

ION BEAM ANALYSIS AND RADIOCARBON DATING

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Abstract

The working principles and main characteristics of the two main categories of nuclear techniques for applications to Cultural Heritage problems, i.e. Ion Beam Analysis for compositional characterisation of materials and Accelerator Mass Spectrometry for ^{14}C dating of archaeological finds, are briefly recalled. The new Florence Tandem accelerator laboratory is presented and some applications described, as examples of the great potential of these techniques in the specific field.

KEYWORDS: NUCLEAR ACCELERATOR-BASED TECHNIQUES, ELEMENTAL ANALYSIS, ARCHAEOLOGICAL DATING

KULCSSZAVAK: NUKLEÁRIS GYORSÍTÓ ALAPÚ TECHNIKÁK, ELEMÖSSZETÉTEL VIZSGÁLAT, RÉGÉSZETI KORMEGHATÁROZÁS

Introduction

The most important contributions of “nuclear” techniques for archaeometrical studies are undoubtedly the analysis of materials (by X Ray Fluorescence and Ion Beam Analysis [IBA]) and the dating of finds by ^{14}C (radiocarbon) measurements.

Let us start from the former and first of all let's clear our mind from the idea that material analysis in archaeometry be just a sort of diagnostic obsession of scientists with no importance for the world of humanists. Quite the contrary: it is the answer to specific demands from that community. Historians of art, archaeologists, historians of science and technology can learn a lot from the knowledge of the materials used: both through the information concerning specific works, specific artists or their artistic environment (e.g. for attribution purposes) and to achieve more general knowledge on historical trends, sources of supply of raw materials, existence in the past of trade routes from countries far away, etc.

Equally important, it is the conservators and restorers that need to know the materials of the original art works, both to detect their degradation and to consciously choose techniques and materials to be used in a restoration procedure.

Ion Beam Analysis (IBA)

Ion Beam Analysis is the most sophisticated and complete of material analysis techniques. It is based on the use of beams of particles, obtained by accelerators, to “bombard” the objects to be analysed, used as a target. The interactions of beam particles with atoms and nuclei of the target induce emission of radiation (X rays, gamma rays, primary backscattered or secondary particles) with energies characteristic of the emitting atom or nucleus. It is

thus possible to reconstruct the composition of the bombarded material, by collecting and energy-analysing the induced radiation. The great analytical power of IBA derives from the fact that one can easily change beam energy, intensity, size, in order to answer the specific problem (each case is in a sense “special” and may require to adapt the technique to the specific demand). Extended performance is also achieved by simultaneously exploiting the different “signals” (the various kinds of emitted radiation) that provide complementary information. Thus, a very broad, often complete, set of data can be achieved in a single measurement, which is typically very fast (100-200 seconds). Among IBA techniques, PIXE (Particle-Induced X ray Emission) exploits the emission of characteristic X rays from atomic elements, PIGE (Particle-Induced Gamma ray Emission) relies on the emission of characteristic gamma rays from nuclei, RBS (Rutherford Backscattering Spectrometry) detects the energy of beam particles after elastic scattering from nuclei (their energy depends in fact on the mass of the scattering nucleus). The most “popular” process is PIXE, just because it is the most probable of beam-target interactions, deriving from an atomic rather than a nuclear collision (and atoms are a much larger target than nuclei for the particle beams! In more rigorous scientific terms, this is expressed by the much larger X ray emission cross sections with respect to all other interaction cross sections).

In Florence, our group started doing IBA already in the first half of the Eighties, using an old single-ended Van de Graaff accelerator “inherited” from basic nuclear physics activities. We got some successful results of non negligible relevance in different fields like the study of environmental pollution, petrologic research and just the applications to Cultural Heritage.

