LASER ABLATION COUPLED TO MASS QUADRUPOLE SPECTROMETRY (LAMQS) APPLIED TO ANCIENT COINS

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Abstract

A Nd:Yag laser operating in second harmonic (532 nm), 3 ns pulse duration, 1-150 mJ pulse energy and 1-10 Hz repetition rate is employed to irradiate different coins placed in high vacuum chamber. The ablated material, in vapor phase, is analyzed by a mass quadrupole spectrometer in the range 1-300 amu with sensitivity up to 1 ppm. The "on line" analysis permits to investigate on the elements, chemical compounds and isotopic ratios characterizing the coin composition.

Focused and unfocused laser beams can be employed to irradiate sub-millimetric or tens millimetric areas, respectively. The first method is employed to determine the elemental depth profiles from surface up to about 0.1 mm. The second method is employed to analyze the average composition of the superficial patina layers. This micro-invasive technique, associated to the characteristic X-ray fluorescence emission due to 20 keV electron impact, was employed to analyze different coins, based on bronze and silver, from VI up to XX sec.

INTRODUCTION

The Laser Ablation coupled to Mass Quadrupole Spectrometry (LAMQS) is becoming an interesting analysis technique useful to investigate on the surface composition of different materials comprised ancient metallic coins [1].

The laser-target interactions give rise to a localized surface vaporization with formation of a crater which dimensions depends on the laser spot, laser energy and number of laser shots [2]. The high energy stability, repetitive beam profile and flexibility permit a controlled material removal from solid surface, layer by layer, till the wished depth.

The choice of the best laser irradiation parameters and the relative rapidity of analysis are the main advantages of the method, which make this technique attractive for elemental depth profile analysis, surface cleaning and non-disruptive surface processes. The ablation yield, given in terms of removed depth per laser pulse, can be measured in a con-trollable manner by using suitable calibration samples irradiated at different laser intensities [3]. The surface analysis is limited by the laser spot, controllable from the optical focusing lens. The penetration depth of the single laser shot depends on the laser and target properties. Thermal effects, mainly induced by infrared and visible lasers, enlarge the penetration depth in conductive targets, due to their high thermal conductivity. Photochemical effects, mainly due to ultraviolet lasers, limit the ablation depth only to the penetration absorption light and can be employed for analysis in insulator samples [4].

The atomic and molecular emissions from the laser irradiated target can be analyzed by using a mass spectrometer, which permits to measure the masses with high sensitivity and high mass resolution, permitting to detect ppm level element and compound concentrations and to distinguish isotopic masses.

By increasing the irradiation time it is possible to remove atoms from depth layers and, by knowing the ablation rate, the mass spectrometry analysis may give the depth profile of the detected masses in the investigated surface. By using micrometric laser spots it is possible to investigate on the sample depth in a micro-invasive mode.

In this work LAMQS and characteristic X-ray fluorescence (XRF) are applied to some coins in order to determine their elemental composition, chemical compounds and isotopic ratios, both in surface and in depth, in order to give interesting information to numismatic field.

MATERIALS AND METHODS

The laser ablation was performed with a pulsed Nd:Yag working at 532 nm, 3 ns pulse duration, 1-10 Hz repetition rate and 1-150 mJ pulse energy. The laser beam was directed on the target placed in high vacuum (10^{-6} mbar) through a thin glass window. The spot diameter is 1 mm^2 and the incidence angle is 45°. The target can be moved vertically with the vacuum feedthrough, so that each laser shot can hit a fresh flat surface. Fig. 1 shows a photo of the experimental setup.

