NUCLEAR TECHNIQUES FOR THE ANALYSIS AND DATING OF CULTURAL HERITAGE WITH THE TANDETRON ACCELERATOR AT THE CEDAD

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1. Introduction

Nuclear techniques for the analysis and dating of cultural heritage have received considerable interest in recent years due to the characteristic of being practically non-destructive. In the field of determining absolute dating chronology by radiocarbon, it was in 2001 that Italy finally bridged the technological gap with Australia, France, Germany, Switzerland, the United Kingdom, the United States and other countries that have had laboratories equipped with particle accelerators for dating cultural heritage since the 80s.

Abroad, some of these laboratories are able to perform either materials analysis or just dating using the Accelerator Mass Spectrometry technique. In Italy, the University of Salento (formerly Lecce University) has set up the CEDAD - CEnter for DAting and Diagnostics, the first Research Center and service for radiocarbon dating and ion beam analysis using a 3MV particle accelerator. Over the years the CEDAD has significantly increased its technological potential becoming a point of reference both in Italy and abroad for studies related to Archaeology, Art History, Materials Science, Geological and Earth Sciences and Forensic Sciences. Hundreds of archaeological sites have been studied and tens of thousands of samples have been dated so far using the Tandetron accelerator at CEDAD.

In this paper we will discuss the advantages of nuclear techniques used in the CEDAD laboratories to establish the absolute chronology of cultural heritage and to determine the composition of archaeological and artistic artifacts. In addition, thanks to the IT@CHA project, an important technological innovation carried out by researchers at the CEDAD will be described which allows us to date a material with only 10 μg of organic material.

2. The CEDAD – Center for DAting and Diagnostics –University of Salento

In 2001, the University of Lecce set up the CEDAD – Center for DAting and Diagnostics, a multidisciplinary Center for dating by AMS (Accelerator Mass Spectrometry) and for the study of cultural heritage using IBA (Ion Beam Analysis) techniques [1- 4].

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The main facility at the CEDAD is the Tandetron, a 3MV ion accelerator connected to six experimental beamlines (Fig. 1) that enable:

a) AMS radiocarbon dating up to 50,000 years;
b) dating and isotopic analysis of 10Be, 26Al; 129I and actinides;
c) materials analysis by Rutherford Backscattering Spectrometry;
d) elemental analysis by PIXE- PIGE in the air;
e) proton microbeam analysis;
f) high energy ion implantation.

The Centre also has laboratories for the chemical preparation of a wide range of samples for radiocarbon dating [5].

Figure 1. The AMS-IBA system at the CEDAD - University of Salento. 6 beamlines and 4 ion sources are connected to the Tandetron accelerator for radiocarbon dating and compositional analysis of materials

3. Radiocarbon dating by Accelerator Mass Spectrometry

Radiocarbon age determination of an organic sample (bones, charcoals, fragments of wood, clothes, etc.) requires the measurement of the residual concentration of ^{14}C in the sample. The method was developed after World War II by W. Libby and has become over the years an important tool of investigation in many fields of research [6]. Radiocarbon produced in the upper atmosphere as a result of the interaction of cosmic rays with ^{14}N, is oxidized to form carbon dioxide $^{14}CO_2$, together with the two stable forms of carbon dioxide ($12CO_2$ and $^{13}CO_2$) in the different carbon reservoirs of our planet (atmosphere, oceans, biosphere and lithosphere). In every living organism, the concentration of radiocarbon remains constant and equal, in a first approximation, to the value present in its reservoir of radiocarbon because of the onset of a condition of dynamic balance

for which the ^{14}C that decays radioactively or that is released outwards due to the effect of biological processes, is offset by the ^{14}C absorbed through diet or, for plants, through photosynthesis. With the death of the organism, this condition of dynamic equilibrium no longer exists and the concentration of radiocarbon begins to decrease exponentially. Therefore the measurement of the residual concentration of radiocarbon in a sample allows us to determine the time that has elapsed since the death of the organism.