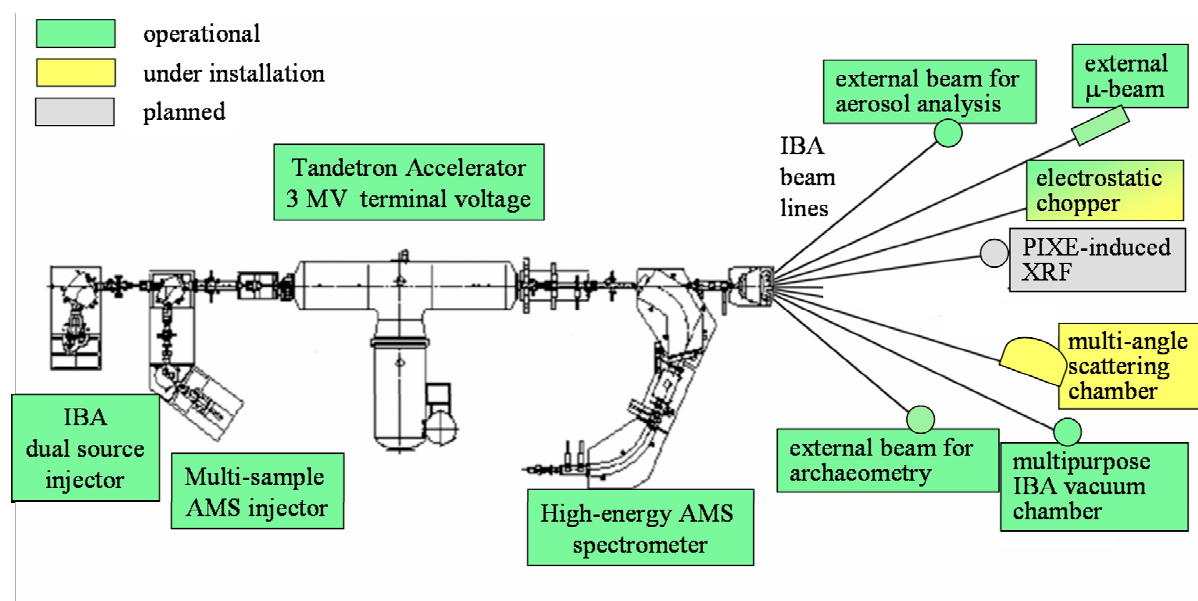


Figure 1. Present layout of the accelerator hall

Also thanks to these results, when recently the Physics Department of the University moved into a new campus where large space and newly built infrastructures were available, the National Institute of Nuclear Physics (INFN) decided to fund the installation of a dedicated laboratory, mainly for applications to C.H. The heart of the new laboratory, named LABEC (Laboratorio di tecniche nucleari per i Beni Culturali) is a new 3 MV Tandetron accelerator, specifically designed to perform both IBA and Accelerator Mass Spectroscopy (AMS), in particular radiocarbon dating. The project started at the end of 2001 (while the building, funded instead by the University of Florence, was still in the early stage of construction); thanks to a hard work of our group and of many more people both in the University and in the INFN management, the installation of the accelerator started already in May 2003, and after one year we were operational with both IBA and AMS. The present layout of LABEC (December 2005) is shown in **Figure 1**, with AMS fully operational, four IBA beamlines already active and a fifth almost completed, plus two more planned to be installed within the next couple of years. **Figure 2** shows a view of the accelerator hall.

It is essential, for a laboratory willing to perform IBA applied to C.H., to be provided with an external beam set-up. We have been using external beams for IBA since the very first activities in the Eighties, developing more and more complete set-ups including more detectors for PIXE and other techniques. The reason why an external beam is a must for C.H. applications is that by such a facility you can investigate in a non-destructive way the

complete quantitative composition of any material you may be interested in, with great ease in handling the “targets” (often fragile, sometimes also rather large!). During over twenty years of experience, we have been analysing hundreds of samples or whole works of glass, ceramics, ancient illuminated manuscripts, historical documents, drawings, paintings on wood or canvas. References to these works, as well as to all the past and present activities of LABEC, can be found in the website of the laboratory, <http://labec.fi.infn.it>¹

