

A new combined IRMS-AMS system for the measurement of small samples at CEDAD

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Abstract – A new system dedicated to the measurement of samples with masses in μg range has been installed at CEDAD-(Centre for Dating and Diagnostics)-University of Salento. The set-up can perform ^{14}C measurements by AMS (Accelerator Mass Spectrometry) on gaseous samples thanks to a new hybrid ion source, capable of accepting both solid and gas samples, simultaneously determining stable carbon and nitrogen isotopic ratio by IRMS (Isotopic Ratio Mass Spectrometer). An Elemental Analyzer (EA) combust organic samples and a gas splitting unit (GHI) split the combustion gases to the two instruments.

The possibility to date samples with mass in the microgram range, significantly lower than that typically used for radiocarbon determinations (of the order of 0.5-1 mgC), has extended the experimental potential of CEDAD. The new experimental set-up has opened new frontiers for the application of AMS technique in several research fields. We present the performances of the system, the results of different tests performed on real samples and some preliminary results.

I. INTRODUCTION

AMS radiocarbon dating together with the analysis of nitrogen and carbon stable isotopic ratios represents a fundamental research tools in different fields. In particular in archaeology, these methods can supply highly complementary information in studies related to paleodiet reconstruction, paleo-environmental analyses and for the assessment of the quality and accuracy of radiocarbon age determinations.

A relevant, instrumental and methodological step in this direction has been achieved at CEDAD though the installation of a new set-up whose main goal was to give the possibility to perform, on the same sample of mass in the micrograms range, both stable isotopes and radiocarbon analyses.

The new system is formed by different functional blocks [1]: an Elemental Analyzer (EA) converts organic solid samples to gas by combustion at high temperature in an

oxygen flow and, by a chromatographic column, separates the different gas species determining N and C concentrations by a TCD (Thermal Conductivity detector). A gas splitting unit (GSU) formed by an attenuated tee connection splits the gas flow coming from the EA into two aliquots: 10% to the IRMS for $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ measurements and 90% to the a gas-accepting ion source through a gas handling interface (GHI) and a silica capillary with a inner diameter of 50 μm for AMS ^{14}C determinations. The GHI works through different phases [1] and was designed, on the basis of previous works [2, 3], to satisfy the required source operating parameters, such as He flow rate and He/CO₂ ratio. The connection of the hybrid sputtering ion source required the modification of the low energy spectrometer with the installation of a rotatable Electrostatic Analyzer [4].

After different experimental tests performed by analyzing samples of know isotopic composition and of different masses in order to define optimal operating conditions [4], the new system is ready for routine operations and for the analysis of unknown samples from different research fields for which the possibility to date very low mass is a crucial advantage.

The first studies performed with the new set-up on samples with historical and archeological interest regard the Capitoline She-wolf and a sample coming from a prehistoric cave in Italy. The bronze statue named “She-Wolf” is the symbol of Rome in the world. It is on display at the Capitoline museums in Rome and represents the Capitoline Wolf feeding two twins (fig.1). The legend tells that the wolf saved and nursed the twins Romulus and Remus that the parents, Rhea Silvia and Mars, abandoned on the Tiber river. Traditionally, the statue of she-wolf was attributed to the Etruscan age (5th century B.C) while it was known that the twins were placed beneath the Capitoline wolf in the fifteenth century AD [5]. During the last restoration campaign anyway, a different hypothesis about the age of the statue was suggested on the base of considerations concerning the casting techniques. To solve the controversy a radiocarbon dating campaign was then initiated. The bronze statue was made with the lost wax casting technique, so it was possible to establish the time of its realization by dating the organics residues still preserved inside the casting cores.



Fig. 1. The Capitoline She-Wolf

II. SAMPLES PREPARATION

From the Capitoline She-wolf different classes of materials were selected and handpicked at the optical microscope among the organic material collected into two different phases: during the restoration works (1997-2000) and during a second sampling campaign performed by the CEDAD researchers by using an endoscope inserted through a hole present below the statue (fig.2a and 2b).



Fig. 2. The sampling phases with endoscope through the hole below the Capitoline she-wolf (a); selection of organic matter at the optical microscope (b); wheat straw (c) and caryopses (d) samples.

Paleobotanical and SEM investigations (carried out at the University of Rome “La Sapienza” by Dr. Alessandra Celant) allowed to recognize two different types of functional structures.

The first one consists of fragments of epidermal tissue formed by elongated cells with wavy margins and numerous silica bodies regularly arranged between the epidermal cells (fig.3a). The second is characterized by vascular tissue, with pits and spiral thickenings along the

longitudinal walls, and parenchymatous cells (fig. 3b).