In order to avoid any damage of the target surface, the laser was employed generally at a low intensity, of the order
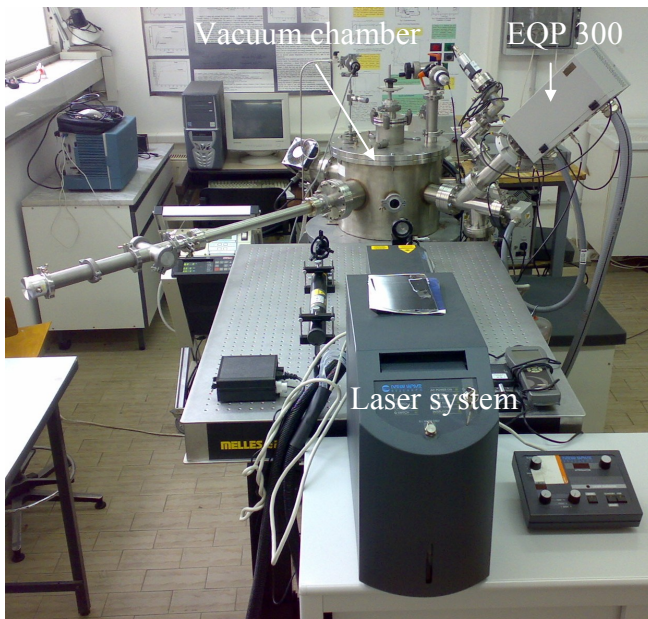
Fig. 1: Photo of the experimental set up.

of 8.3×10^8 W/cm^2 corresponding to 25 mJ pulse energy, and at 10 Hz repetition rate mode for times of the order of 20 seconds or less. In such conditions only the most superficial atomic monolayers can be removed, without damage of the surface and the ablation rate on a Cu and Ag calibration samples demonstrated that the removing depth is about 10 nm/s [6]. During depth analysis the laser energy generally is increased to 150 mJ at which the removing depth increases to about 1 mm/s.

Two different bronze coins of archaeological interest coined in the Mediterranean basin, coming from Antinopoulis (Egypt) and coined in the VI-VII century a.D. and Syracuse (Sicily, Italy), coined in the same historical period, were analyzed. The Egyptian and Syracuse coins are reported in the photo of Fig. 2a and Fig. 2b, respectively. Moreover, two different silver coins, consisting in a Greek tetradrachm from Messana (Messina-Italy) dated to 470–

Fig. 2: Photo of the four investigated old coins: The Alexandria bronze coin of VII-VII sec. a.D. (a); the Syracuse bronze coin of VII-VIII sec a.D. (b); the Greek silver coin tetradrachm of IV sec B.C. (c) and the recent Italy silver coin of XX sec. (d).

466 B.C. and coined under the ruling of Anassila, and from Italy of 1937, coined under the Vittorio Emanuele III re d'Italia, were also analyzed.

The Greek and Italian coins are reported in the photo of Fig. 2c and Fig. 2d, respectively.

A Balzer-Pfeifer MQS spectrometer, 300 amu full scale, less than 1 amu mass resolution and less than 1 ppm sensitivity, was interfaced to the vacuum chamber in order to detect the masses emitted from the laser ablation process. The MQS mass selection occurs thank to a selective radiofrequency applied to four parallel rods, while the high sensitivity is obtained by the use of a secondary electron multiplier. The quadrupole operates by plotting the mass yield vs. the mass value or, by fixing the masses of interest, by plotting the masses vs. the irradiation time. Characteristic X-ray fluorescence (XRF) analysis, induced by 20 keV electron beam, was performed with a high vacuum SEM microscope and a X-ray Si(Li) detector. XRF permitted to analyze the elemental composition of the investigated samples and to furnish the input masses parameters for the MQS spectrometer. XRF analysis is limited to the electron range depth in the metal which is about 600 nm for Ag and 800 nm for Cu. LAMQS analysis depends on the ablation yield and on the number of the laser pulses employed to ablate the metal surface. A surface profiler, Tencor P-10, with high horizontal and vertical resolution, has been employed to measure the surface roughness on the surface of the two coins. It uses 1 mg tip force sweeping on the selected zones of the sample, especially in correspondence of the craters produced by the laser ablation on the coins. The crater profile permits to measure the ablation yield in terms of ablated depth/pulse and to correlate the MQS profile with the real sample depth.