Let me here briefly mention just the analysis of tens of hand-written notes by Galileo concerning the problems of “natural motion”, which are a sort of record of his way of thinking throughout his life, from wrong beliefs to the final modern achievements that he reported in the printed works. It is of the utmost interest to reconstruct and locate in time the steps of his “conceptual path” towards these achievements, but these notes are not dated and it is not obvious to derive their chronology from just their content; the idea was then to provide a support to the historians’ hypotheses through the analysis of inks. They were not a standard industrial product at Galileo’s times, so that each time a batch of ink was over, the new ink (self-prepared or bought from shops) although being made of the same ingredients was never quantitatively equal to the previous. In other terms, we showed that ink composition can be correlated to the period when it was used, and by the matching of ink composition in dated documents (we analysed a large number of dated writings, e.g. letters) and in the undated notes, a chronological reconstruction of the latter was in several cases possible.

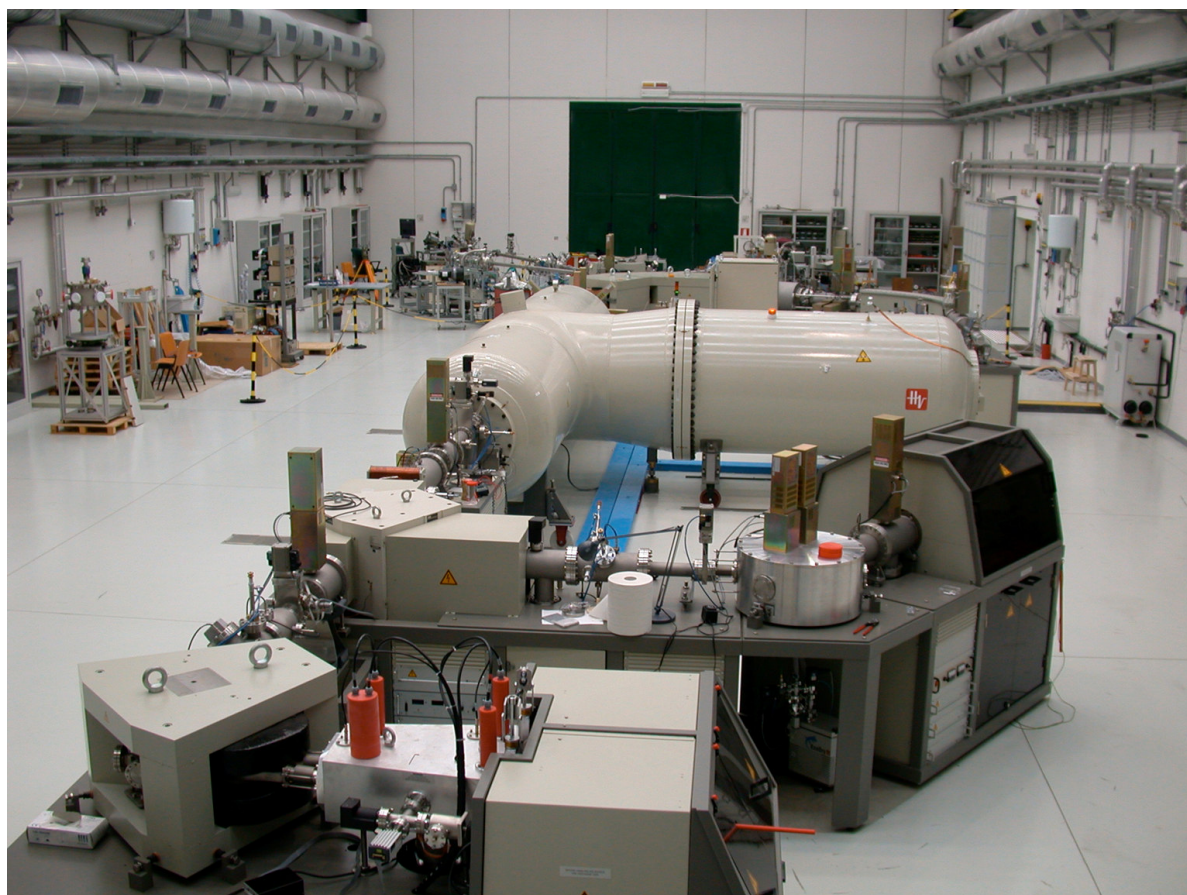


Figure 2. Overall view of the LABEC accelerator hall

Among our IBA measurements for C.H., another case that I wish to mention is the analysis of a famous painting by Leonardo, the *Madonna dei fusi* (ex-Reford version). In the analysis of materials in paintings on wood or canvas, in general, the analytical problem is connected with the layer structure of these works, and with the presence of the surface protective varnish, if it cannot be removed (as in the case of this painting; sometimes instead the varnish can be removed, when e.g. a restoration must be performed). The problems are:

1) within the beam-induced radiation, you cannot discriminate which come from the varnish, or from the paint layers (you may also have a superposition of more), or from the *imprimatura* and painting preparation. All signals are mixed in the radiation energy spectrum; in particular, one is usually NOT interested in varnish composition, while it is the paint layers that one would like to characterise. Thus, the varnish contributes a sort of undesired background;

2) the surface layer of varnish absorbs the X rays of lower energy (associated to low-Z elements) produced by the beam penetrating into the paint below. Thus, low-Z elements in the paint layers remain undetected by PIXE, while for the identification of some pigments (e.g. lapis-lazuli) it

would be essential to detect them: for instance, in the case of lapis-lazuli, the detection of sodium would be a sort of fingerprint of its presence.

As to point 1), the solution has been found by applying what may be called “differential PIXE”, which consists in performing measurements on the same area with beams of different energies. At different energies, beam ranges are different and probed depth also changes, thus by comparing X ray spectra taken at different energies, stratigraphic information can be obtained.