These structures suggest that the samples are formed by fragments of vegetative and reproductive elements of cereals: the presence of caryopses and wheat straw has been indeed determined (fig. 2c and d). The selected samples were chemically processed at CEDAD by following the standard Acid-Alkali-Acid protocol in order to remove contaminants.

The sample from the prehistoric cave consisted of a human bone from which collagen was extracted by following the Longin protocol. The collagen was, then, freezer-dried for 24 hours in order to evaporate water and acid.

The processed samples excreted from both the Capitoline statue and the human bone were dated by using the standard “solid” procedure (after conversion to graphite at 600°C by using iron powder as catalyst and hydrogen as reducing agent) while some fractions (approximately 50 µg according) were sealed into tin capsules and placed into the EA autosampler. The solid samples were converted into gas by the elemental analyzer for IRMS and for AMS analysis by using the hybrid ion source.

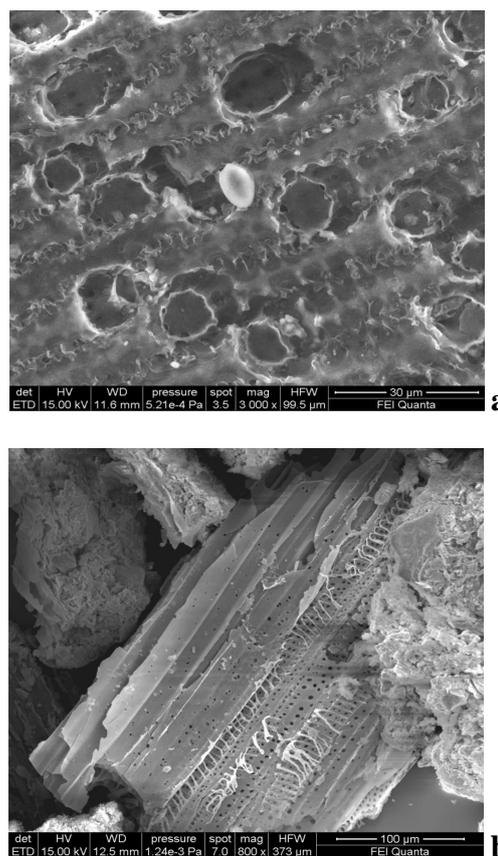


Fig. 3. Epidermal (a) and Vascular tissues (a) observed at SEM microscope.

III. RESULTS AND DISCUSSION

Twenty-eight different solid samples, collected from the casting cores of the bronze statue, were investigated and dated with the standard AMS technique. The radiocarbon dating campaign accomplishes samples collected on internal part, from the head to the tail, allowed the definition of the absolute chronology of the Capitoline she-wolf.

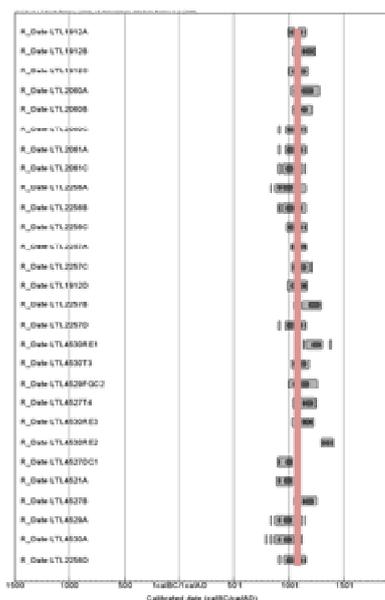


Fig.4. Calibrated radiocarbon ages

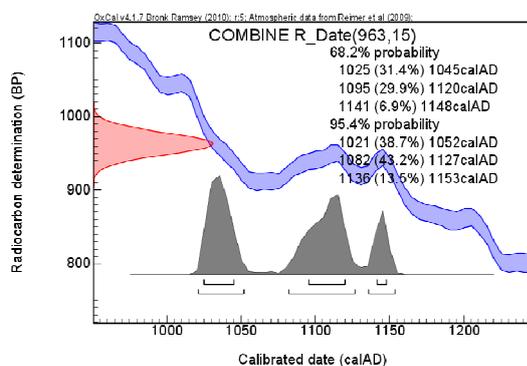


Fig.5. Combination of 28 ¹⁴C ages

Fig 4 summarizes the results of the 28 organic samples; in particular, the results place the artifact between 1021 and 1153 AD with a confidence level of 95.4 % (fig.5). The three gaseous samples measured with the new hybrid ion source gave results which are consistent with those obtained on the corresponding samples dated by using the standard graphite technique (Table 1).

