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## Laser ablation coupled to mass quadrupole spectrometry for analysis in the cultural heritage

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**Abstract.** A Nd:YAg laser operating at 1064 nm, 150 mJ, 3 ns pulse duration, 1-10 Hz repetition rate and  $10^9$  W/cm<sup>2</sup> intensity is employed to irradiate ancient metallic and ceramic samples in high vacuum. A mass quadrupole spectrometer (MQS), operating between 1-300 amu with sensitivity better than 0.1 ppm, analyzes elements and compounds. Repetitive laser ablation removes in controlled manner the first surface layers of the irradiated samples so that the irradiation time can be correlated to the layer depth. MQS can be fixed to peculiar masses so that during the laser irradiation the mass yields can be plotted as a function of the sample depth. The technique permits to give the depth profiles of elements, chemical compounds and isotopes characterizing the composition of the analyzed samples. The analysis of ancient coins based on bronze and silver alloys and of old vitrified colored ceramics has been investigated to identify peculiar elements of the colored layers. Particularly, the lead isotopic ratios  $^{208}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{207}\text{Pb}$  were measured in bronze coins. Measurements were compared with the database of lead isotopic ratios in lead minerals extracted from old mines in the Mediterranean basin. In some cases, of special interest for Archeologists, the comparison has indicated that the lead employed for the coin production could have been extracted from mines of particular geographic sites.

### 1. Introduction

Ancient bronze coins coming from Mediterranean basin are of special interest in numismatic and archeology in dependence of the historic period of their coinage and use. The archeological bronze generally is based on an alloy containing: copper, lead, iron, tin and zinc. These coins are the best indicator for tracing the ore sources and the trading of the huge amount of copper used to realize the bronze alloy, thus their investigations permit to improve the archeological knowledge. Recently the use of the physical technique LAMQS (Laser Ablation coupled to Mass Spectroscopy) can be employed to analyze the bronze elemental composition both in the bulk and in the superficial patina, to detect special chemical compounds vs. depth and to measure the isotopic ratios of some peculiar elements [1]. Particularly interesting is referred to the Pb content of the bronze alloy, that can be different depending on the geographic area and on the historical period of coinage and to the lead isotopic ratios that permits to characterize the specific mineral used and sometimes to go back to the geographic area of the origin mine [2, 3]. The analysis is applied to some coins from IV – X century



AD coming from different Mediterranean sites: Egypt, Greece and Italy. LAMQS is applied also to ancient silver coins and vitrified ceramics of the Mediterranean basin.

## 2. Materials and methods

In this section we discuss how to format the title, authors and affiliations. Please follow these instructions as carefully as possible so all articles within a conference have the same style to the title page. This paragraph follows a section title so it should not be indented.

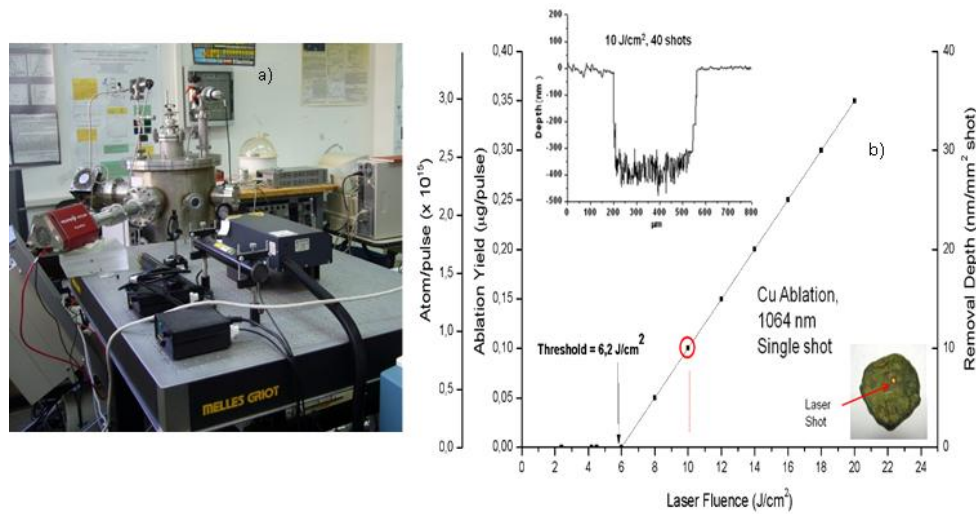
A set of analyzed bronze coins are the reported in the photos of Fig. 1. Characteristic-X-ray fluorescence (XRF) technique, induced by 20 keV electrons of a SEM microscope (Zeiss EVO), was employed to identify the elemental composition of the sample surface.



