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The Florence accelerator laboratory for Ion Beam Analysis and AMS radiocarbon dating(*)

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Summary. — On the occasion of the transfer of the Physics Department of the Florence University to the new scientific campus in Sesto Fiorentino, INFN decided in 2001 to provide our group with a large laboratory dedicated to applications of nuclear techniques, based on a new 3 MV Tandetron accelerator, which would greatly improve the performance of existing Ion Beam Analysis (IBA) applications (for which we were using since the 1980s an old single-ended Van de Graaff) and in addition would start an activity of Accelerator Mass Spectrometry (AMS), in particular for ^{14}C dating. The new laboratory, LABEC, is hosted in a dedicated building purposely constructed by the University of Florence. LABEC has been installed within three years from the decision to fund it, and after a commissioning phase has become in 2004 fully operational for both IBA and AMS. Switching between the two kinds of operation is very easy and fast, which allows us high flexibility in programming the activities. The paper shortly describes the facilities presently available in the laboratory, their technical features and some recent applications.

PACS 01.52.+r – National and international laboratory facilities.
PACS 29.17.+w – Electrostatic, collective, and linear accelerators.
PACS 89.20.-a – Interdisciplinary applications of physics.

1. – Introduction and overview of the Laboratory

Our group in Florence has been involved in research with nuclear techniques applied to the Cultural Heritage for more than twenty years. Using an old 3 MV single-ended Van de Graaff accelerator, "inherited" from previous use in basic nuclear physics experiments, we developed great experience in the so-called Ion Beam Analysis (IBA), which can provide complete and quantitative compositional information on any material in a non-invasive way. The latter characteristic is of course especially important in applications aimed at discovering the composition of materials used to produce precious art works, or more in

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general works of historical or archaeological relevance, which are often unique so that picking up samples or damaging them anyway cannot be tolerated.

After some success we had obtained in the solution of important problems (*e.g.*, the chronological reconstruction of undated Galileo's handwritten notes using ink composition as a dating criterion [1-4]), and also exploiting the opportunity offered by the dislodgment of the Physics Department to modern buildings in the new scientific University campus, the National Institute of Nuclear Physics (INFN) decided in 2001 to support the installation of a dedicated laboratory. A new accelerator was acquired from High Voltage Engineering Europe: a 3 MV Tandetron, capable of greatly increasing the potential of the existing IBA activities and, in addition, designed to perform Accelerator Mass Spectrometry (AMS) aimed in particular at radiocarbon dating.

The Laboratory, named LABEC (LAboratorio di tecniche nucleari per i BEni Culturali) has become operational in 2004. We are currently performing both AMS and IBA activities, with an ease of switching between the two modes, which is beyond any optimistic expectation (no dead times, therefore great flexibility in programming the laboratory's activities).

The Tandetron system is equipped with three independent ion sources: two are used for IBA (a Duoplasmatron source, HVEE mod 358, and a Cs-sputter source, HVEE mod 860) and one is dedicated to AMS (a 59-sample Cs-sputter source, HVEE mod 846B). AMS is performed in the sequential-injection mode. On the high-energy side is installed a rare isotope line (where the searched isotopes are analysed through a 115° magnet and a subsequent 65° electrostatic analyser); so far it has been used for ^{14}C measurements, although measuring other rare isotopes such as ^{10}Be, ^{26}Al and ^{129}I is also possible. For IBA, four beam lines have been so far completed, including two collimated external beam lines, an external micro-beam system based on strong focusing, and a multipurpose in-vacuum IBA chamber. A fifth beam line with an electrostatic beam chopper for ultra-fast pulsing is also already available; two more are designed to be installed in the future for other applications.

Sources, accelerator and beam lines are located in a large hall of about 500 m^2; operation control console and data acquisition stations are in separate rooms nearby (250 m^2 altogether), as imposed by Italian safety regulations. Figure 1 shows an overall view of the Tandetron hall; in fig. 2, a view of the line with the standard external beam set-up for applications to Cultural Heritage is presented.

