Muonic atom X-ray spectroscopy for non-destructive analysis of archeological samples

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Abstract
The implementation in the RIKEN-RAL negative muons facility of a new muon beamline monitoring and novel digital data acquisition system for gamma and X-ray spectroscopy are presented. This work also shows the high potential of the muonic atoms X-ray spectroscopy technique in non-destructive elemental characterization of archaeological samples.

Keywords Muonic atom X-ray spectroscopy · Pulsed muon beam · Non-invasive elemental analysis · SIPM-fibers scintillating hodoscope

Introduction

The muon is an elementary particle belonging to leptons family has mass of 105.7 MeV/c^2, about 200 times heavier than electron mass. The interaction of muons with matter has been used in various research fields. The greater mass of the muons makes that entering into the matter, lose their kinetic energy by "bremsstrahlung" radiation emission much lesser than electrons with same energy; the muons can penetrate several thicknesses of materials in function of the density and atomic number Z of the target material.

The CHNET_TANDEM collaboration aim is to characterized elemental composition of archeological samples detecting characteristic high energy X rays emitted following a negative muons irradiation. The muons "implanted" in matter can form "muonic atoms" along the particle range up to the stopping depth; the muon atoms thus formed, following the cascade transitions from the greater to the lesser energy states of the "trapped" muon, emit characteristic X-rays. The distance of the muonic orbit from the atomic nucleus is much smaller than that of electrons, giving rise to characteristics X-rays emissions with energies 200 times higher than those due to electron transitions (several tens of keV even if implantation occurs in light elements such as Li, F, B....). The muonic X-rays are therefore enough energy to pass through material thicknesses even of some tens of mm, also in materials with elements with high atomic number Z and high density, giving the possibility to analyze much greater depths than the "classical" XRF, PIGE, PIXE. These peculiarities together with the possibility to modulate the muon beam momentum, suggests in a completely natural way the use of MAXRS for non-destructive elemental characterization of samples such as for example

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the archaeometric ones, with the possibility to perform both superficial and deep elemental characterization surveys along the vertical profile from the surface to depths of tens of mm.

Archeometry is the area of applications of scientific disciplines that have as scope the characterization of ancient finds. By extension, under the term "archeometry" we understand the methods of analysis useful for the characterization of the material or for the diagnosis of the state of conservation of the objects (ancient and not) of interest for the cultural heritage.

Whenever scholars, as well as are art historians, archaeologists, restorers or researchers in general, involved in the field of the study and protection of cultural heritage, face a relic of artistic or historical interest, a series of questions regarding dating, origin, production techniques and materials used for their fabrication need arises for answer.

The aim of scientific analysis, in the field of Cultural Heritage is therefore not only directed to the protection, conservation and restoration, which are obviously of primary importance, but is also to provide a materials characterization that integrate the data of the historical and stylistic study that, in principle, regardless completely to conservation and restoration purposes.

The chemical and physical analyzes on artistic or archaeological heritage, very often, are aimed at the characterization of the materials or elements present in the analyzed samples to understanding for example the processing techniques used for its manufacture, but with this type of investigation moreover it is possible to carry out a study of origin, determine the historical-artistic "location" of the finds or validate its authenticity [1].

The choice of the type of analysis depends on the kind and quantity of sample that can be analyzed and the nature of desired information. Not all the techniques created for the material characterization can be satisfactorily applied in the field of archeometry since finds are generally rare (sometimes unique) and precious both from economic and historical/cultural point of view.

An archaeometric technique that are able to characterize a find in both surface and bulk analysis, in a non-invasive manner, are of great interest for archaeological and historical reasons, pointing to the "historical" reconstruction (temporal and spatial collocation) of the find and to identify the techniques used for the realization of ancient manufacts [2–4]; the aim of this work is to demonstrate the usability of muonic atom X-ray spectroscopy in the characterization of elemental content in metallic archeological samples.

ChNet-TANDEM experiment

The *ChNet-TANDEM experiment* is funded by INFN [5] the Italian National Institute for Nuclear Physics and in particular by the Scientific Commission V [6] and Cultural Heritage NET of INFN [7].

