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Laser ablation mass spectrometry (LAMS) technique for isotopic ratio measurements.

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Abstract

A Nd:YAG laser operating at 532 nm, 3 ns pulse width, 150 mJ maximum pulse energy, 1-10 Hz repetition rate, is employed to ablate solid targets placed in high vacuum. An electrostatic deflection mass quadrupole spectrometer, 1-300 amu mass range, less than 1 amu mass resolution, with SEM detector, is employed to analyze the mass particles ejected from the laser-generated plasma along the direction normal to the target surface.

The laser ablation coupled with the mass spectrometer is a powerful technique in order to investigate the first superficial layers ablated by repetitive laser pulses. Elements, chemical compounds and isotopes can be detected properly. A special attention is devoted to the analysis of the isotopic ratios of peculiar elements. The laser ablation mass spectrometry (LAMS) technique, in fact, measures isotopic ratios with high precision permitting to correlate the target elements with the mineral from which the elements is extracted. Applications in the field of geology, cultural heritage and numismatic will be presented and discussed.

Introduction: Laser Ablation coupled to Mass Spectrometry (LAMS) is a new technique of analysis useful for surface compositional and depth profile analyses of different solid materials placed in high vacuum [1]. This technique represents a powerful tool to measure the mass-to-charge ratio of the vapour composition of the ablated matter. The four charged rods of the quadrupole induce the arrival of the appropriate ions, with a given mass-to-charge ratio, at the secondary electron multiplier detector (SEM) for counting, while all others are lost. Different elements can be detected with high resolution and sensitivity by changing the sinusoidal voltage applied to the rods [2]. LAMS can be used as a micro-invasive technique useful in different scientific fields, such as geology, cultural heritage and microelectronics. In this work the technique is applied to the isotopic ratio measurements in calibration samples and bronze coins of archaeological interest.

Materials and Methods: The laser ablation was performed with a q-switched Nd:Yag working at 532 nm wavelength in single pulse and at 10 Hz repetition rate. The single pulse duration is 3 ns. It was possible to change the laser pulse energy in the range 1 - 150 mJ. The laser beam was directed on the sample (target) placed in high vacuum (10^{-6} mbar) through a focusing lens and a thin glass window. The spot diameter is 1 mm^2 and the incidence angle is 45°. Fig. 1a shows a photo of the experimental setup at Messina University.

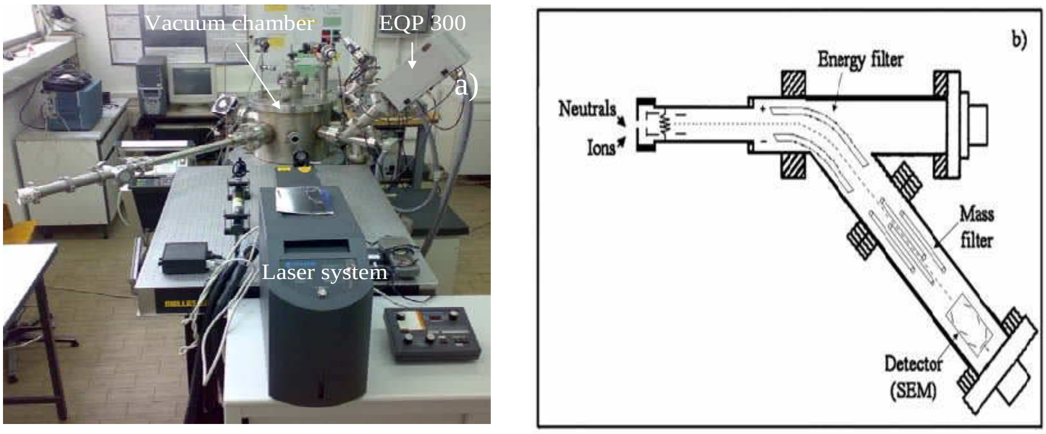

Fig. 1: Photo of the experimental setup (a) and scheme of the EQP instrument (b).

A special mass quadrupole spectrometer, the Hiden Electrostatic Quadrupole Plasma (EQP) 300, was employed to monitor the isotopic ratios for the selected elements in the mass range 1-300 amu. The EQP is placed along the normal to the target surface, i.e. along the direction which corresponds to the maximum detectable ion yield. The instrument consists in four main sections: the ionisation source, the electrostatic energy filter, the mass filter and the SEM detector, as reported in Fig. 1b. EQP system sensitivity reach less than 1 ppm and its mass resolution is below 1 amu.

In order to not damage the investigated samples, the laser ablation duration is below 2 min, during which the mass spectra are acquired.