As to point 2), the solution comes from using PIGE simultaneously with PIXE. Gamma rays, even though produced below the varnish, are not absorbed since their energy is much higher than the one of X rays. Since it is just from the low-Z elements that gamma ray emission can be more easily induced, the combined use of PIGE and PIXE is of great use to guarantee the detection of low-Z elements even when they are “buried” below some surface layer.

Both ideas were applied in the analysis of the *Madonna dei Fusi*, leading to a complete characterisation of Leonardo’s palette in this work and to the reconstruction of the layer sequence: it came out e.g. that Leonardo’s technique was so

delicate that ultra thin layers of only 10 to 20 micron thickness were laid to produce chromatic shades!

The most recent implementation of our laboratory in the way to perform IBA has been the use of beam scanning procedures on the work to be analysed, in order to reconstruct the concentration map of the various elements. Indeed, most of the materials in the field of C.H. are inhomogeneous, and details of small size or inhomogeneous structures in the order of 100 μm or so are not always easily recognised by visual inspection. From single-spot measurements, the risk of misleading information exists: using too broad beams, one may mix information referring to different materials, using too small beams, one might inadvertently analyse anomalous, non-representative “points”. For this reason, in the standard way of performing IBA, measurements are always repeated on several points assumed to be of equal composition, to check how homogeneous is the structure.

A really dramatic improvement in significance, reliability and completeness of information can now be obtained, using methodologies providing “compositional maps”. This can be e.g. realised by the scan of relatively large areas ($\sim$ some mm^2) with beams around 100-200 μm size, using a data acquisition system that not only records energy signals from detectors, but associates them to the instantaneous x-y position of the beam on the target when the signal was produced. The element-characteristic energies of X rays, gamma rays, etc. are thus coupled to the “pixel” from which they originated on the scanned area, and stored as energy-x-y triplets in the computer memory (list-mode acquisition). It is subsequently possible to replay the acquired data and reconstruct concentration maps of the detected elements. Then, by selecting *a posteriori* homogeneous sub-areas within the scan in such a way as to avoid the compositional “anomalies” discovered thanks to the maps, one reconstructs “safe” energy spectra from which the composition of really representative areas is quantified.

