The use of Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICPMS) in the study of Cultural Heritage

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Abstract

Several analytical techniques are actually employed for the study of Cultural Heritage and permit to identify production methodologies, constituent materials, degradation products, dating and provenance of the objects examined; elemental analyses provide precious information to archaeologists, art historians, restorers and analysts, opening a door into the past.

Those techniques capable of ensuring versatility of application, sensitivity and non-destructive or micro-invasive analysis are generally requested. Laser ablation–inductively coupled plasma–mass spectrometry (LA-ICPMS), by virtue of its effective lateral resolution, sensitivity to most elements and capacity of outdoing limitations due to the low quantity of accessible samples, fulfils these requirements. Multivariate statistical techniques applied to the elemental data permit classification and provenance of artistic objects and allow to confute or confirm historical hypotheses.

In the present work several case studies, addressed recently by the authors concerning objects of artistic and historical value, are outlined: pottery and glazes of Vesuvian area (Campania, Italy), *fibulae* of Egnatia (Puglia, Italy), inks of painting of *Sant'Irene* by Giuseppe Verrio and lime mortars from Siponto (Puglia, Italy). For each of the presented activity, results, advantages and drawbacks of the LA-ICPMS were discussed.

Introduction

The study of Cultural Heritage is highly interdisciplinary and involves different professions, each with their own skills. This approach, based on the harmony of Art and Science, resolves questions relating to the use of ancient materials and technologies, to dating, to provenience of raw materials, to diet, to the trade routes of the past. However the Cultural Heritage that survives from the past are unique objects, for this reason scientific analysis involve a series of requirements, for example versatility of application, sensitivity and non-destructive or micro-invasive analysis.

Laser ablation–inductively coupled plasma–mass spectrometry (LA-ICPMS), by virtue of its effective lateral resolution, sensitivity to most elements and capacity of outdoing limitations due to the low quantity of accessible samples, fulfils these requirements.

The LA-ICPMS is a type of mass spectrometry which is capable of detecting multi-elements (metal and non-metals), at concentrations as low as one part in 10^{12} (part per trillion). This is achieved by ionizing the sample in a inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions; the instrumental configuration which is most often employed is reported in Fig. 1.

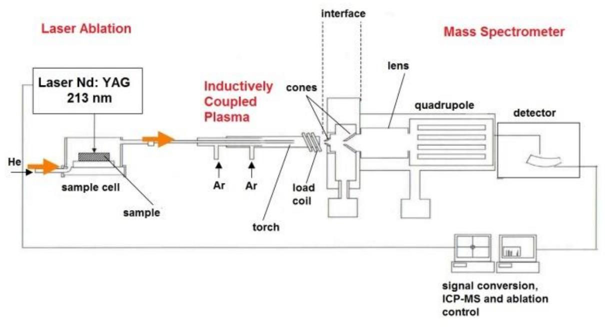

Fig.1.Instrumental configuration most commonly used.

Basically, the sample to be analyzed is placed in a closed chamber (ablation cell) and the laser beam is focused onto the sample surface, through a transparent window (typical diameter between 10 and 100 µm). A flow of inert gas (Argon or Helium) transports the material ablated by the laser, out of the cell to the plasma torch. The laser produced particles are then decomposed in the plasma, the elements ionized and the generated ions separated and measured according to the mass analyzer used, i.e. quadrupole, sector field or time of flight.

The technique allows the isotopic and multi-elemental determination (trace and ultra-trace elements), without any pre-treatment of the sample, respect to the conventional ICP-MS technique. Moreover, the coupling to other analytical techniques, provides a complete characterization of heterogeneous materials and the data processing with multivariate statistical techniques, provides a classification and a provenance of artistic objects.

In the present work several case studies addressed by the authors, were presented, with the aim of highlighting the advantages and disadvantages of the LA-ICPMS, in the studies of Cultural Heritage.

Materials and methods

The LA-ICPMS instrumentation of the Laboratorio di Spettrometria di Massa Analitica ed Isotopica (Università di Lecce) consists of Thermo Electron Corporation XSeriesII mass spectrometer, coupled to NewWave Research UP213AI laser ablation system. The ablating beam is generated by a pulsed laser which operates at 213 nm and is focused onto the sample surface, through the window of a quartz sample cell (5 cm x 3 cm). The diameter of the laser beam is adjusted by a set of ceramic apertures and optical lenses, and varies between 4 to 110 µm. The repetition rate of the laser varies between 1 to 20 Hz and the maximum energy of the beam is 3 mJ. Viewing of samples is allowed by a high resolution CCD camera and colour monitor. The products of laser ablation are carried away from the sample cell to the ICP-MS by a flow of Helium.