This determination can be carried out by measuring the radioactivity of the sample, i.e. by counting the β- particles emitted during the decay. This is the so called "Radiometric or Conventional" technique developed by Libby in the 50s and for which he was awarded the Nobel Prize for Chemistry in 1960.

At the CEDAD, however, the determination of absolute chronology is performed using accelerator mass spectrometry (AMS), introduced at the end of the 70s [7].This technique is based on the direct measurement of radiocarbon by a particle accelerator. The AMS technique has an efficiency which is a million times higher than the radiometric technique and thus allows dating using less than one milligram of carbon with results obtained in just a few tens of minutes.

The main advantages of this technique are to reduce both the sample mass required for dating and the measurement time. Some laboratories for AMS radiocarbon dating are able to measure bulk samples of the order of 0.1-1 mg, with uncertainty about age ranging from 20-30 years, in just 10-15 minutes of measurement with the accelerator. In paragraph 7, a major technological innovation will be described achieved through the project IT@CHA at the CEDAD which allows us to date materials of interest of cultural heritage with a few tens of micrograms of carbon, i.e. a hundred times less than the amount currently used in similar laboratories abroad.

The AMS system consists of an ion source, a low energy mass spectrometer, a 3MV Tandetron accelerator and a high energy mass spectrometer for the separation and analysis of carbon isotopes. In the ion source, an ion beam is extracted from the graphite sample prepared in chemical laboratories, accelerated to an energy of 35 keV and sent to the low energy system where the separation of the components of the beam occurs according to the energy/charge and mass/charge ratios, prior to injection into the acceleration system. In the central part of the accelerator (stripper) the particles collide with argon gas of low density losing electrons, thus allowing the dissociation of carbon isobars. In the high-energy spectrometer the separation and analysis in mass and energy take place together with the measurement of the isotopes ^{12}C, ^{13}C and ^{14}C.

4. Ion Beam Analysis techniques at the CEDAD

Determination of the composition of elements in materials is carried out at the CEDAD with Ion Beam Analysis (IBA) techniques with the same accelerator used for determining the absolute chronology of organic materials. The Group of Applied Physics of the Department of Engineering for Innovation was among the first to follow the IBA-AMS integrated approach for the determination of the chronology and composition of materials of cultural heritage interest using the same facility. IBA techniques are essentially based on the study of interaction processes, atomic and nuclear, between MeV charged particles and the surface of the sample.

The main analytical IBA techniques, which find applications in the field of cultural heritage, are the PIXE (Particle Induced X-ray Emission) and PIGE techniques (Particle Induced Gamma Ray Emission,) and RBS (Rutherford Backscattering Spectrometry).

Figure 2 shows the experimental set-up for IBA in the air developed at the CEDAD. A particle beam, typically protons or α particles, accelerated to energies of 2-4 MeV is focused onto the surface of the sample to be analyzed by inducing the emission of characteristic radiation (x-rays and gamma) and the backscattering of incident particles. The simultaneous detection and analysis of the energy of x-rays, gamma rays and backscattered particles is used to determine, both qualitatively and quantitatively, the elemental composition of the material analyzed.

The ability to detect and analyze simultaneously, and not destructively, the various products of the interaction of the incident beam with the sample, allows PIXE, PIGE and RBS measurements to be carried out at the same time, providing additional information in terms of detectable elements, depth of analysis and sensitivity.

Although IBA techniques are applied in numerous fields of research such as Materials Science, Biology, Science of the Earth, and environmental monitoring, they have become, especially in recent years, an analytical tool used in the field of cultural heritage diagnostics. In this field, in fact, the possibility of compositional analysis of both major and trace elements, without the need for sampling, represents the fundamental advantage of these analytical techniques as witnessed by the numerous applications in the analysis of Renaissance paintings, manuscripts, miniatures, ceramics, glass, jewelry and textiles, to name just a few examples.

