deposits and oxidation products trapped within the complex surface texture of the metal surface showing high roughness and interstices (fig. 3.e). These were not removed since they required too high fluences and then involved the risk of micro-melting.

3.2 Numismatic Analysis:

Following the optimized laser cleaning of the coin, the numismatic analysis to the study coin's features shows that the coin was minted in the Abbasid period and represents written Arabic Kufic inscriptions only (no depictions). The silver dirham from Kofa (Iraq) dates to the Abbasid Caliph Al-Mustakfî billâh (333-334 A.H.; 944-946 A.D.)[6]. The coin thickness is ˜ 0.89 mm with a wighet of ˜ 3.68 gm and diameter

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of ˜ 25.5-25.8 mm which is sligtly higher than the earlier Umayyad period[1]. The observe of the coin has the inscriptions in three annulets where the outer margin shows circular qur'anic inscriptions: "God commands in the past and the future; and on that day the believers will rejoice in God's Victory" (يفرح لله الأمر من قبل ومن بعد ويومئذ المؤمنون بنصر الله) while the inner margin shows the place and date where the coin was made "In the name of Allah, this dirham was struck in El-Kufa in 333 A.H. (بسم الله ضرب هذا الدرهم بالكوفة سنة ثلاث وثلاثين وثلثمائة). The center shows inscription of "there is deity but God Alone; al-Muzaffar Abu'l-Wafâ" ("أبو الوفا المظفر لا شريك له الله وحده لا إله إلا"). The reverse has inscriptions in two annulets where the margin shows qur'anic inscriptions: "Muhammad is the messenger of Allah, he sent him with guidance and the religion of truth to manifest it over all religions even if polytheists dislike it" (محمد رسول الله أرسله بالهدى ودين الحق ليظهره على الدين كله ولو كره المشركون") while the center shows inscription with the name of the Caliph: "Belongs to God; peace be upon him; Caliph Al-Mostakkfi Bellah" ("لله محمد رسول الله صلي الله عليه وسلم المستكفي بالله الخليفة").

4. Conclusion:

In conclusion of this research, the application of LIPS, XRF, XRD and EDS analysis techniques allowed the characterization of the silver dirham coin as Ag-Cu alloy with high percentage of silver and slightly high content of copper (which maybe deliberately added to harden the alloy or for economical purposes). The absence of gold may indicate of the use of different extraction technique of silver ores, but such hypnosis requires further analysis on Abbasid dirhams collections. LIPS provided depth profiling of the coin alloy to better understand the chemical composition of the Ag-Cu alloy and deterioration mechanism comparing the surface analysis techniques such as the XRF and EDS. The nanosecond laser (1064nm) has removed the unwanted layers safely as attested by the morphological and elemental study of the surface showing the selectivity of the laser that allowed to protect the cuprite layer. Following the laser cleaning, the numismatic analysis of the silver dirham proved that the coin dates to the Abbasid period and was struck in Kufa in 333 A.H.

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