The heart of the ICPMS is the inductively-coupled plasma ion source. Since the source operates at temperatures of 7000 K, virtually all molecules in a sample will be broken into their component atoms. A radio frequency signal (RF) is fed into a tightly wound water-cooled coil where it generates an intense magnetic field. Within the center of this coil is a quartz plasma torch where the plasma if formed. The ions produced by the plasma are introduced into the mass spectrometer via the interface. The interface consists of two cones: sample and skimmer cones. The ions that successfully pass through the skimmer cone orifice are first accelerated by a high voltage potential gradient, and then are passed through a series of focusing lenses into the quadrupole. The ions are separated on the basis of their mass-to-charge ratio and a detector receives an ion signal proportional to the concentration.

The LA-ICPMS analysis, reported in individual case studies presented below, were carried out on small fragments of sample or on cross-sections, under microscope observation and experimental conditions of ablation were optimized, depending of individual cases.

Case studies

1. Ceramic finds from Vesuvian area (Campania, Italy)

Chemical characterization of Roman glazed pottery (Fig.2) from archaeological sites of Pompeii and Herculaneum (Campania, Italy) was carried, aiming to identify: materials, production technologies, mechanisms of degradation and provenance of raw materials.

Fig.2. Image of some finds. Scale bar = 3 cm.

Small size fragments (~0.5-1.0 mm) of archaeological objects (skyphoi, oil lamps, bowls, askoi, amphorae, krateres, statuettes) were sampled, and LA-ICPMS technique was carried on cross sections, to overcome the problems of heterogeneity of the samples and to obtain stratigraphic information. Calibration was performed using the standard reference materials NIST 610, 612, and 614 (National Institute of Standards and Technology, Gaithersburg, MD, USA) and Corning C (Corning Museum of Glass, Corning, NY, USA). Coupling with optical microscopy (OM), SEM-EDS analysis and micro-Raman Spectroscopy, provided additional information on the mineral phases, degradation products and firing temperatures. Provenience and classification of archaeological objects were obtained by processing the results through multivariate analysis (Principal Components Analysis PCA). The chemical composition of glazes and ceramic bodies showed significant differences: lead and sodic-calcic glazes, chromophores (such as Cu for green/blue glaze, Fe for brown-ocher glaze, Co for blue glaze), opacifier (Ti, Sn, Sb-based) and production methods (lead plus quartz or a frit), have been identified. Two types of ceramic pastes (not calcareous and calcareous) have been used, but chemometric techniques (PCA) support the hypothesis of a Campanian archaeological provenance of raw materials for lead-glaze pottery, while, with the exception of 3 samples (samples 1, 12, 13-Fig. 3), blue faiance have Egyptian origin (Fig.3).

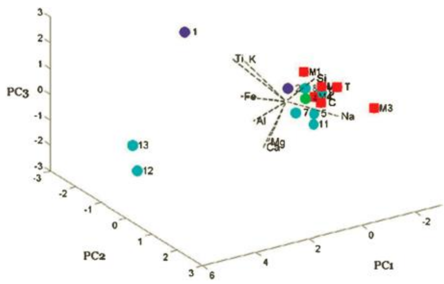

Fig.3.Scores and loadings diagram for the first three principal components related to the ceramic bodies from Pompeii (circles) and from different Egyptian sites: Cairo (C), Memphis (M), Tell el-amarna (T)-92% of the total variance.

2. Fibulae from Egnatia (Puglia, Italy)

Twenty-one *fibulae*, dated from the 6th–4th centuries BC (*fibulae* 1-8) and from the Republican and Imperial Roman Ages (*fibulae* 9-14), from the archaeological site of Egnatia (Puglia, Italy) were examined, aiming to identifying: types of alloys used, techniques employed in the manufacturing processes, and corrosion products. Due to the need to analyze objects of a few millimeters and in a bad state of conservation (encrustations, patina and corrosion layers on the surface, caused by the burial conditions), and to reduce the sampling to a minimum, we preferred to use the LA-ICPMS technique, directly on the bulk sample; to obtain additional information, the same fragments were subjected to metallographic analysis. Compositional and morphological information were obtained using different complementary techniques, in addition to LA-ICPMS: Optical Microscopy (OM), Scanning Electron Microscopy (SEM) with Energy Dispersive Spectrometry (EDS) and Raman Spectroscopy. *Fibulae* composition is very varied and includes unalloyed copper and different copper-based alloys, such as low and high tin bronze, brass, and Cu–Zn–Ag alloy. The use of different production methods has been established (simple casting, forging or annealing), allowing to outline the changes over time. The existence of two different types of copper-alloy patinas has been confirmed.

Besides, this study made it possible to give archaeologists comprehensive answers to questions regarding the classification, dating and provenance of some items, supporting the integration of Egnatia in a complex commercial network.

Fig.4.Sample 11 (a) and ternary diagram Sn-Pb-Zn (b).