The idea behind the CHNET_TANDEM experiment is to develop and optimize non-invasive and non-destructive analysis techniques to be used in the archaeometric searches for the elementary characterization of artifacts [8]. One of the techniques utilized is the muonic atom X-ray spectroscopy (MAXRS): a technique that analyze the constitutive elements of a sample in a non-destructive and non-invasive way, detecting prompt X-ray emissions by cascade processes in muonic atoms that follow the muon capture in the orbitals of the target atoms [9–13].

In archeometry recently but also in the past, other non-destructive and non-invasive techniques have been successfully used for the characterization of materials, such as XRF X rays fluorescence [2], PIXE (particle induced X-rays emission) PIGE [14], or neutron based analytical methods such as PGNAA [15] and others. These techniques generally have very different depths and areas of irradiation and in the case of neutron spectroscopy they can leave the sample radioactive with non-negligible radioactivity amounts. MAXRS is the only non-invasive, non-destructive technique that does not make the sample radioactive (or in negligible and it's usable for both superficial and in-depth elemental analysis, with the possibility of delimiting the analysable area and depth with great precision.

The RIKEN-RAL muons source

The RIKEN-RAL muons sourc facility has been constructed by RIKEN [16] at Rutherford Appleton Laboratory in the UK [17]. The facility utilizes intense pulsed proton beam provided by the ISIS synchrotron accelerator [18]. The superconducting solenoid in ISIS facility beam line has the necessary features for produces intense source for positive and negative muons in the momentum range from 20 to 120 MeV/c. A pulsed magnetic kicker split is used to split in double-pulsed structure the muon beam, enabling to execute two experiment simultaneously at each channels. Important research activities such as investigations related to muon catalyzed fusion [19] and studies of condensed matter by muon spin rotation/relaxation/resonance are being actively pursued [20] at RIKEN-RAL muon facility. The tipically intensity of RIKEN-RAL muon source is about 8×10^4 muons per

spill at 60 MeV/c^2, with a time structure made of two successive 70 ns wide spills (with an inter-peak distance of 320 ns) and 50 Hz repetition rate; a good control of the beam focus z-position, and hence a good spatial resolution along z, is achieved via fine momentum tuning/sensitivity of 1 MeV/c.

Muonic X-rays spectroscopy system development

The experimental setup consists of 2 hodoscopes for beam monitoring made by 64 squared scintillating fibers read by SiPM and a high energy resolution spectroscopy system which consists of 5 HPGe detectors. A new full digital Data AQuisition (DAQ) system for an HPGe detectors was also tested for "nuragic" archeological bronze samples and Standard Materials targets analysis in order to test and validate the set-up for quantitative non-destructive bulk elemental analysis of metallic archeological artifacts.

The Muon beamline monitoring system is based on 2 different hodoscopes (Fig. 1) with different fiducial areas: one is 3.2×3.2 cm^2 placed before the sample and the other one 10×10 cm^2 placed after, both with similar design. The 2 Array for X–Y beam profile are made by Bicron BCF12 square single clad scintillating fiber planes (32 + 32 channels) read by 3×3 mm^2 Hamamatsu (Advansid) SiPM with EMA coating with Al film wrapping in order to avoid light cross-talk in adiacent fibers.

The mechanics is realized with a 3-D printer and have electronics with common high voltage biasing system for fibers plane (V_{break} in a large SiPM sample is very similar) and a DAQ system based on CAEN V1742 F-ADC that give us information about the waveform of the signal: total area, rise and decay time.

The use of two hodoscopes design for measure X–Y profile and monitor beam intensity, proved to be very precise in centering the sample, measuring the muons fluxes before and after the sample, allowed not only the optimization of the position with respect to the beam center, but also to improve the number of muon implantations in the target volume as shown in Fig. 2.