5. PIXE (Particle Induced X-Ray Emission)

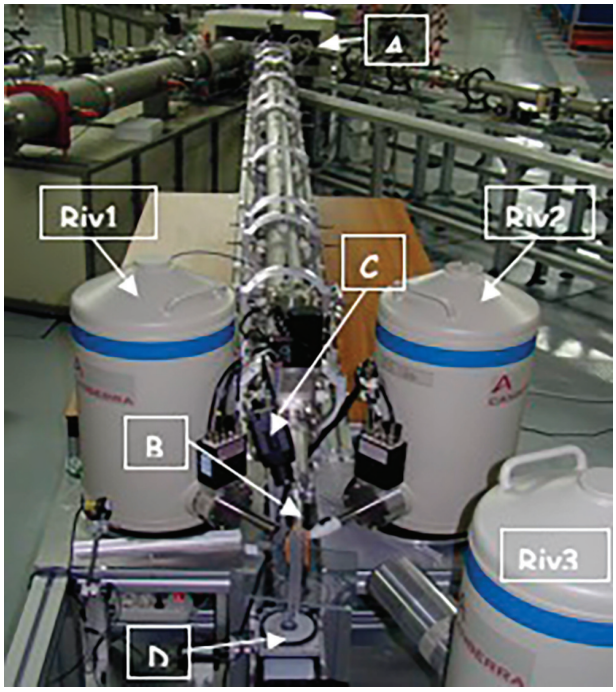

Figure 2. The PIXE-PIGE external beamline for cultural heritage at the CEDAD. A: Switching magnet; Riv1: 30 mm² Si(Li) X-ray detector; Riv.2: 80 mm² Si(Li) X-ray detector; Riv3: Gamma Ray Ge detector; B: external window; C: TV camera; D:sample x-y stage

The PIXE technique is based on the detection and analysis of the characteristic x-ray energies emitted by a material when subjected to bombardment with particle beams with (typically protons) energy of the order of MeV [4]. The interaction of the incident proton with an electron of one of the atomic inner shells, has a certain probability it will be ejected, leaving the atom in an ionized state. The vacancy left by the electron in the inner shell is "filled" by the transition of an electron from an outer shell, which corresponds to the emission of a photon by the atom of energy equal to the difference between the two shells. Since the energies of the electrons in the various shells are characteristic of each atomic species, so are the differences between them, and thus the energy of the emitted photon x is too. In the field of cultural heritage diagnostics, the PIXE technique has the following advantages:

a) Multi-element analysis: this technique makes it possible to determine at the same time, in a single measurement, all elements with an atomic number greater than that of sodium.

b) Analysis in air: this technique has the considerable advantage of being used either in air or in a helium atmosphere thanks to the reduced loss of energy in air of the protons exiting the accelerator.

c) High sensitivity: the use of appropriate energy of the incident beam, of suitable geometry detection and experimental set-up enables detection of both the major elements in the sample (for example, the matrix elements) and the trace elements, with sensitivity in the order of parts per million (ppm).

d) Non-destructiveness and reduced measurement times: the high value of the ionization cross section allows the use of reduced currents in the ion beam probe and therefore, leads to a reduction in measurement times (typically a few minutes), and damage caused to the material.

e) Complementarity with other IBA analysis techniques: the interaction of the incident proton beam causes not only the emission of x-rays from the material but also gamma rays and the backscattering of protons. The detection of x-rays occurring at the same time as the analysis of these additional products of interaction is used to detect elements lighter than sodium which cannot be determined with PIXE. In particular, the detection of gamma rays is used to determine elements such as fluorine, sodium, magnesium and aluminum, while the analysis of the backscattered protons allows the detection of carbon, oxygen and nitrogen.