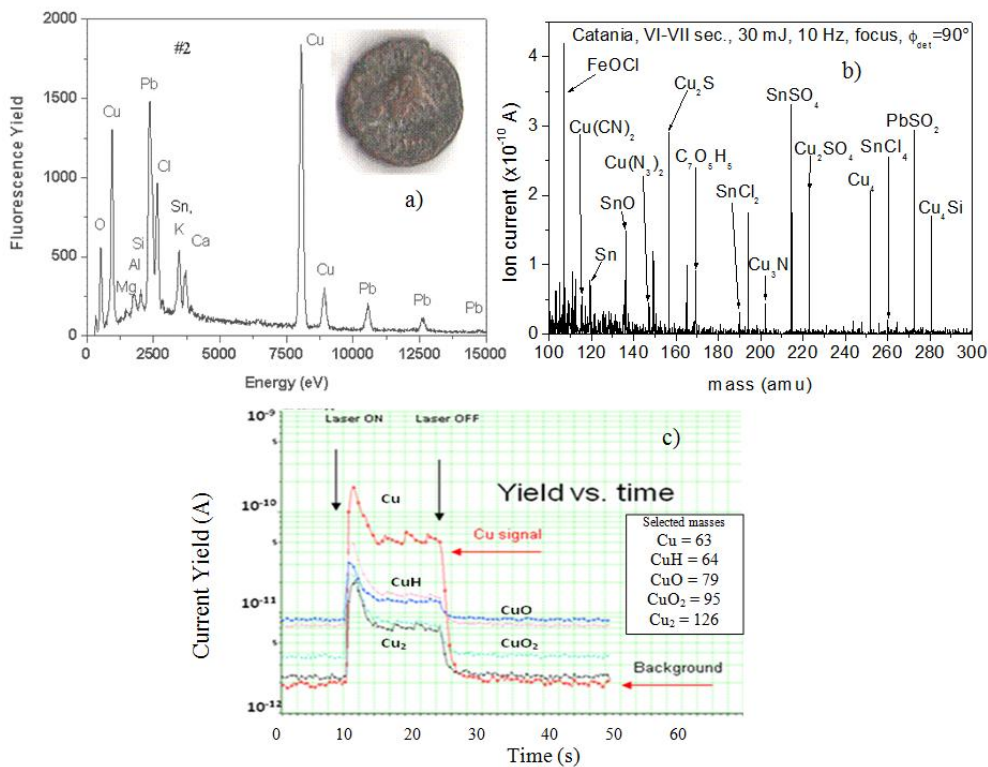
**Figure 1.** Photos of the analyzed coins base on Silver (a) and Bronze (b) and of the vetrified ancient pottery (c).

A Nd:Yag laser, operating at 1064 nm, with 3 ns pulse width, 1-150 mJ settable pulse energy, single pulse or 1-10 Hz repetition rate, was employed. The laser was focussed on the target (sample) up to a spot size of 0.5 mm<sup>2</sup>. A preventive calibration on a bronze alloy permitted to evaluate the ablation yield in terms of removed thickness per laser shot. The calibration uses a surface profile meter to measure the ablation depth with a resolution of 10 nm [4]. Generally the analyses are performed at the pulse energy of 30 mJ at which the ablation yield is of about 10 nm per laser shot.

A mass quadrupole spectrometer (MQS), Pfeiffer Vacuum-Prisma 300, with 1-300 amu mass range, mass resolution less than 1 amu and sensitivity less than 0.1 ppm was employed to measure the mass of the particles emitted from the laser ablation process. Depth profiles can be measured operating with a laser ablation at 10 Hz repetition rate and analyzing, contemporary, the mass yields of the element of interest. A special attention is given to the detection of the masses of the four Pb isotopes: <sup>204</sup>Pb, <sup>206</sup>Pb, <sup>207</sup>Pb and <sup>208</sup>Pb. Fig. 2 shows a photo of the experimental set-up (a) and the Cu ablation yield vs. laser fluence (b). Measurements were performed at 10 J/cm<sup>2</sup> at which the removal depth is of 10 nm/mm<sup>2</sup> shot.



**Figure 2.** Photos of the experimental set-up (a) and Cu ablation yield vs. laser fluence (b).



**Figure 3.** XRF spectrum typical of a bronze coin (a), LAMQ spectrum in bronze coin (b) and relative to some elements and compound of interest (c).