3. *Picture of "Sant'Irene" by Giuseppe Verrio.*

The painting was done in the 17th century by the local artist Giuseppe Verrio; it represents St. Irene and 19 paper sheets on linen (from the size of 57x43 cm or 44x43 cm) were used for its construction. Chemical analysis were carried out in order to understand techniques and materials used, and to program a correct restoration. The coupling of LA-ICPMS with other diagnostic techniques (optical microscopy, Raman spectroscopy and gas chromatography/mass spectrometry GC/MS) has allowed us to identify production methods and materials used.

In particular LA-ICPMS analysis were performed on cross sections of samples in qualitative modality. Pigments used were identified with LA-ICPMS: the presence of copper resinate in the green, yellow tin and lead in the yellow areas, cinnabar in red zone, and azurite in blue points was demonstrated thank to the detection of 63Cu (with traces of 120Sn), of 208Pb and 120Sn, of 202Hg, and of 63Cu, respectively. Spectroscopic analysis have also indicated the presence of indigo, white lead and calcite, while chromatographic analysis the use of a mixture of animal glue, linseed oil and resin as an adhesive for paper sheets.

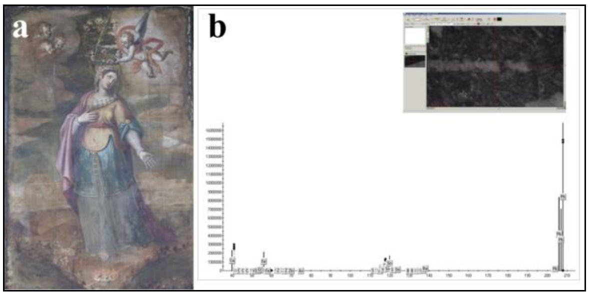

Fig.5.Painting of St. Irene (a) and ablation line and results of LA-ICPMS (b).

4. *Lime mortars from Siponto (Puglia, Italy)*

The medieval archaeological site of Sipontum (Foggia, Italy) was recently investigated and partially excavated. The excavated structures show a complex stratification, which points to functional transformation (from production to dwelling site) and a further abandonement of the investigated urban area between the 11th and the 13th century A.D. The LA-ICPMS analysis was made on the lime lumps detected in the mortars on thin section, aiming to verify the wall stratigraphy identified by the archaeologists. About 33 samples of bedding mortars were also subjected to petrographical (OM), X-ray diffraction (XRD) and X-ray fluorescence spectrometry (XRF) analysis. Two groups of mortars (group A and B) were identified with LA-ICPMS technique: the mortars of group A show a quite homogeneous lime composition, which slightly differs from that of group B in MgO, MnO and Fe2O3 concentration; the same differences are visible from the petrographic analysis, that have determined the presence of nummulites in group B, XRD analysis that showed different mineral phases and XRF analysis, that have indicated a different lime/aggregate ratio in the two groups. The samples belonging to the group A correlate with stratigraphic units archeologically attributed to the period of urban expansion (11th-12th century A.D.). The samples of group B put in evidence an extended reconstruction and modification of the existing structures in a later period (first half of 13th century). The use of local calcarenite as aggregate and a different lime in the mortars of group B shows a change in the choice of raw materials with respect to those of group A, probably due to a critical period occurred at the half of the 12th century as consequence of earthquakes and wars.

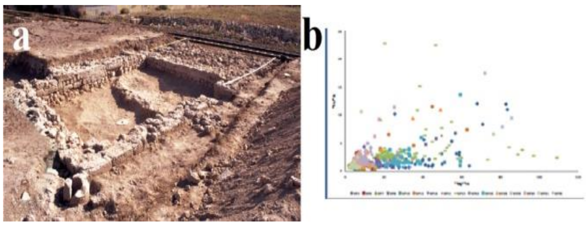

Fig.6.Photography during excavation in 2002 (a); diagram of 57Fe/44Ca versus 24Mg/44Ca (b).

Conclusions

In this work we have tried to show, through the presentation of several case studies, the many advantages of the LA-ICPMS technique, in the field of Cultural Heritage. The analysis of various materials, not only ceramics, glazes, mortars, metals, pigments, but also coins, glass, stones materials, stuccoes, human remains, black crust, patinas etc., makes this technique very versatile. Through the use of the laser, no sample preparation is required, obtaining a reduction of the overall analysis times and minimizing the risk of contamination due to the handling of the object; also stratigraphic information can be obtained by a deeper ablation; alternatively it is appropriate to work on thin or cross sections, which can also be used for additional diagnostic methodologies. LA–ICPMS features micrometer spatial resolution as well, enabling the analysis of heterogeneous samples. This feature fosters the investigation of particular components in a sample and the objects may also be studied through depth profiling. The surface damage caused by the laser ablation is in most cases invisible to the naked eye, having typical diameter of 4–110 μm, for these reason the analysis is micro-invasive and the integrity of the precious objects is preserved. In addition to performing multi-elemental, qualitative and quantitative analysis and to determine trace and ultra-trace elements, the LA-ICPMS is the only technique able to measure the isotopic ratios, directly on the sample, obtaining important information for dating and provenance of the artifacts.

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