6. Application of IBA-AMS techniques to Cultural Heritage

6.a Detail of the statue of St. Francis

As part of the collaboration between the CEDAD and the Department of Arts and History at the University of Salento several parts of various sculptures which underwent analysis were dated by radiocarbon method and analyzed using the IBA techniques at the CEDAD. As an example, the study reports on a detail of the statue of St. Francis of unknown author which is preserved in the Church of Santa Chiara in Lecce. The purpose of the analysis was to obtain information on the elemental composition of the original painting pigments and on the layer beneath the original pigments and to determine the time of realization. Two analyses were performed on the hand of the statue of St. Francis (Fig. 3) which is characterized by the presence of stigmata.

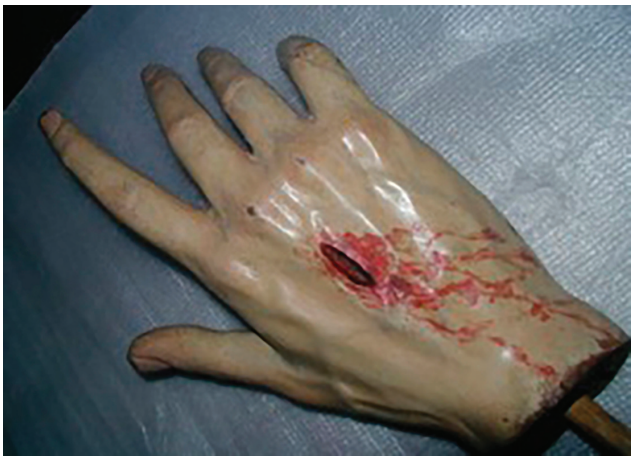

Figure 3. Detail of St. Francis's hand.

A first analysis was carried out on the inside of the stigmata to obtain information on the pigment used to reproduce the blood. In addition to the lines of lead, the X-ray spectrum shows those of mercury, a chemical element found in cinnabar red (Fig. 4a). Furthermore, in a particularly abraded area, one point of the analysis shows the presence of white lead, used for the flesh tones (Fig. 4b).

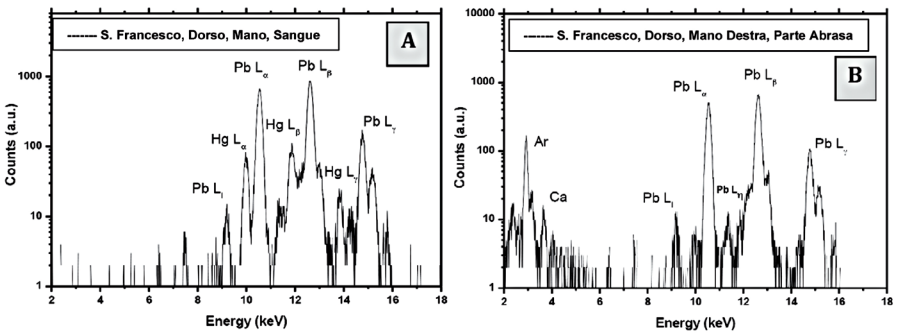

Figure 4. Hand of the St. Francis statue: (a) blood, (b) flesh tones

Investigations carried out on various parts of the hand made it possible to acquire information about the elements used for the pigments in the original paint layer (especially lead white, and cinnabar for the reds and flesh tones). In the abraded areas, elements such as titanium and zinc were detected, probably attributable to modern restoration and the use of titanium dioxide, and zinc oxide for the white. The presence of emission lines x for calcium may indicate the use of a gypsum for restoration. In the case of the analyzed samples, finally, given the high intensities of the lines of lead (and the overlap of line Mα1 of lead at 2.345 keV with line Kα of sulfur at 2.307 keV) it was not possible to discriminate unequivocally the presence of sulfur and obtain, therefore, unique and conclusive information about the existence of an original plaster-based preparation. Radiocarbon dating was carried out by taking some tiny fragments of wood from the statue of St. Francis of Assisi. By using the AMS dating technique the amount of wood taken was reduced to 10-20 mg, minimizing the destructiveness of the analysis. Dating results are shown in Figure 5.