The X-rays detection system (Fig. 3) is made by two GEM-S semi-planar 30×20 mm^2 HpGe crystals, for detection of low and medium muonic X-rays energy, one GLP planar 9×7 mm^2 HpGe crystal, for X rays up to 150 keV and two GMX n-type coaxial 49×57 mm^2 crystals for energy up to 6 MeV. The detectors are connected to ORTEC amplifiers, one 579 fast-filter amplifiers with 250 ns of shaping time and 4672 amplifier with shaping times ranging from 0.5 to 6 µs.

A new full digital Data AcQuisition (DAQ) system for HPGe detectors has been also implemented. The DT5780 is a compact desktop system integrating 2 Independent 16k Digital MCA and featuring HV and Preamplifier capabilities for digital nuclear Spectroscopy: 2×100 MS/s 16-bit waveform digitizer (based on CAEN 724 series).

The characteristics of DAQ module are:

- 2 separate channels with pulse height histogram of 1k–2k–4k–8k–16k channels selectable by software and "list" mode file output with pulse height and time stamp for each event with 10 ns time resolution.
- 2 independent high voltage and pre-amplier power supply;
- different triggering and coincidence data acquisition modes;
- Digital pulse processing (DPP) features: possibility to choose all the acquisition, filtering, triggering and coincidence parameters by software;
- simple USB and fast optic fibres input/output;

With digitizer it is possible to set, through the M^{2}C software, the high Voltage bias provided to the detectors and the shaping time parameters of the trapezoidal filter to achieve the best triggering and resolution performances. The output file contains two columns with the X-ray calculated energy and the time of arrival or time stamp. To perform time cuts in coincidence with the muon beam, the proton synchrotron