Besides the accelerator system, a large laboratory is available for the preparation of samples to be measured by AMS at LABEC. Here, the raw materials taken to the lab for radiocarbon dating undergo the standard preparation procedures of pre-treatment, combustion and graphitisation. Combustion is made using an elemental analyser, following which four reactors for final reduction to graphite are available in parallel, to speed-up the overall processing times; a second complete combustion + multiple graphitisation line is under construction. Laboratories for R&D of electronics, detector repair, and tests of ultra-high vacuum equipment are also available, as well as a dedicated mechanical workshop (which adds to the large workshop shared with the other groups in the Physics Department).

In addition to applied research for the Cultural Heritage, applications to atmospheric pollution monitoring and to geology are extensively performed at LABEC. A large number of collaborations with research groups in Italy and abroad have been established, as well as with governmental or regional organisations such as the main Italian institutions for Cultural Heritage preservation and some regional environmental protection agencies.

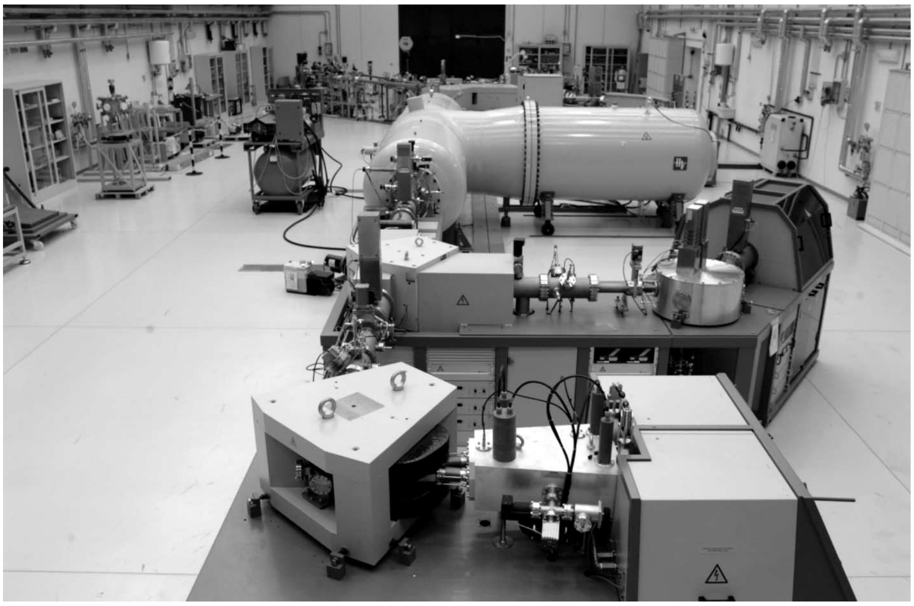

Fig. 1. – General view of the Tandetron hall at LABEC, Florence.