Table 1. Comparison between the AMS results of solid and gas samples

Sample ID	Results on Graphite	Results on gas
LTL2256A	1051 ± 60	1201 ± 150
LTL4529A	1066 ± 50	903 ± 200
LTL4530RC/1A	1070 ± 50	1138 ± 150
AVERAGE	1062 ± 30	1080 ± 90

The results obtained on gas samples are statistically consistent with those obtained on graphite samples, thus confirming the good accuracy achievable by the new ion source and further extending the confidence on the results obtained for the absolute dating of the statue.

Simultaneously to the radiocarbon age, also stable carbon isotopic ratios were measured for the three gas samples. Table 2 reports the values of the $\delta^{13}\text{C}$ obtained with the IRMS technique. The range of the $\delta^{13}\text{C}$ obtained proves that all the plant remains found in the Capitoline Wolf statue belong to plants with a C3 photosynthetic pathway.

Table 2. The $\delta^{13}\text{C}$ values for three gas samples of Capitoline she-wolf obtained by the IRMS technique

Sample ID	$\delta^{13}\text{C} \pm \sigma$
LTL 2256A	-26.0 ± 0.9
LTL 4529A	-26.2 ± 1.5
LTL 4530RC/1A	-25.6 ± 0.6

Also for the samples LTL 17200 A, coming from a prehistoric cave in Italy, the ¹⁴C age was measured by the new hybrid ion source.

Fig. 6 shows the extracted beam current and isotopic ratio as a function of the measurement time for the sample.

The result of radiocarbon dating shows a Radiocarbon Age=14013±300 BP, well consistent with the age measured by using the standard graphite approach which was 13961±75 BP.

The age was then converted to calendar age by using INTCAL13 curve and the software OXCAL ver 4.3; the bone sample was dated between 15878 and 14250 cal BC with a confidence level of 95.4% (fig.7).

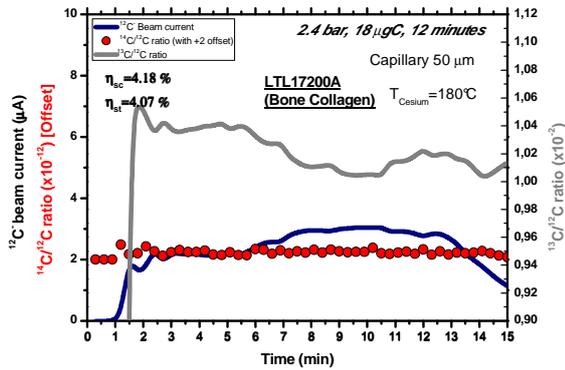


Fig. 6. Test on bone samples. The extracted beam current (blue line) and isotopic ratio (grey line) are shown as a function of the measurement time. The red points represent the $^{14}\text{C}/^{12}\text{C}$ ratio.

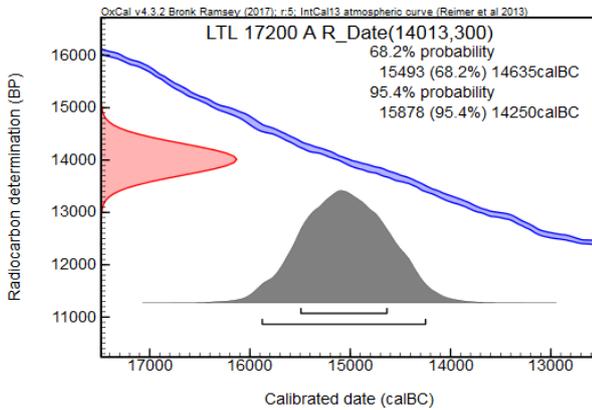


Fig. 7. Calibrated age for bone sample coming from a prehistoric cave

Table 3 reports the $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C/N values obtained simultaneously to the radiocarbon dating. The C/N ratio is within the optimal range for good quality supporting the accuracy of the obtained results.

Table 3. The EA-IRMS results obtained for the bone sample

LTL 17200 A		
$\delta^{13}\text{C}$	$\delta^{15}\text{N}$	C/N
-19.83 ± 0.05	13.59 ± 0.15	3.33 ± 0.11

IV. CONCLUSIONS

Radiocarbon dating results, obtained at CEDAD on gaseous and solid samples, firmly anchor the bronze statue of Capitoline she-wolf in the Middle Ages. The she-wolf is then more than 15 centuries younger than what traditionally believed.

The potential of the new hybrid IRMS-AMS system installed at CEDAD, for both typology of samples with historical and archaeological interest, has been proven as well its good performances on samples with reduced mass ($\sim 20\mu\text{gC}$) and demonstrate that the system is ready for routine measurements.

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