### 3. Results

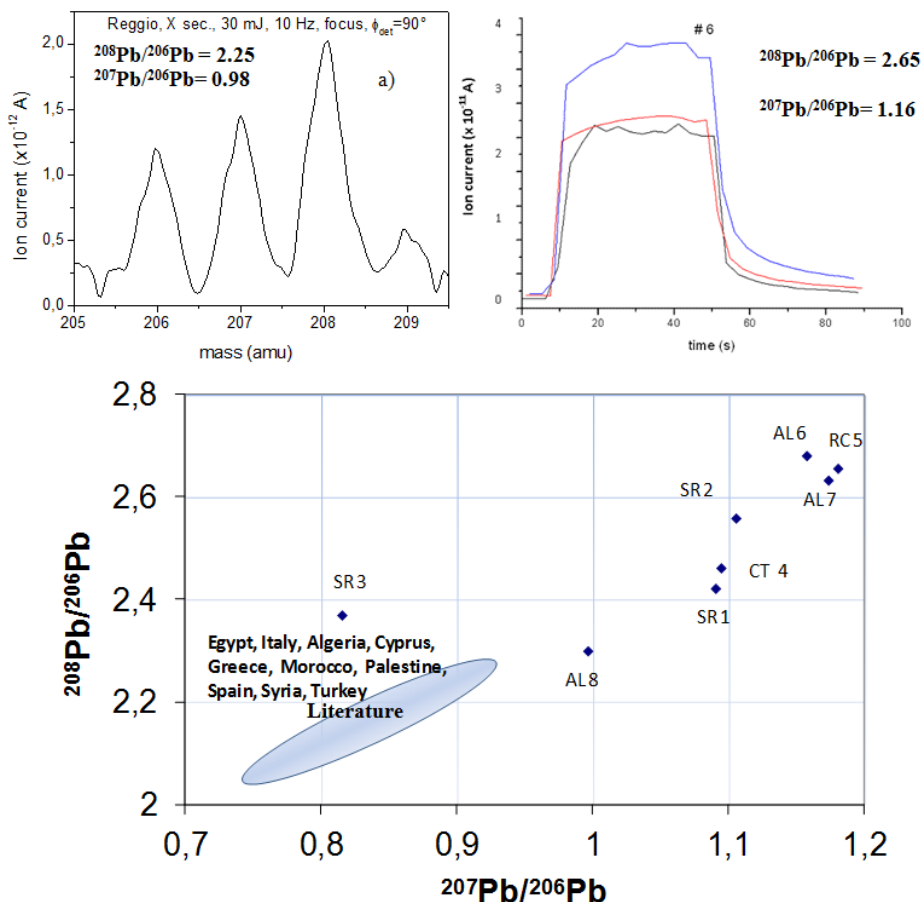
Fig. 3a shows a typical X-ray spectrum relative to the sample #2 in bronze (a) which composition is based on Cu (~70-80%), Pb (~10-20%) and Sn (~6-10%) and that is rich in oxygen, carbon and trace elements in the superficial patina.

The higher lead concentration is found in the bronze samples of Catania #1 and Syracuse #4. Fig. 3b shows a typical LAMQS spectrum, in the mass range 100-300 amu, of the analysis relative to the

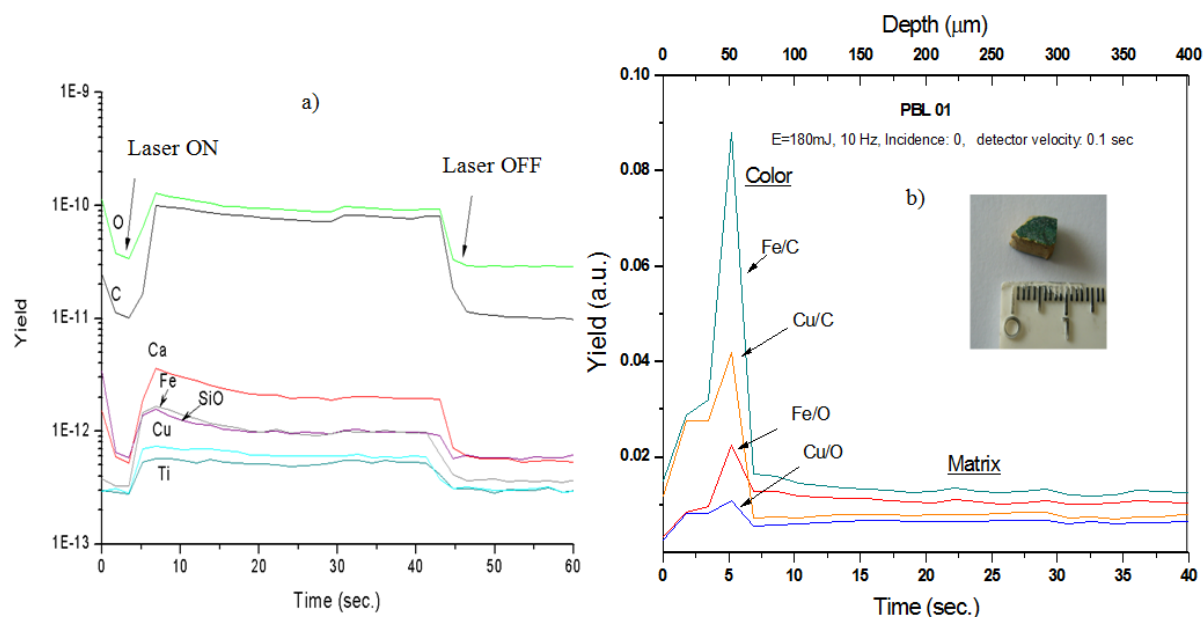
bronze sample #1. The spectrum shows many chemical compounds based on Cu, Fe, Sn, Pb, O, S, Cl and N [4]. Spectrum can be acquired during laser ablation to have information about special masses as a function of the laser irradiation time (3c).