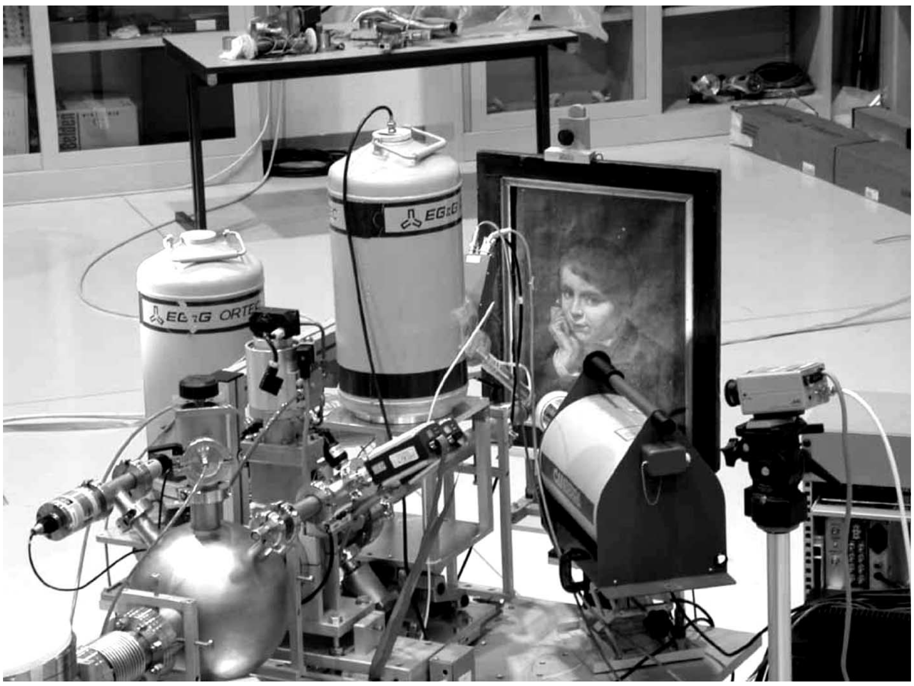

Fig. 2. – The end station for external IBA measurements dedicated to the Cultural Heritage, at LABEC, Florence.

2. – IBA applications at LABEC

A sort of mandatory pre-requisite to perform IBA in the field of Cultural Heritage (but also a great advantage in all other IBA applications) is to install an external beam facility, in order to be able to measure the objects in atmosphere. We have been using an external beam set-up since we started these activities over twenty years ago; our basic set-up has been described in many papers (*e.g.* [5-7]) and similar set-ups have now become a standard in all laboratories worldwide involved in such activities. It is obvious that by using external beams one can analyse all kinds of objects, whichever their kind and size, with great ease of handling them and further reducing any risk of beam-induced damage. Such risk is however negligible anyway, since very low currents can be used and measurement times are short (few pA are often sufficient for 100 s or so) thanks to the high cross-sections of the beam-target interactions exploited (this applies in particular to PIXE, Particle-Induced X-ray Emission). In the past, we have analysed a wide variety of artworks or historical documents, from hundreds of miniatures in medieval or Renaissance manuscripts, to the inks in the above mentioned hand-written notes by Galileo and in many other documents, to glazed ceramics by the Della Robbia family, to Renaissance drawings on paper, to oil paintings by Leonardo and Antonello da Messina. Often the problem posed by the humanists pushed us to explore new analytical possibilities beyond the standard techniques. This has been the case of the analysis of a painting by Leonardo, the Madonna dei Fusi, ex-Reford version; here, we exploited PIGE (Particle-Induced Gamma ray Emission) to detect sodium as a "marker" of the use of ultramarine, based on lapis-lazuli, as a blue pigment. The presence of sodium was otherwise undetectable using the more standard PIXE technique, because of the very low energy (1.04 keV) of its X-rays and of the presence of a coating varnish that we were not allowed to remove (the surface varnish layer totally absorbed the very soft X-rays, while gamma-rays were unaffected) [8]. The analysis of this masterpiece by Leonardo was also the first occasion to apply a variant of PIXE, so called "differential PIXE", which consists in repeating the measurement on the same spot at different beam energies, therefore probing different depths from the surface. The layer structure of paintings can be detected from the comparison of the data obtained at different energies; this way, we were able to get—in a fully non-invasive way—an indirect measurement of the paint layer thickness, which came out to be as thin as 15–20 micron: a witness to Leonardo's highly sophisticated pictorial technique [9].

With the new Tandetron, higher beam energies are now available and the potential of differential PIXE can be greatly extended, probing much deeper layers. A decisive advantage also derives from the very easy and fast procedures of beam energy change. In fact, the optimum tuning is preliminarily found for the different energies and all parameters are stored in the control computer; thus, subsequently, a given configuration can be recalled and one has again the beam on target in a few seconds after deciding to change energy.