RESULTS

The preliminary analyses performed through XRF permitted to evince the elemental composition of the patina layers of the different coins. As an example, Fig. 3 shows typical XRF spectra coming from the surface analysis of the Egypt bronze (a) and Greek silver (b) coins.

The first indicates the typical bronze content in Cu, Pb, Fe and Al with trace elements of Si, Cl, K and Ca, probably present as oxides in the ancient patina. The second shows a high Ag characteristic peak indicating that the silver was employed as pure in the phase of coin. Also in this case the patina layer contains many trace elements, such as C, Cu, Zn, Mg, Al, Si, S and Cl and oxygen probably present as oxide compounds.

A confirm of these elements was given by MQS analysis. As an example Fig. 4 shows two typical MQS spectra obtained detecting the removed species from the Syracuse ablated coin. The first is relative to the mass range 60-100 amu (a) and the second to the mass range 100-300 amu (b). In both cases many chemical compounds are indicated as

content of the patina surface which appears rich in oxides, carbides and chlorides of the main bronze elements Cu, Fe, Sn and Pb.

A particular attention was given to the measurements of the isotopic ratios of the lead in the bronze samples.

Lead has four isotopes and their relative ratios are suitable of little variations, characteristic of the mineral used for the coin.
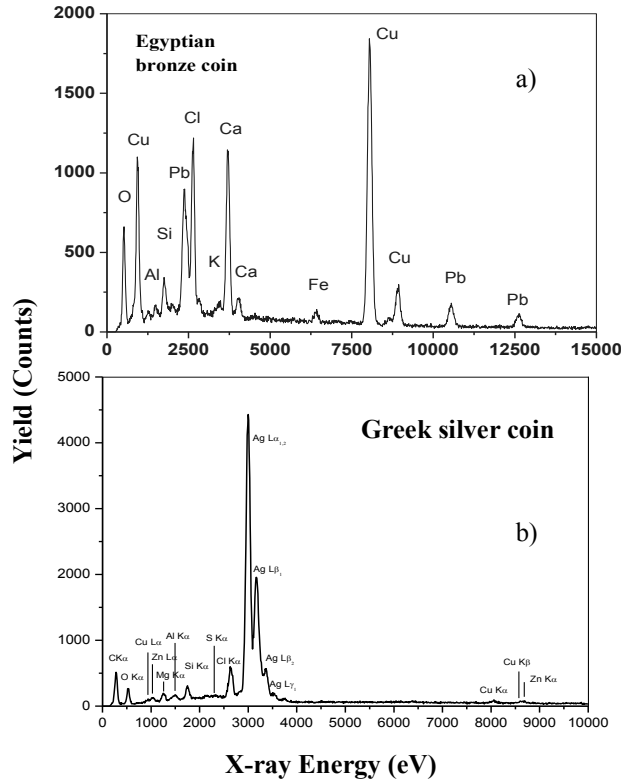

Fig. 3: XRF spectra relative to the patina analysis of the Alexandria bronze coin (a) and of the Greek silver coin (b).

Fig. 5 shows two typical MQS spectra relative to the characteristic lead isotopic masses measured in Alexandria (Egypt) (a) and Syracuse (b) bronze coins. The measured isotopic ratios are reported in Tab. I and compared with the expected ratio values coming from the global measurement on the terrestrial crust [5].

The little difference values of the isotopic ratios are very important because they are typical of the used minerals employed during the coin phase. Thus, from the point of view of archeology, numismatic and historic, the comparison between different coins and coins and mineral contents permit to deduct important information for the scientific and cultural communities.

In order to have more information of the depth composition of the coin, depth profile investigations were conducted by using the laser ablation at 1 Hz repetition rate.