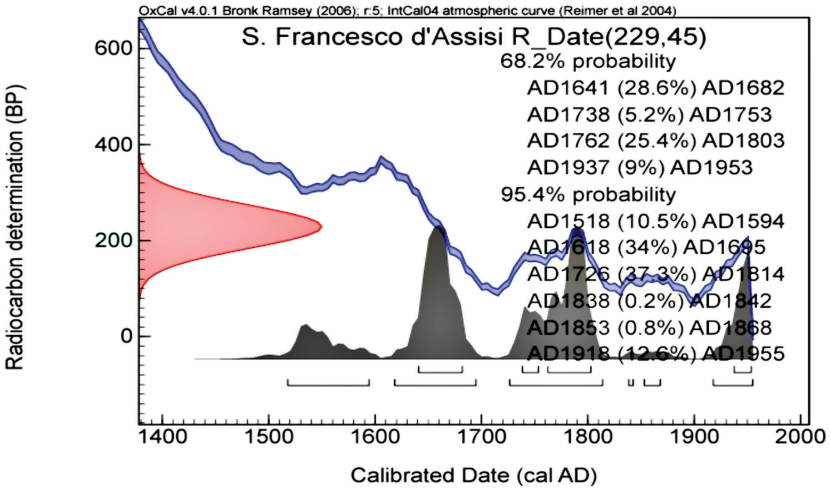

Figure 5. Results of radiocarbon dating of St. Francis's hand

6.b Radiocarbon dating the Capitoline She-Wolf

The Capitoline Wolf is a bronze statue known throughout the world as the symbol of Rome and preserved in the Capitoline Museums of Rome in Italy. Historically, it has been attributed to the Etruscan age (5th century B.C.). It has a significant symbolic and cultural value because its creation can be traced back to the legendary foundation of Rome. The statue represents the Capitoline Wolf suckling the twins Romulus and Remus, the sons of Rhea Silvia and the god Mars. Legend tells that the twins were abandoned on the Tiber river and were then saved and suckled by the wolf. The twins placed beneath the Capitoline Wolf were added in the fifteenth century, perhaps by Pollaiuolo

Figure 6. The Capitoline She-Wolf during investigations by the CEDAD team

Doubts about the realization of the bronze statue during the Etruscan era were also advanced in the nineteenth century by various researchers. The restoration of 1997-2000 commissioned by the direction of the Capitoline Museums was given to Anna Maria Carruba [9]. The Capitoline She-Wolf was made with the technique of lost-wax casting. The casting contains numerous plant remains which were added to give firmness to the mixture and to facilitate the expulsion of fumes during its treatment with high temperature. There have been numerous debates and study days over the years on the Capitoline Wolf, organized to refute Anna Maria Carruba's thesis about the Carolingian origin of the she-wolf [10].

Researchers at the CEDAD were contacted directly by the direction of the Capitoline Museums, and carried out a systematic study to determine the absolute chronology of the she-wolf by using the Tandetron accelerator. The organic materials taken from the wolf were dated making it possible to establish the time of its realization. The study lasted almost five years and was held in two phases. In the first phase, the organic materials collected during the restoration were dated. In the second phase, the Group of Applied Physics of the University of Salento removed further samples using an endoscope inserted through the center hole below the statue (Fig. 7) with specifically designed equipment.

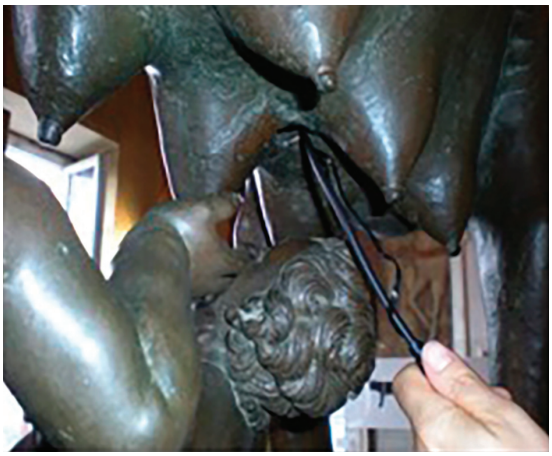

Figure 7. The phases of sampling from the casting through the hole under the belly of the Capitoline She-Wolf