Results: In this investigation the irradiated targets consist in standard samples based on bronze alloys (containing Cu, Sn, Pb) and in a lot of ancient coins coming from Antinopoulis (Egypt), coined in the VII century a. C. and here named PAN 2. Fig. 2 shows the experimental results obtained for the stable isotopes of pure Pb from calibration sample (a) and PAN 2 coin (b) ablation, respectively.

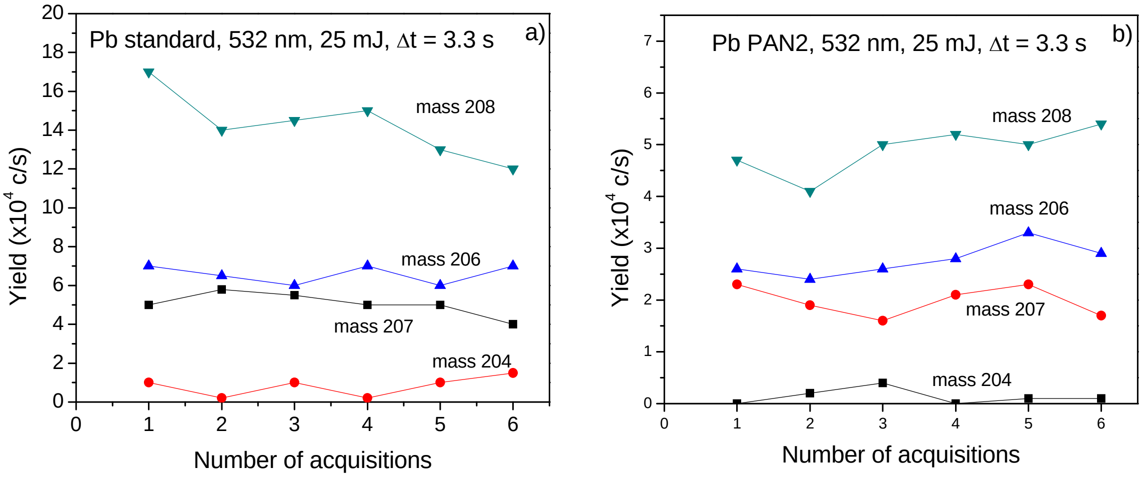

Fig. 2: Mass yield as a function of the acquisition number for four isotopes of the lead and for the standard (a) and PAN 2 (b) irradiation.

The experimental abundance was 1.3%, 23.8%, 21.2% and 53.7% for ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, respectively, for pure Pb calibration standard. These experimental values are in very good agreement with the theoretical ones obtained from the natural isotopes abundance (1.4% for ^{204}Pb, 24.1% for ^{206}Pb, 22.1% for ^{207}Pb and 52.4% for ^{208}Pb, respectively). For the PAN 2 coin ablation the mean value of the Pb isotopes abundance is 1.3% for ^{204}Pb, 26.3% for ^{206}Pb, 18.9% for ^{207}Pb and 53.5% for ^{208}Pb, respectively. The measured PAN2 lead isotope ratios are in agreement with the literature values for galena mineral coming from the Taleit Eid mine, in east Egypt, on the red sea side (see map of Fig. 3) [3].

Fig. 9: Egypt map reporting the site of Antinoupolis, where the coin PAN 2 was found, and the site of the Taleit Eid were a galena mine can give minerals similar to that used to build the bronze coin.

The galena of this site shows the isotopic ratios reported in Tab. I, very similar to that of PAN 2 coin [4]. The map indicates also the geographic position of Antinoupolis where the PAN 2 coin was found.

Isotopic ratios	**PAN 2 (Measurements)**	**Taleit Eid mine (Galena)**
Pb^{204}/Pb^{208}	**0.0243**	**0.0634**
Pb^{206}/Pb^{208}	**0.492**	**0.506**
Pb^{207}/Pb^{208}	**0.353**	**0.384**

Tab. I: comparison of the lead isotope ratios in PAN 2 coin and in the galena mineral coming from Taleit Eid mine.

Discussion and Conclusions: The use of a power laser beam to ablate, in a controlled manner, a solid target in high vacuum, coupled to the mass quadrupole spectrometer analysis of ablated particles assumes a relevant meaning to study the surface composition of samples with archaeological and geological interest. The analysis gives information of the atomic elements, on the chemical compounds and on the relative isotopes concentration. Moreover the use of laser spots with low intensity and of low irradiation times produces negligible effects on the irradiated surface, non inducing macroscopic damage of the surfaces. This technique is based on a complex synchronization between the laser beam and the mass quadrupole, making a very careful and sensitive mass analysis. Our LAMQS laboratory analyses have furnished further and more substantial tests in comparison to the numismatic indicators. The encouraging results of the initial research now necessitate an extension of the analyses, with the goal to realize a coins data-base, which can serve as a point of reference for numismatic and archeological studies.

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