Scanning IBA should always be preferred to single-point measurements, whenever possible. Sometimes it is really essential; an example is in the analysis of metal-point drawings on prepared paper, a drawing technique extensively used by the greatest Renaissance painters in Italy and Europe.

Knowledge of materials (the metal alloy used for the drawing stylus and the pigments used for the preparation of the coloured substrate paper) is needed for conservation purposes: one is dealing with very fragile and precious works, so far little studied, and mainly from the art-historical point of view.



Figure 3. Track left by a Pb stylus on paper prepared using a mixture of cinnabar (HgS) and lead-white ($(2\text{PbCO}_3 \text{ Pb}(\text{OH})_2)$)

There is a problem however: the track left by the metal stylus is not uniform as can be seen by **Figure 3**, and - especially when the paper is prepared using compounds of the same metal used for the stylus - it is difficult to discriminate the track from the paper and quantify the composition of both. By compositional mapping (through the scan over an area of the drawing) the problem is solved and any ambiguity is eliminated (**Figure 4**).

Radiocarbon Dating

Let's briefly talk also about radiocarbon dating. The principle is very well known: the age of an archaeological find (of organic origin, such as wood, seeds, burnt carbon, cloth, remains of an animal or of a man, etc.) can be obtained by measuring the residual concentration of isotope 14 of carbon with respect to the stable isotope 12.

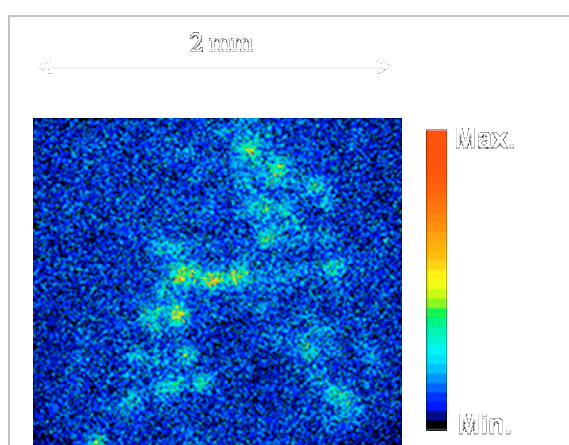


Figure 4. Map of Pb concentration on the surface of Figure 3. The highest values (brighter areas) match exactly the pattern of the stylus track as seen from the optical photograph.

This concentration in fact decreases in time from the death of the organism from which the find originates, with an exponential decrease characterised by a well known lifetime τ of about 8200 years (which corresponds to 5730 years for the so-called half-time $T_{1/2}$). Assuming as known also the initial concentration, the date of the find can be immediately obtained (the assumed initial value is not necessarily correct but the date thus obtained can be recalibrated).

The real problem is that the concentration to be measured is terribly small (one atom over thousand billions or even much less for an old sample), and in addition, in order to have a sufficient accuracy in the date, such a low concentration must be measured with great precision (1% uncertainty in measured concentration reflects into ± 80 years on radiocarbon date). Until about twenty-five years ago, to achieve such a precision and sensitivity, one needed to sacrifice a large mass of the find (tens or hundreds of grams). This was in fact the quantity of material necessary to achieve sufficient counting statistics in reasonable measuring times, using the β counting technique (according to the general radioactive decay law, the number of β decays of ^{14}C per unit time is proportional to the number of ^{14}C isotopes in the sample, so you can measure such decays and deduce ^{14}C concentration). Starting some twenty-five years ago, progressively an alternative method has been introduced, which is based on the direct measurements of the number of ^{14}C isotopes by mass spectrometry, using Tandem accelerators as ultra-sensitive, selective mass spectrometers. The great advantage of Accelerator Mass Spectrometry (AMS) is that the quantity of material needed for a dating is very low, in the order of milligrams. Dates back to 50000 years can be obtained, and for historical or pre-historical finds (back to 10000 years) the uncertainty on radiocarbon date can be kept within ± 40 years (the overall uncertainty on the date is often higher however, due to the recalibration procedure).