Fig. 1 2 Hodoscopes with different fiducial areas: one is 3.2×3.2 cm^2 and the other one 10×10 cm^2, both with similar design
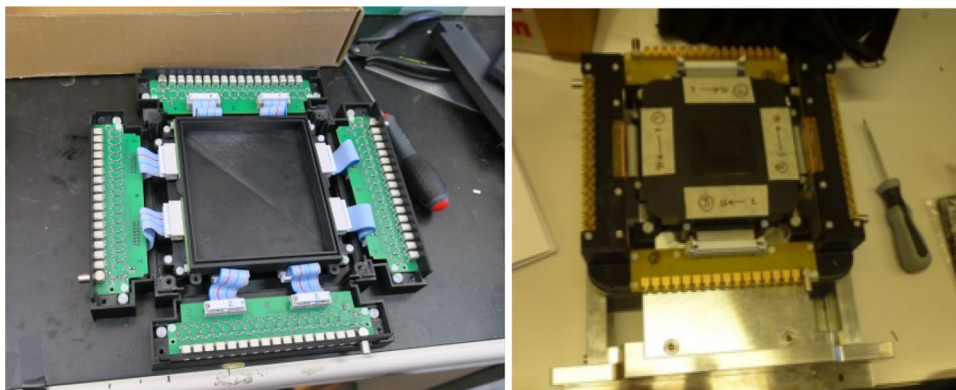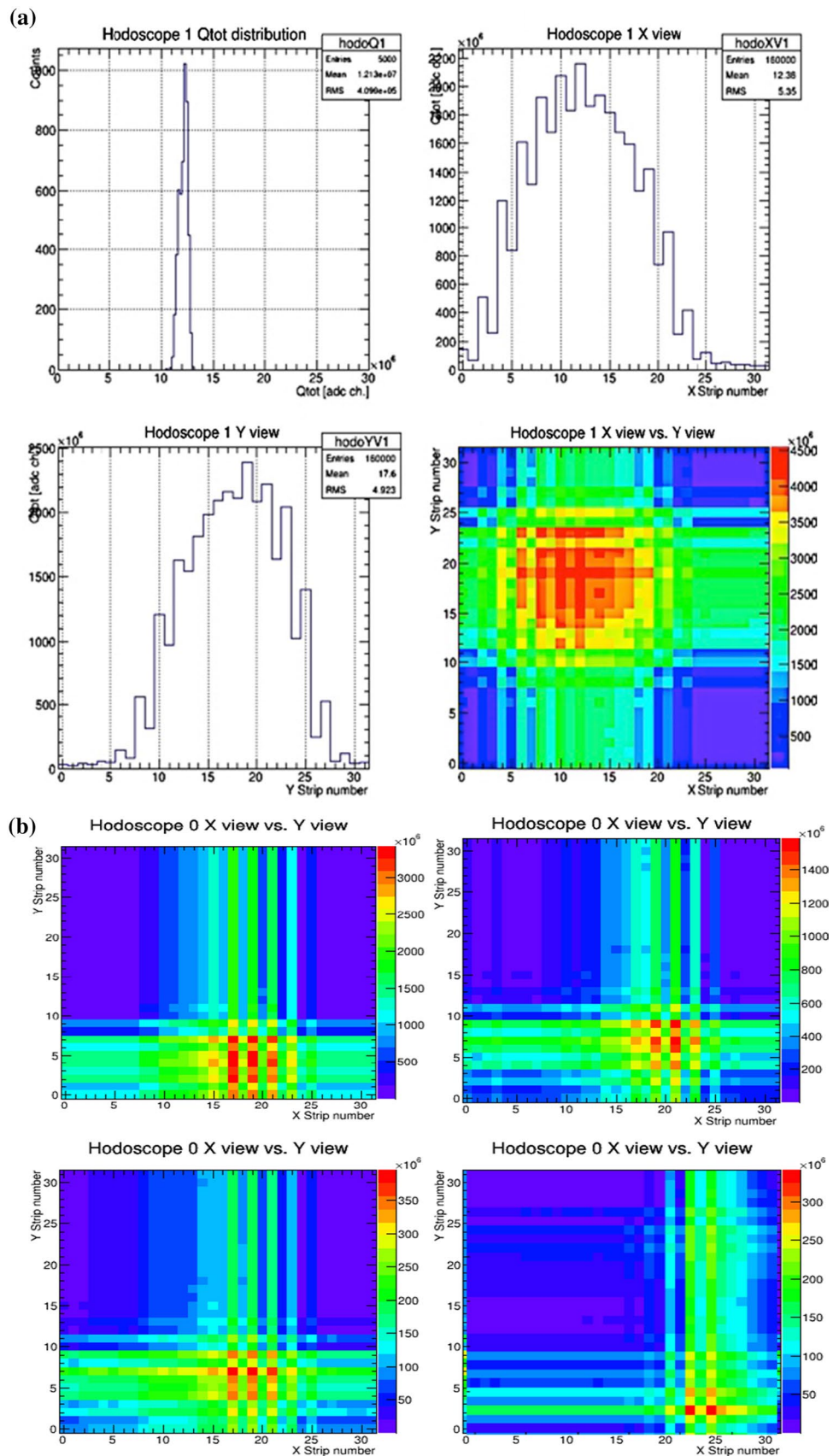
Fig. 2 **a** Muon flux distribution in *X*–*Y* plane of a typical run at 60 MeV/c: $8 \times 10^4 \, \mu \, s^{-1}$; **b** decrease in the outgoing muons flux from an archaeological sample (A1280) during the various phases of centering A1208
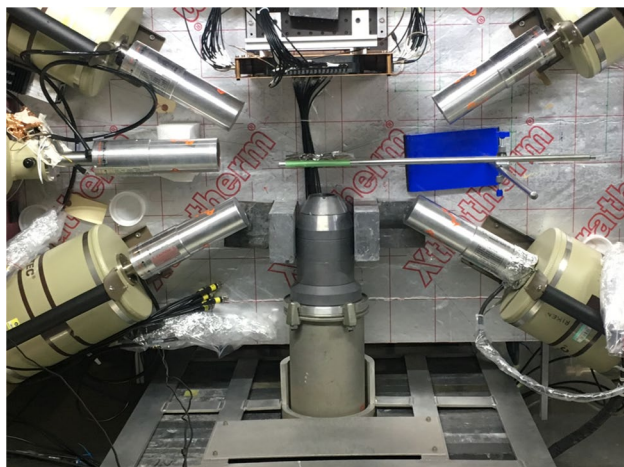
Fig. 3 System detection: 5 HpGe for X-ray spectroscopy measurements and SiPM Hodoscope during sample centering operations

trigger signal is used as "time zero" of the acquisition. The shaping parameters were chosen reproducing the gaussian ones already used in analog acquisition system. In particular,

chosen τ as a gaussian shaping time, the time to peak (τ_{peak}) is approximately 2.2 τ. The produced ASCII output file is imported and processed in the MATLAB environment.