Fig. 4a shows an example of mass spectrum in the range 205-210 amu obtained reporting the yield as a function of the mass in order to measure the Pb isotopic ratios. Fig. 4b shows an example of mass spectra obtained by fixing the masses of interest, relative to the Pb isotopes 206, 207 and 208 amu, and reporting the yields as a function of the laser ablation time. Low ablation times, below 60 s, are used to reduce the laser invasively. Measurements indicate that the main Pb compounds in the surface of bronze coins are due to PbO, PbSO<sub>2</sub>, and PbCl<sub>2</sub>. The range of variability for the isotope ratios <sup>208</sup>Pb/<sup>206</sup>Pb and <sup>207</sup>Pb/<sup>206</sup>Pb is in the range 1.86 - 2.70 and 0.64-1.13, respectively. The lead isotope masses may interfere with different compounds, such as the Pb-H and Cu<sub>3</sub>NH, however an accurate analysis using the maximum MQS resolution reduces the uncertainty. Fig. 4c shows the comparison of experimental data (points) with literature (ellipses) [5, 6, 7]. Measurements indicate that the lead used to realize the coins may comes from different mines giving minerals, such as galena, with similar isotopic ratios but their geographic place may be different with respect to the literature data.

Further investigations are in progress in order to investigate about the literature-experimental data differences that can be attributed or to the lead employed for the coinage of the analyzed samples or as colorant of the vitrified ceramics. A better investigation will be performed increasing the number of collected data and comparing isotopic ratio measurements with literature mineralogical data.



**Figure 4.** Mass spectra (a), time (depth) profile for the <sup>206</sup>Pb, <sup>207</sup>Pb, <sup>208</sup>Pb isotopes (b) and measure comparison with literature data (c).



**Figure 5.** Typical LAMQS spectra of elements in vitrified ceramics (a) and measurement of their color layer thickness (b).

#### 4. Discussion and conclusions

The LAMQS analysis can be employed to analyze the elemental composition, chemical compounds and isotopic ratios of ancient coins and ceramics. Obtained results demonstrated that coins composition is different between patina and bulk, that the Cu, Pb and Sn concentration in bronze is different for different set of coins. Major differences in the elemental composition is found for the sample #5 from Syracuse (VII sec A.D.) that have higher Cu content, for #1 from Catania (VI-VII sec A.D.) that has the higher Pb content, for the sample #2 from Alexandria (IV sec A.D.), that has higher concentrations of  $PbSO_2$  and  $PbCl_2$ . The XRF analyses only to the first micron of the patina coin surface (corresponding to the range of 20 keV electrons) while the LAMQS analyses about 10 ns per laser shot, thus, operating at 10 Hz repetition rate, the yield is depending on the laser irradiation times. After 60 s irradiation the composition is relative to a depth of about 6 microns. The major difference are found for the coin #3 from Reggio Calabria (X sec A.D.), having higher  $^{208}Pb/^{206}Pb$  and  $^{207}Pb/^{206}Pb$  ratios, and for the coin #6 from Syracuse (VII sec A.D.), having the lower  $^{207}Pb/^{206}Pb$  ratio. Other analyses with LAMQS technique has permitted to study the elemental composition of some ancient Sicilian colored pottery and measured their thickness. Further measurements are in progress in order to improve the statistical data.

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