A major improvement is also obtained in the use of IBA at LABEC thanks to the upgraded version of the external micro-beam facility (first developed at the old accelerator [10]) based on strong focusing rather than bare beam collimation. Through the use of a quadrupole doublet and an ultra-thin beam exit window (Si_3N_4, 100 nm thick) a beam spot on target of less than 10 μm is achieved, still keeping the work to be analysed in atmosphere. The use of a x-y beam scanning system coupled to a list-mode acquisition system (the energy of the detected radiation is associated to the x-y coordinates of the beam impact point when radiation is detected) makes it possible to reconstruct not only the average composition over the probed area, but also the spatial distribution of the different

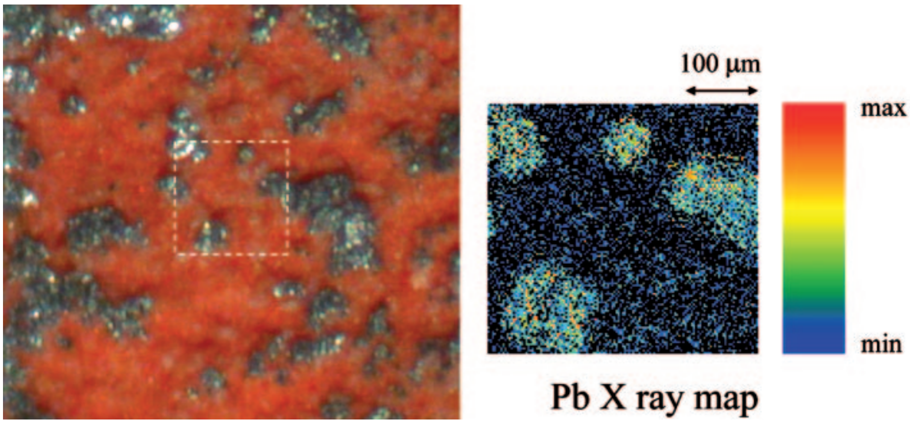

Fig. 3. – Metal-point drawing (Pb stylus) on a lead-white + cinnabar prepared paper. Optical image of the irregular trace left by the stylus, and elemental map of Pb obtained by PIXE over a $0.4 \times 0.4\,\mathrm{mm}^2$ area at the external micro-beam facility at LABEC.

detected elements. Elemental imaging is thus possible using PIXE, PIGE and even RBS (Rutherford Backscattering Spectrometry) without placing the object in vacuum [11].

An example of useful application of this technique to Cultural Heritage is the analysis of metal point drawings on prepared paper. The metal point drawing technique was widely used by the most celebrated artists in the Renaissance period, both in Italy and in northern Europe. Often the paper, on which the artist made the drawing, was preliminarily prepared by colouring it in red, or blue, or green, or white; different metals, or metal alloys, were used for the drawing stylus. Not so much is known about which materials were used by the different artists, and in addition conservation problems require their knowledge. Measuring the composition of the trace left by the stylus on the prepared paper, however, is not straightforward. The trace is not homogeneous, often made of very small grains of metal residues, and the pigments used for preparing the paper may contain significant amounts of the same metal (*e.g.*, lead stylus—lead white preparation; copper stylus—malachite green preparation, etc.). Thus, when measuring by PIXE on a spot in the metal trace, it is difficult to discriminate whether the detected elements are due to the metal point trace or to the paper preparation. In these cases, a scan over the area can be performed by means of the external micro-beam and maps of elemental concentrations constructed thanks to the list-mode acquisition. The patterns of metal concentrations, compared to the optical images of the same areas, clearly and unambiguously identify the metal point areas and those to be referred to paper (see the example in fig. 3), and the quantitative compositional analysis is performed extracting X-ray spectra from the respective areas and just from them, avoiding spurious contributions from surrounding materials. In other terms, it is like choosing *a posteriori* the target area in an appropriate selective way, being fully aware (from the maps compared to optical images) of what it is referred to.

Other applications of the various IBA techniques with the LABEC external micro-beam facility are in the field of petrography and material analysis. Examples can be found in refs. [12-14].

3. – First applications of AMS at LABEC

The first period after commissioning of the new Tandetron at LABEC was dedicated to perform a large number of reproducibility tests for the AMS determination of ^{14}C in many standards; background level measurements were also performed under different conditions in both the preparation laboratory (*e.g.*, the influence of "memory effects" due to previous preparations was checked), and in the accelerator settings.

