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LASER AND ELECTRON BEAMS PHYSICAL ANALYSES APPLIED TO THE COMPARISON BETWEEN TWO SILVER TETRADRACHM GREEK COINS

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Abstract

Physical analyses by Laser Ablation coupled to Mass Quadrupole Spectrometry (LAMQS), and Energy Dispersive X-ray fluorescence (EDX) induced by electron beam are applied to the investigation of two silver Tetradrachm Greek coins. Quantitative analysis of elements, silver compounds and isotopic ratios have been investigated in the two samples. Significant differences in the elemental content and in the morphological aspects are observed.

1. Introduction

Laser Ablation coupled to Mass Quadrupole Spectrometry (LAMQS) is a technique useful for compositional analysis of different materials. It can be associated to X-ray fluorescence (EDX) and scanning electron microscopy (SEM). These analyses have been applied to two silver coins, one presumably true and one false. The coin is a rare silver tetradrachm from Messana (Messina, Italy), dated to 470 - 466 B.C. and coined under the ruling of Anassila [1]. The flexible laser control conditions and the relative rapidity of analysis are the main advantages of the method. The laser ablation of the coin is preceded by investigations on silver calibration samples in order to know the ablation rate vs. laser pulse energy [2].

The mass quadrupole spectrometry, coupled to the laser system, is a powerful tool for measuring the mass-to-charge ratio of the vapour composition. The energy of the laser pulses deposited onto the sample surface induces desorption and vaporization of the most superficial layers. The vapor is then ionized and the quadrupole analyzer permits to detect, on-line, the mass-to-charge ratios of removed atoms and molecules.

2. Materials and Methods

The object of this investigation is a true silver tetradrachm from Messana. The coin weight is 17.50 grams, the average diameter is 23 mm and the average thickness is 2.5 mm. The false coin shows similar figures. The two coins are of the same historical period and issued by the same issuing authority. The insets of Fig.1 show the photos of the two faces of the investigated coins, the true in the top inset and the false in the bottom one.

The samples have been analysed by means of a SEM and EDX facility using 30 keV electron beam. The penetration depth of the electron beam in silver is about 1.6 μm. The quantitative analysis was obtained taking in account the different X-ray production cross-sections of the elements, the Si(Li)-detector efficiency vs. the X-ray energy and the X-ray self-absorption corrections in the investigated silver depth [3]. The laser ablation was performed in high vacuum (10^{-7} mbar) with a Nd:Yag pulsed laser working at 1064 nm wavelength in single pulse and at 30 Hz repetition rate. The single pulse has a duration of 9 ns. The incidence angle of the laser beam is 45° and the spot area is about 2.3 cm^2. In order to avoid any damage to the original coin patina, the laser was employed at a very low intensity of the order of $4.8x10^6$ W/cm^2, using 100 mJ pulse energy, 0.04 J/cm^2 laser fluence, 30 Hz repetition rate and an irradiation time of about 10 s. In such conditions only the most superficial atomic mono-layers can be removed, without damage of the surface [2]. Measurements demonstrated that, in the above mentioned conditions, 10 s laser irradiation time remove less than 10 nm Ag thickness. A Balzer-Pfeifer MQS spectrometer, 200 amu full scale, less than 1 amu mass resolution and less than 1 ppm sensitivity, was interfaced to the vacuum chamber. MQS permits to separate the isotopic masses of the detected elements.

3. Results

The EDX spectra of the true and the false coin are reported in Fig. 1. Spectra show a very good agreement. The main elements detected in both samples are very similar. Their concentrations in the true coin with respect to the false one are: Ag = 66.64/74.65; C = 17.01/13.14; Mg = 4.55/4.90; O = 4.13/1.66; Cl = 2.32/0.62; S = 1.47/0.96; Fe = 1.04/1.09; Al = 0.97/0.30; Cu = 0.94/2.10; Si = 0.51/0.15; Ni = 0.41/0.42. The true coin contains higher concentration of C, O, Mg, S, Cl and Cu with respect to the fake. This comparison indicates that the patina of the true coin is more rich in silver oxides, sulphides and chlorides, as expected in the case of old silver coins. Moreover, the bulk composition of the true coin contains more copper, about twice the fake concentration.