The measurements, correlated with the ablation yield, permit to know the patina thickness, the presence of segregation effects and, in general, to have information of the
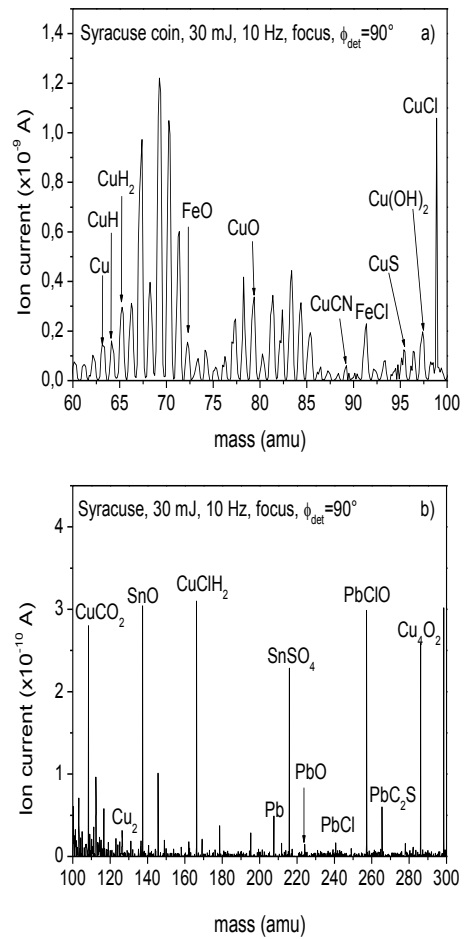

Fig. 4: MQS spectra analysis of the Syracuse bronze coin in the mass range 60-100 amu (a) and 100-300 amu (b).

depth profile of elements, chemical compounds and isotope ratios. As an example, Fig. 6 reports two MQS plots relative to the masses 16 (a) and 107 amu (b), representative of the O^{16} and Ag^{107}, respectively, for the Italian silver coin (Fig. 2d).

Both spectra, recorded irradiating with 150 mJ pulse energy and 1 Hz repetition rate, show a yield decreasing with the irradiation time, due to the crater depth effect which reduces the laser focusing and the particle emission towards the MQS detector. It is the ratios between the two spectra yields, in terms of Ag^{107}/O^{16}, that shows an interesting result in terms of elemental profile with the irradiation time, as reported in Fig. 6c. Finally, the data elaboration obtained by using a smoothing process cancels the background peaks due to the 1 Hz ablation repetition rate and it gives a clear profile with the irradiation time, as reported in Fig. 6d. This last plot contains also a depth scale which permits to correlate the element profile with the sample depth. This correlation between the irradiation time and the depth is obtained measuring the ablation yield in the coin, i.e. the crater depth per each laser shot.

Two typical crater shapes obtained by using the surface depth profiler in the Alexandria bronze (Fig. 2a) and Italian silver coins (Fig. 2d) are reported in Fig. 7. By using

pulse laser energy of 150 mJ, the first crater is due to 25 laser shots and the second crater to 50 laser shots, both have a diameter aperture of about 1 mm. In these conditions the measured ablation yield is of 3.2 μm/pulse and 1 μm/pulse, for the bronze and silver coin, respectively, which correspond to 3.2 μm/s and 1 μm/s of ablation rate, by using 1 Hz repetition rate, in the two cases, respectively.
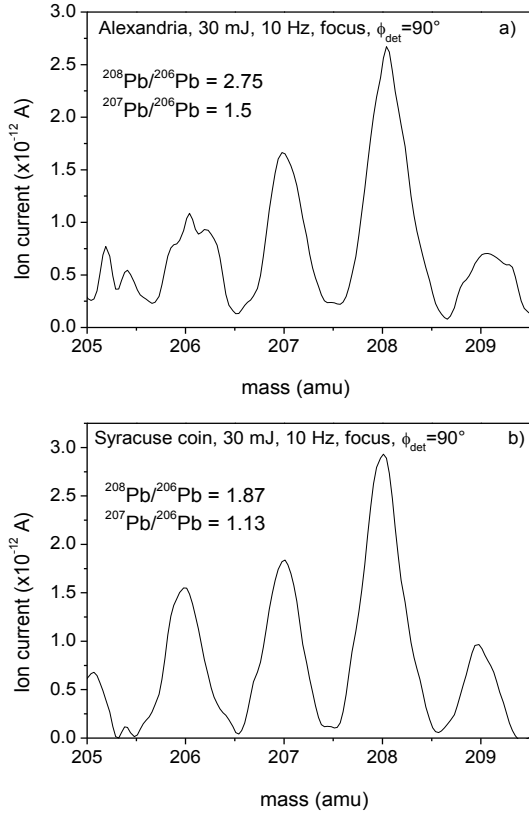
Fig. 5: Comparison of the MQS spectra relative to the isotope mass peak detected in the bronze