The plant remains found in the Capitoline Wolf belong to the category of C3 plants, that is, during photosynthesis carbon atoms form chains of three atoms. Paleobotanical investigations carried out at the University of Rome "La Sapienza" by Dr. Alessandra Celant have determined the presence of caryopses and wheat straw (Figures 8a and b).

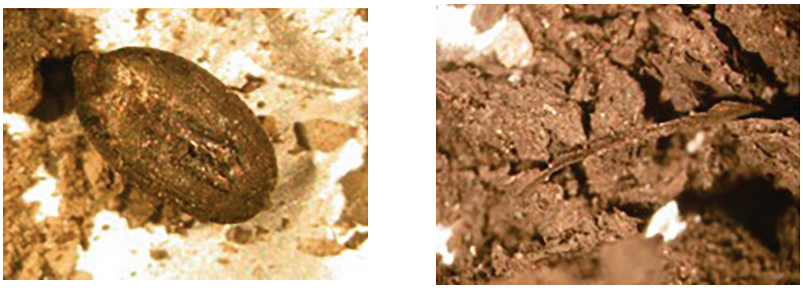

Figure 8. (a) caryopses, (b) plant remains

Putting aside the controversy that sought to obscure the results of the CEDAD researchers, the radiocarbon dating using the AMS technique enabled us to establish definitively that the Capitoline She-Wolf was made in the Middle Ages. In particular, the resulting average of the 28 datings made on internal parts, from the head to the tail, led to establishing the absolute chronology of the she-wolf between 1021 and 1153 with a confidence level of 95.4%. Therefore the realization of the wolf is about 17 centuries later than the wrongly attributed dating based on historical and stylistic considerations.

6.c AMS-IBA investigations on the Riace Bronzes

The Riace bronzes are two famous masterpieces of great importance for the history of art. They were found off the coast of Riace in Calabria in 1972. The dating of the "elder" is attributed archaeologically to between 470 and 460 BC, while the second statue, the "youth", is archaeologically dated to between 440 and 430 BC.

Figure 9. The Riace Bronzes, (a) the youth, (b) the elder

After the discovery of the Riace Bronzes, they were restored first in Florence and then in Rome at the Central Institute for Restoration. In order to carry out the absolute determination of the bronzes using the radiocarbon method, with the CEDAD accelerator AMS technique, numerous organic samples were extracted from the casting core of the two bronzes - fragments of wood, plant remains, charcoal and animal hairs were found inside the casting cores of the Bronzes (Fig. 10).

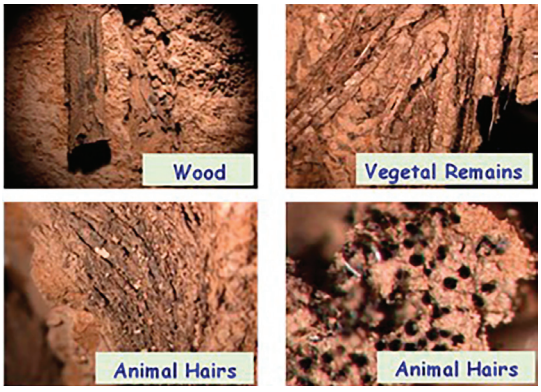

Figure 10. Organic materials found in the casting core of the Riace Bronzes

13 samples were dated for statue A and 12 for statue B. The combined dating results made it possible to attribute statue A to 512-398 and statue B to 510-400 BC, an age calibrated in years with a confidence interval of 95.4%. The radiocarbon dating results are therefore consistent with expected archaeological methods.