This allows to define the time windows after the acquisition keeping the file size quite small (order of 100 MB per 12 h of acquisition) and to construct, as shown in Fig. 4 spectrum with prompt and delayed events, the corresponding scatter plots with energy and time information and obtain a 3D energy-time spectrum as shown in Fig. 5.

Results and discussion

Multi Layer sample for muon beam momentum scan

In order to calibrate the muon implantation depth inside the different materials a detailed scanning (from 28 to 72 MeV/c with 1 MeV/c step) of the muon beam momentum was carried out using a multi-layer sample made by PTFE, Al, Si, Sn, Fe, Cu, Zn, Ag, Ta, Au, layers of variable thickness (250 μm to 1.3 mm); the results were compared with a simple model for the muon stopping calculation in materials
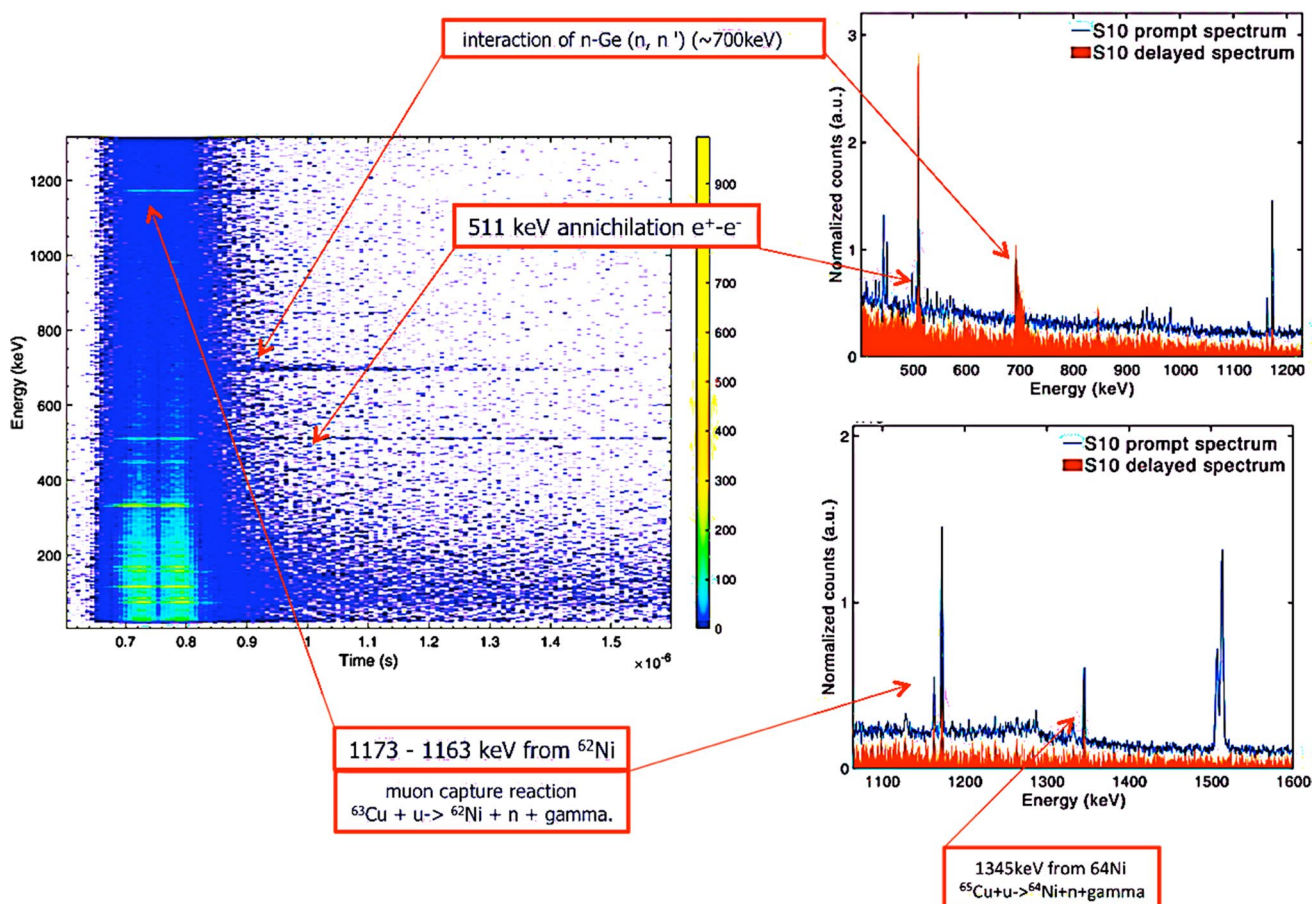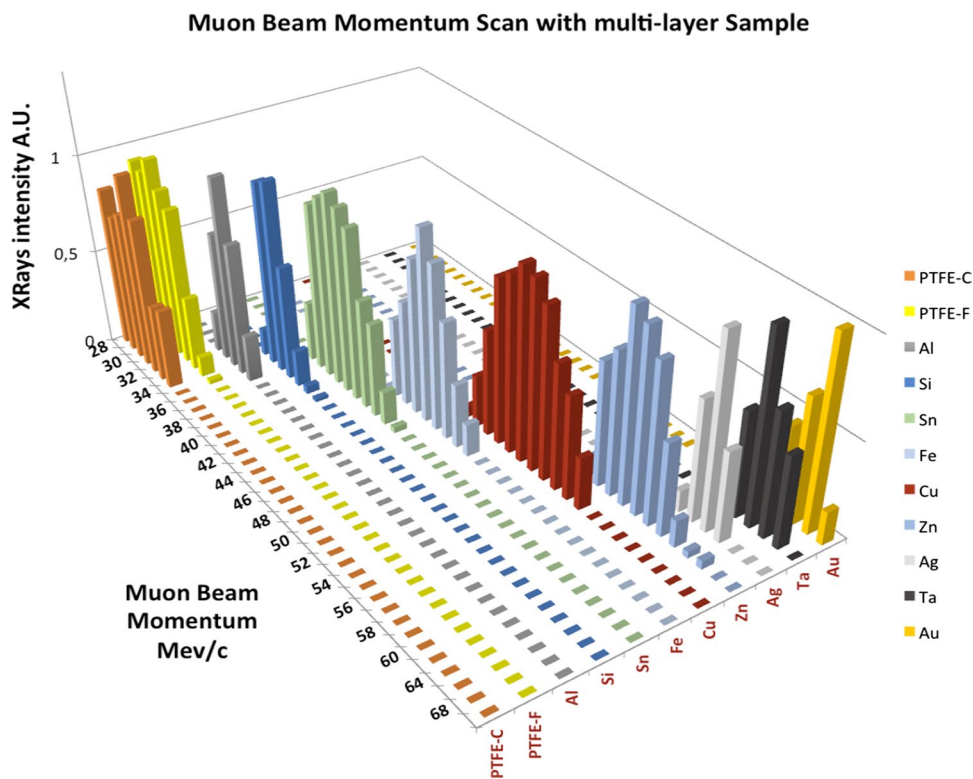

Fig. 4 Scatter plot of all events and delayed and prompt spectrum of copper sample

Fig. 5 Distributions for different materials of characteristic muonic atom X-ray intensity

such as SRIM-TRIM software. A detailed quantitative analysis and comparison with the simulations did provide a better understanding of the correct value of the muon momentum and distribution of muon implantation in materials; such information coul be used profitably by other experiments.

In Fig. 5 characteristic muonic atom X-rays intensity distributions for different materials are shown in a 3D graphics.