AMS has now almost totally ousted the traditional β counting method for radiocarbon dating. Presently, over forty laboratories in the world perform AMS to a larger or lesser extent, some of them being entirely dedicated. Over ten thousand dates per year are produced: the basic, hard, "obscure" work for the archaeologists.

In Europe, at least ten laboratories are active with AMS; many of them have a long experience, high qualification and a large throughput of dates per year. Recently, the possibility has been demonstrated of using even very compact tandems (< 1 MV terminal voltage) for precision ($< 1\%$) ^{14}C dating.

In Italy, until three years ago no laboratories were equipped for routine AMS radiocarbon measurements. Today, three laboratories are active in this field (Naples and Lecce besides Florence). As mentioned above, the new 3 MV Tandatron of our LABEC laboratory is now fully operational, not only with IBA but also with AMS. We have also installed a well equipped sample preparation laboratory for radiocarbon measurements: indeed, the finds must be pre-treated, combusted and finally reduced to graphite before using them as pellets in the ion source of the Tandem where their ^{14}C concentration will be measured through AMS. The preparation procedure is very delicate because, due to the ultra-low concentrations of ^{14}C , any contamination with external carbon can modify significantly the final results.

For this reason, before we started with real dating campaigns, we spent months to check our reliability in the overall (preparation plus AMS) procedures needed to attain a radiocarbon date: in the first period of AMS operation, after accelerator commissioning was completed, only a large number of reproducibility tests with standards and background level measurements were indeed performed. Our ^{14}C background (i.e. the apparent amount detected in completely "dead", radiocarbon free, standards) corresponds to around 60000 years (AMS only), or 50000, also including contamination effects during sample preparation. This means that we are very competitive, at the highest level. Precision is also very good ($< 0.5\%$, i.e. ± 40 y on radiocarbon age); the tests with standards of certified radiocarbon concentration are reproducible and satisfactory.

Following these reliability tests, a systematic activity of dating campaigns has started and about 200 dates of archaeological finds have been measured in the last few months. Among the first, let me quote studies aimed at authenticating some Medieval and Renaissance wood paintings, in collaboration with Opificio delle Pietre Dure in Florence; archaeo-metallurgical studies in northern Etruria, in collaboration with Sovrintendenza archeologica della Toscana, Department of Archaeology in Sienna, Department of Earth Science in Florence; dating of finds from excavations around Palazzo Vecchio and the Uffizi, in Florence, in collaboration with the Italian Ministry of Culture and the Department of Archaeology in Sienna. As I mentioned, more details on all our (old and new) activities can be found in our website, to which the reader is referred also for a list of references.

Acknowledgements

I wish to thank all the group of people working hard at LABEC: Luca Carraresi, Agnese Cartocci, Massimo Chiari, Mariaelena Fedi, Lorenzo Giuntini, Novella Grassi, Franco Lucarelli, Marco Manetti, Mirko Massi, Antonio Mirto, Silvia Nava, Francesco Taccetti. It is only thanks to them that the task of establishing the new lab in Florence and of having it so well operational in a short time has been successfully completed.

¹As a suggested general reading for non-specialists wishing to learn about IBA applied to Cultural Heritage, I wish to mention a book published in the frame of a European COST action (G-1), i.e. *Applications of Ion Beam Analysis Techniques to Arts and Archaeometry*, Eds.: M.A. Respaliza and J. Gómez-Camacho, Universidad de Sevilla, 1997.