9 samples from statue A and 13 from B were also analyzed with the IBA techniques at the CEDAD. We found various elements Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, As, Rb, Sr, Y, Zr, Pb with PIXE and F, Na, Al, Si with the PIGE technique. The concentration of SiO2, Sr, and S is shown in Figure 11 from which it was possible to confirm the hypothesis that the right arm of statue B has been restored or replaced, as evidenced by the significant composition with respect to its casting cores.

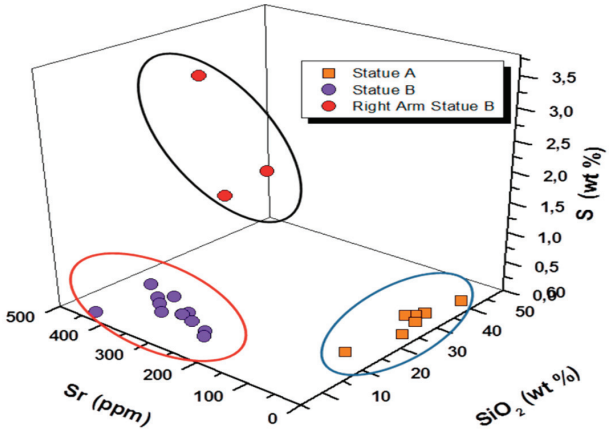

Figure 11. Three-dimensional plot of Sr, S and SiO_2. The different composition of the casting cores from statue A and B and the arm of statue B is clearly shown

7. IT@CHA Project: Italian Technologies for Advanced applications in Cultural Heritage Assets

An important innovation is in progress at the CEDAD thanks to the IT@CHA Project (Italian Technologies for Advanced applications in Cultural Heritage Assets). It is an industrial research project for the development of innovative Italian technologies in support of cultural heritage. The CETMA Consortium coordinates the project with the participation of the University of Salento and the CEDAD, Palermo University, and the University of Calabria together with many industrial partners. In relation to radiocarbon dating by accelerator mass spectrometry, the CEDAD, is currently working on a gas ion source capable of the direct dating of gaseous samples. AMS dating is usually performed once the sample has undergone various physical and chemical treatments on samples of graphite. An extremely small quantity of material is then taken from the object which is then treated until production of CO_2 occurs by acidification or combustion. The sample is subsequently reduced to a graphite, pressed and inserted in the accelerator for the measurement. At the CEDAD the dating of organic materials can be done with just one milligram of carbon in the graphite for routine measurements.

The CEDAD Group of Applied Physics within the framework of the IT@CHA project has designed a new ion source capable of injecting the CO_2 produced from the sample directly into the accelerator. This will result in a considerable reduction in the quantity of material necessary for dating. Preliminary measurements have brought the amount of carbon necessary for dating from 1 mg to 10 µg, i.e. with a quantity one hundred times lower than that usually used for dating with an accelerator.

The new gas source connected to the TANDETRON accelerator is interfaced with an IRMS spectrometer (Isotope Ratio Mass Spectrometry) capable of measuring the stable isotopes of carbon, ^{12}C and ^{13}C, directly on the same gases. In fact, the sample is first loaded into an elemental analyzer, burned, and sent to the IRMS spectrometer connected to the gas source of the accelerator. The IRMS spectrometer measures the effects of the natural isotopic fractionation and is therefore also able to check the status of residual contamination, if any by measuring the $\delta^{13}C$.

In the gas ion source, the CO_2 is injected through a syringe and a capillary on a target of Al provided with an insert of Ti. On the latter a complicated chemical-physical phenomenon takes place leading to the formation of carbon by sputtering with Cs ions on the surface of the Ti. Figure 12a shows the block diagram of the gas ion source interfaced with the IRMS spectrometer and the diagram (Fig. 12b) of the system of gas injection and trapping in the accelerator. Some details of the interior of the new source are shown in Figure 13.