Bronze Coin	**Period**	**Pb^{208}/Pb^{206}**	**Pb^{207}/Pb^{206}**
Alexandria	VI-VII sec. a.D.	2.75	1.5
Syracuse	VII-VII sec. a.D.	1.87	1.13
Expected mean values		1.86-2.70	0.64-1.13

Tab. I: Comparison of the measurements of the isotopic lead ratios in the two bronze coins with the expected values based on the mean isotopic abundances.

Thus the Ag/O increment vs. depth indicates that the surface patina is rich of Ag oxides while the bulk is rich of pure Ag. The depth profile reported in Fig. 6d shows that the oxides layers of the patina have a thickness of the order of 100 mm, in good agreement with literature [6].
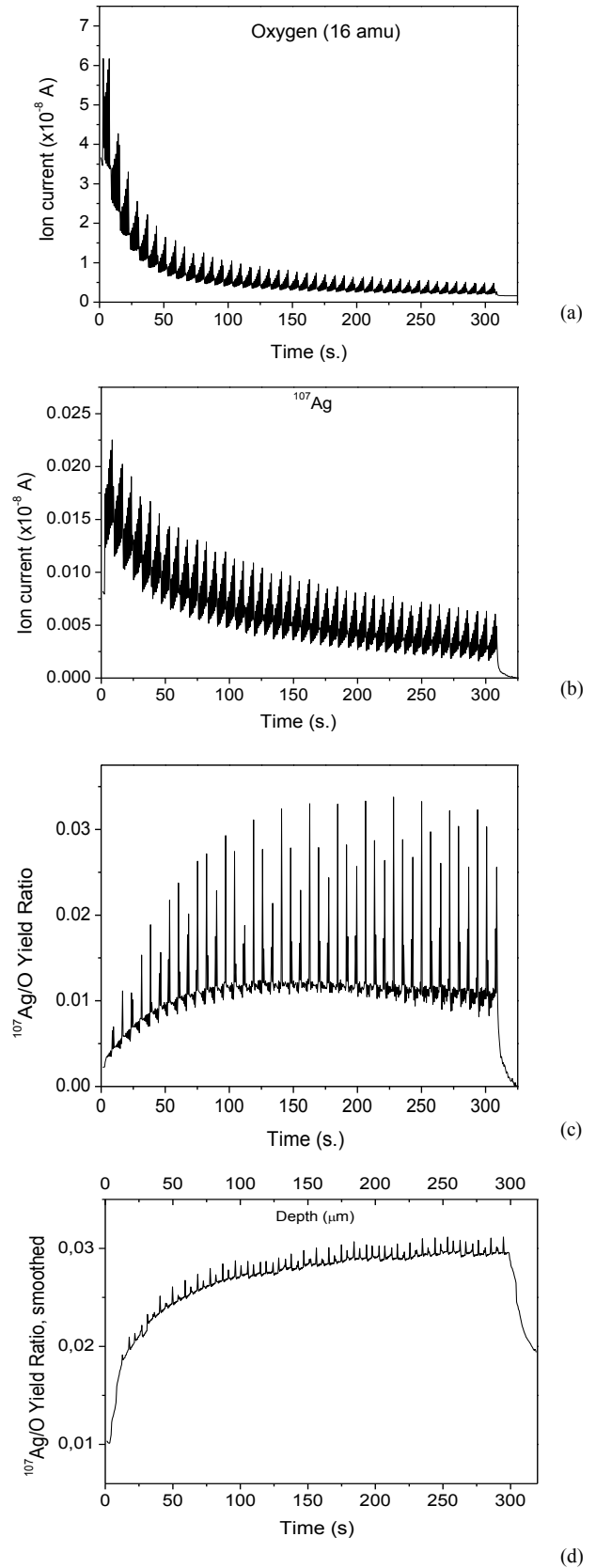
Fig. 6: LAMQS irradiation profiles in the Italian silver coin relative to the Oxygen (a), Silver (b), Silver/Oxygen ratio (c), and data elaboration of the depth profile of Ag/O ratio (d) in the first superficial 300 micron depth.
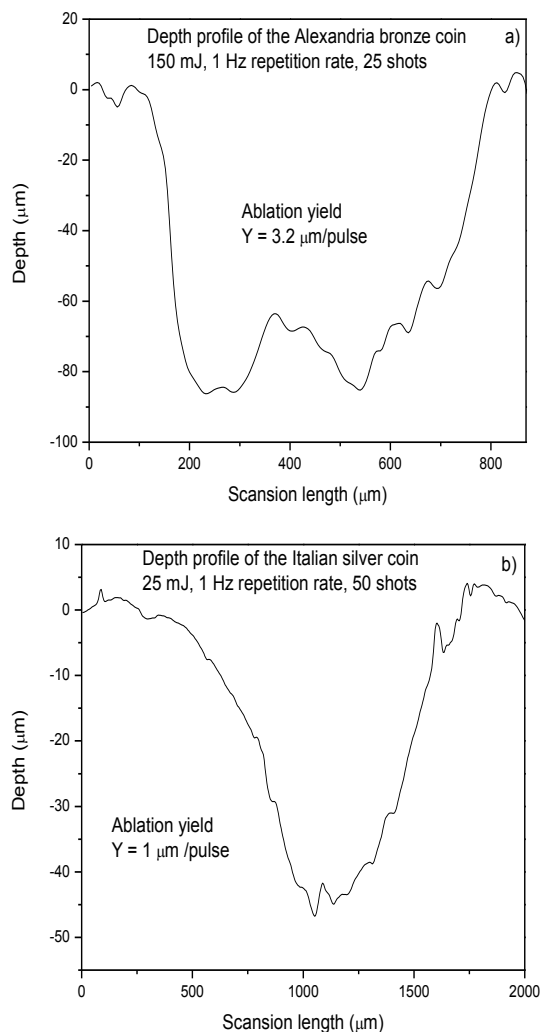
Fig. 7: Crater depth profiles relative to the silver coins coming from Alexandria (a) and Italy (b).