The tests on standards yielded satisfactory results; the precision achieved (reproducibility over many preparation from the same original material) is definitely better than 0.5% (*i.e.* $< \pm 40$ y on the radiocarbon age), and the intercomparison among different standards is also very good, *i.e.* using a standard as unknown, *vs.* another used as a reference, yields a radiocarbon concentration closer than 0.5% (often much closer) to the certified value. These tests have been reproduced at subsequent times over several months, always producing the same satisfactory results.

The measured background level of ^{14}C, as resulting from just the AMS measurement in the accelerator, corresponds to an age of around 60000 years. This was reproducibly checked by directly inserting pellets of dead graphite powder into the sputter source. To test the overall measuring procedure, *i.e.* to include also the possible contaminations deriving from preparation, the same material was preliminarily processed through the standard preparation procedures of carbon samples (*i.e.* pre-treatments, combustion and final reduction to graphite). The background level is obviously slightly worse in this case, but still remains as good as over 50000 years-equivalent, which is definitely very competitive.

Following these reliability tests, over 100 dates of archaeological finds measured in the last few months (as to December, 2005). Several dating campaigns were undertaken, the most relevant of which concerned:

- medieval and Renaissance paintings on wood, for the purpose of authentication, in collaboration with Opificio delle Pietre Dure in Firenze;
- smelts from archaeometallurgical sites in northern Etruria, in collaboration with Sovrintendenza archeologica della Toscana, Department of Archaeology (Univ. of Siena), and Department of Earth Sciences (Univ. of Florence);
- medieval finds from excavations around Uffizi, in collaboration with Department of Archaeology (Univ. of Siena).

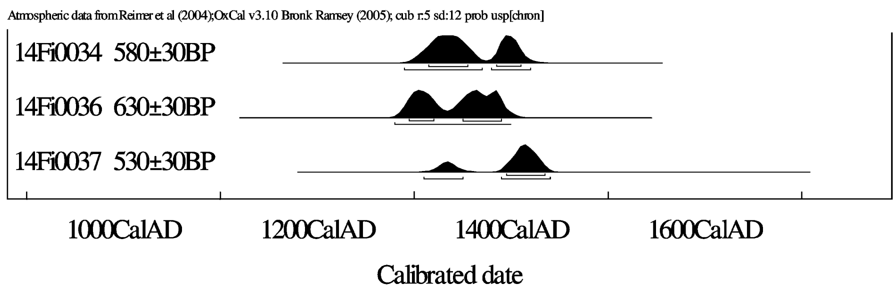

Fig. 4. – Radiocarbon dating, performed at LABEC on three wood samples from the support of two Renaissance paintings; the first two dates refer to a painting of undoubted attribution, the third to a suspected modern fake. This suspicion is not confirmed (see also text).

First results from these activities are now in press [14, 15]. As an example of the good quality of the radiocarbon measurements at LABEC, fig. 4 shows the results from three wood samples, the first two of which taken from the wooden support of an oil painting of a well-known Renaissance painter, and the third from the support of another painting of the same subject, suspected to be a modern fake. The date of the first two samples is perfectly compatible with the attribution (it is normal—and quite understandable—that the wood support of a painting comes out to be some decades older than the painting, what is known as the "old wood problem"). However, as can be seen, also the radiocarbon measurement of the third sample gives an age that, although slightly less old, is still perfectly compatible with the Renaissance period. So, these measurements have not positively supported the suspicion that the latter painting was a modern fake. The measurement however is not conclusive in the merits of the specific art-historical problem. Indeed, apart from having just one sample measured, the fact that the wood support comes out to be old, in itself, does not necessarily imply that the painting is also old. Further measurements are thus underway both on other wood fragments and on the canvas used as "*incamottatura*" in between wood backing and paint preparation layer, which would be a more representative sample to deduce the real age of the painting.

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