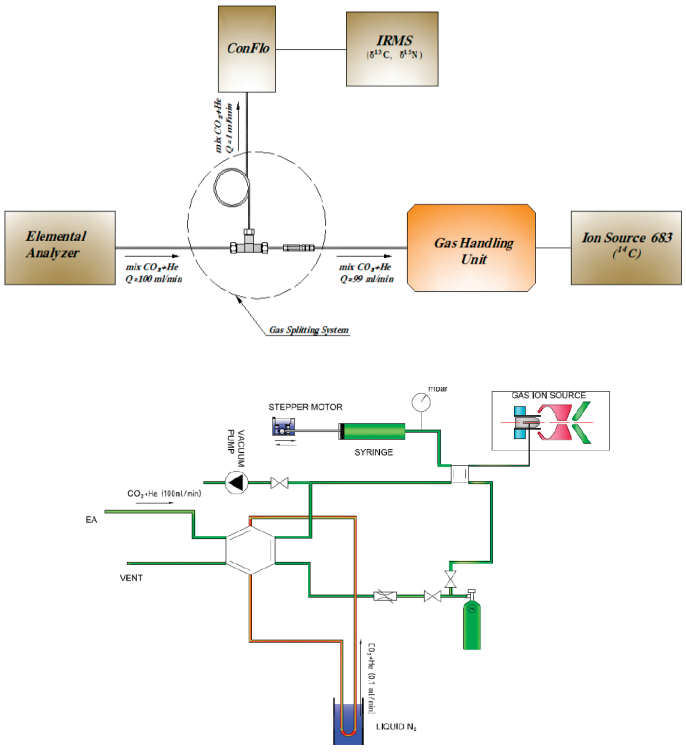

Figure 12. (a) Diagram of the source gas connected to the IRMS spectrometer and the elemental analyzer EA, and (b) diagram of the gas injection system using a syringe in a sputtering source

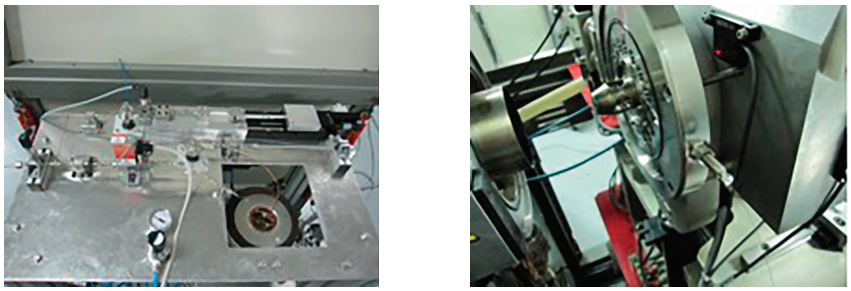

Figure 13. Details of the injection system for the gas ion source

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Biographical Notes

Lucio Calcagnile has been Full Professor of Applied Physics at the University of Salento, Department of Engineering for Innovation, since 2005. His research activity concerns the study of ion-matter interactions, the development and applications of nuclear techniques for non-destructive analysis and dating of materials, accelerator mass spectrometry, applications of cosmogenic isotopes in Archaeology, Geology, Environmental science, Forensic science. He has conducted research at Legnaro National Laboratories of Nuclear Physics, at the FOM Institute for Atomic and Molecular Physics in Amsterdam, the Tandetron Laboratory Gif sur Ivette the AGLAE-CNR Laboratory in Paris, and the Leibniz Labor in Kiel. In 1999 he created the CEDAD – CEnter for DAting and Diagnostics, the first Italian center for research and service using radiocarbon dating, which he currently heads.

He has given numerous talks at schools and conferences in Italy, France, Belgium, Malta, Egypt, Holland, Australia and the USA. He has been Chairman of international workshops and co-chairman of the 11th International Conference on Accelerator Mass Spectrometry held in Rome from 14th to 19th September 2008. He is a member of Advisory Committees of international conferences, including Radiocarbon and AMS Conferences. He is author and co-author of over 100 publications in international journals.