The LAMQS relative quantitative analysis in the true coin surface indicates the following experimental atomic ratios: C/Cu = 0.38; Fe/Cu = 0.19; Mg/Cu = 0.088 against the EDX values of 18.11; 1.11 and 4.84 for the three ratios, respectively. These three ratios for the false coin surface assume the values: C/Cu = 4.5; Fe/Cu = 4.0; Mg/Cu = 3.0 for the LAMQS analysis and 6.27; 0.52; 2.34 for the EDX analysis, respectively.

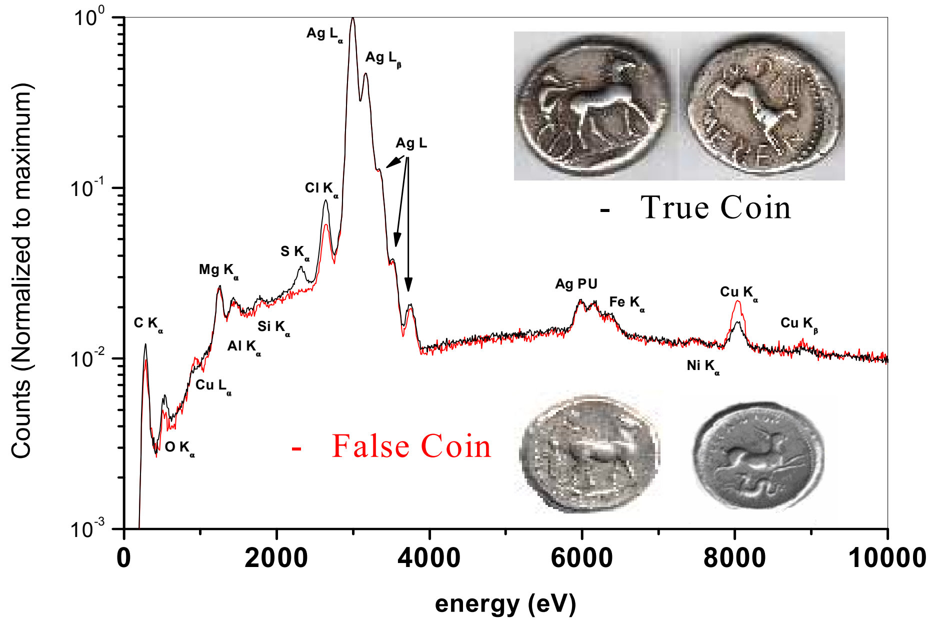

Fig. 1: EDX spectra comparison between true and false coins and photo of the front and back faces of the true greek tetradachm (top inset) and of the false coin (bottom inset).

The apparent differences in the measurements are due to different depth analysis of the two techniques: LAMQS is relative to the first superficial layers, up to a depth of about 10 nm, while EDX is relative to deeper layers, up to about 1.6 μm (range of 30 keV electrons). The differences indicate that the false coin patina is more recent and thinner with respect to that of the true coin. The MQS mass spectra reports the presence of some compounds in the patina of the two samples: 123 (AgO), 139 (AgS) and 142.5 (AgCl). The Ag-oxide and the Ag-cloride are present in both patinas but higher concentrations are found in the true coin. The Ag-sulphured compound, AgS, typical of old patinas, is present only in the true coin.

LAMQS analysis allows the measurement of the isotopic ratio of the detected elements. Ag has two stable isotopes, Ag-107 with an average abundance of 51.84% and Ag-109 with an average abundance of 48.16% [4]. Thus the expected isotopic ratio is Ag-107/Ag-109=1.076. In order to distinguish the type of silver used to produce the two coins, the Ag isotopic ratio was measured as indicated in the LAMQS spectra of Fig. 2c and 2d for the true and false coin, respectively. These spectra show an anomalous experimental isotopic ratio ranging between 1.19 and 1.22 for the true coin and a normal isotopic ratio of 1.072 for the false coin. The morphology of the two coin surfaces also shows a significant difference. The colour of the old patina in the true coin is dark, due to the natural ageing of the tetradrachm surface, while the colour of the fake patina is clear and bright, indicating a recent time of coinage. The edges of the represented figures are very smooth in the true coin and more defined and sharp in the false coin. Moreover, the microscope images show that the true coin contains many large surface irregularities while the surface of the false coin appears more uniform.