The calibration of muon beam momentum has been possible correlating the maximum intensity of the characteristic X-rays due to an element and related mass thickness with the muon beam momentum, establishing a relationship of muon beam momentum as a function of the mass density (density per thickness in g/cm^2) of the multi-layer sample, to be used as calibration for the irradiations of samples having known materials and density.

"Calibration Curve" with alloys and pure elements

In order to perform a quantitative analysis a calibration curve was obtained using several reference materials containing different percentage of known element. For instance we use different targets of copper alloys from GoodFellow: $^{94}Cu/^{6}Sn$; $^{63}Cu/^{37}Zn$; $^{62}Cu/^{18}Ni/^{20}Zn$; $^{55}Cu/^{45}Ni$; $^{72}Ag/^{28}Cu$. The results are reported in Fig. 6.

After the calibration of the muon beam momentum and sample centering system, we proceeded to irradiate and analyze "true" archaeological samples.
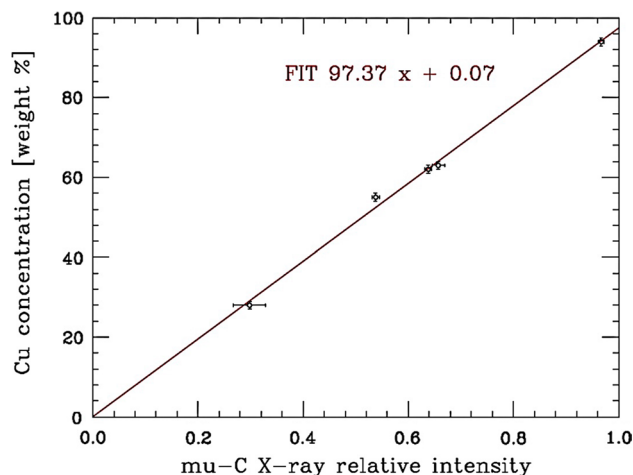

Fig. 6 Calibration curve for copper samples

In particular, 2 bronze fragments (see Fig. 7) of votive lamps of Nuragic age (VII–VIII century B.C.) in the form of little ships, coming form Sardinia (Italy) with prolonged (12–18 h) irradiations were analyzed to reach the sensitivity of 1%.

Archaeologists agree that the first fragment n. A1449 represents a piece of the side wall of the ship, while the second fragment n. A1208 represents the bow of the ship.

The results of the analysis show a presence in both samples of a ternary Cu–Sn–Pb alloy: in the first case the ratio

Fig. 7 Bronze samples: a later wall (A1449) and bow (A1208) of "nuragic" votive ships

is 91(2):7.0(5):2.1(2) against 89(2):10.0(6):1.0(1) of the second one.

Conclusions

The CHNET_TANDEM experiment have been obtained the following results: using a prolonged irradiations the characterization of 2 bronze archeological samples has been charcterized revealing the presence of Pb–Sn–Cu ternary alloy as constituent material; the implementation of a new data acquisition system (Multichannel/Digitizer) which allowed to acquire not only the energy spectrum but also the temporal spectra of the acquired signals identifying a series of muon capture reactions followed by prompt gamma emission; this type of data acquisition permits moreover, to get a better signal to noise ratio; the irradiation of standard bronze samples with different concentrations of Cu allowed us to construct a quantitative calibration curve. MAXRS has proved to be a non-invasive, simoultaneous multielemental analytical technique employable profitably on archeological samples; high energy X-rays emissions has low auto- absorption also with elements with high Z and high density values.

The MAXRS is potentially applicable for the quantification of all elements (from Li to U) without any vacuum system; by muon beam momentum scan is possible to select the depth, providing the possibility to perform depth profile of elemental characterization and as the final goal the possibility to obtain a 3D elementary mapping of the whole sample.

The characteristics above mentioned in addition to those such as its high specifity (energetic and temporal signatures) and the negligible radioactivation, it will be able to become in the future the MAXRS as technique of election for the elemental characterization of cultural heritage samples. For sure, nowaday it could be used as complementary technique to other well-established non-invasive techniques such as PGNAA or XRF.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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