DISCUSSION AND CONCLUSIONS

LAMQS represents an useful technique to analyze the surface of metallic samples such as coins. Although the technique is micro-invasive, the crater diameter is of the order of 1 mm and the depth of the order of 300 mm, the analysis can be applied to many samples of interest in archeology and numismatic.

A very important parameter of this analysis is represented by the control of the ablation yield in order to not damage the analyzed sample. To this low laser energy and number of laser shot should be employed. In this direction the preliminary use of XRF technique has been used to have preliminary information about the elements, possible chemical compounds and isotopes that can be searched by using MQS.

Generally the analysis of one sample take a time of about 15 min but the data analysis and elaboration can take also 1 hour. However the investigation can be developed with

relative simple and economical instrumentations.

The analysis of bronze coin demonstrated that their composition is different, that the chemical compounds of the patina are different and that the lead isotope ratios can be employed as characteristic property of the employed lead for the coin. Similarly, the two silver coins have different patina composition with different chemical compounds and different patina thicknesses.

However, in this work the potentiality of the analysis technique is mainly discussed and not the obtained characteristic of the coin composition. At the moment the composition results are less interesting because they are relative only to four samples coming from different country areas and to different historical periods. Only the application to many samples will permit to have a good statistical data analysis in order to deduct scientific interest conclusions because it will be possible to compare different coins from the same period, coin composition with mineral composition and to distinguish true coins from false ones.

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