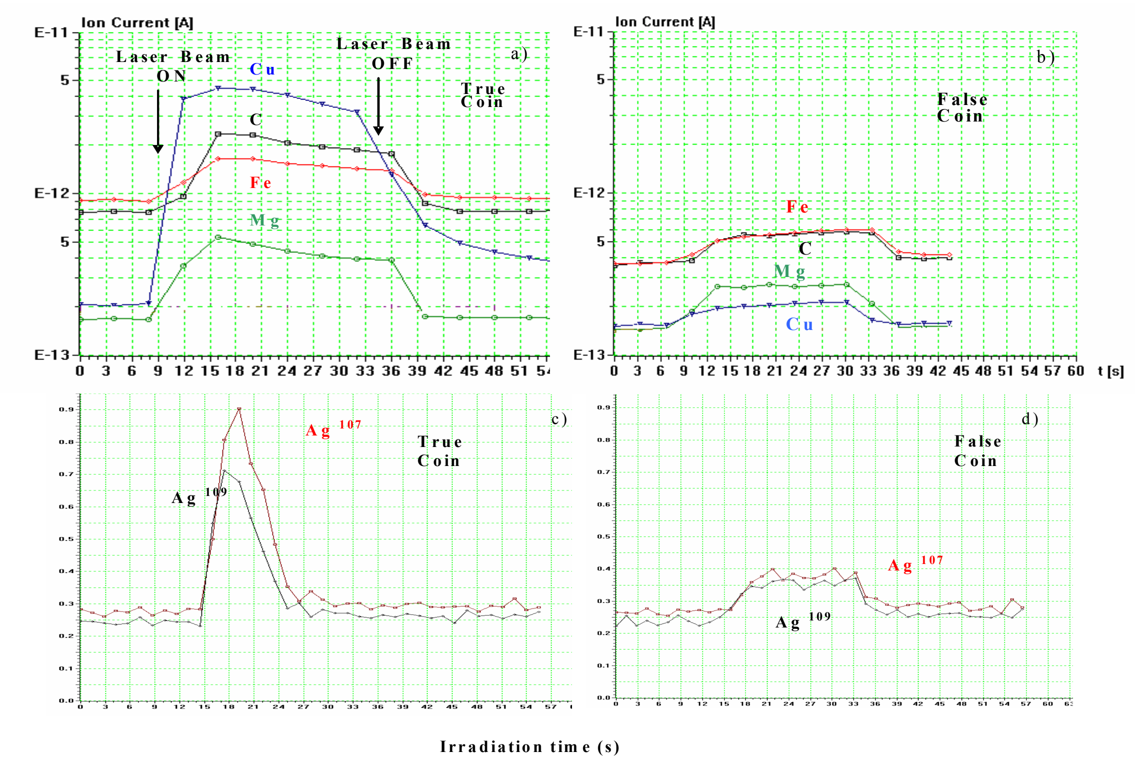

Fig. 2: LAMQS mass spectra vs. time for the elemental masses 12(C), 24(Mg), 56(Fe) and 64 (Fe) in true (a) and false (b) coins at the laser switch ON and OFF and for the Ag isotope masses 107 and 109 in true (c) and false (d) coin.

4. Discussion and Conclusions

Although the false coins are produced with high-level scientific approaches, showing a very similar elemental composition to the true ones and reproducing figures very similar to the originals, the deep investigations with modern physical techniques (SEM, EDX and LAMQS) allow to distinguish false from true coins. An autoptical analysis, particularly in doubtful cases, must be associated, when possible, to a set of proper physical-chemical analyses in order to achieve the better level of certainty in evaluating the authenticity of an ancient coin as well as of other types of metallic pieces of archaeological interest.

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