

The present role of small particle accelerators for the study of Cultural Heritage

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Abstract. The role that small particle accelerators play in the field of applications to Cultural Heritage (for material analysis and dating) is critically discussed also in comparison to other techniques, pointing out pros and cons. As to material analysis, some peculiarities of ion beam techniques may be now less unique than they were perhaps ten years ago, but these techniques can still reach unrivalled results thanks to a smart use of their potential: for instance, they can provide elemental maps and resolve layer structures. Concerning Accelerator Mass Spectrometry, its unique performance for radiocarbon dating — as to sensitivity, precision and quasi non-destructivity — is described, and perspectives for further improvements are presented.

1 Introduction

Scientific diagnostics for Cultural Heritage has gained a lot, in terms of quantity, quality and acknowledged importance, in the recent past. Among the employed techniques, those based on the use of “small” particle accelerators are by now, so to say, classical, but still they play a crucial role owing to the kind of problems which they succeed in solving. Yet, they can be further improved and the way can be paved for new applications.

Indeed, the very basic principles and possibilities of these techniques in the field of Cultural Heritage are themselves sometimes not entirely known outside the small community of the specialised physicists. It can be worthwhile, therefore, to briefly recall preliminarily what one is dealing with and in which problems these techniques play an important role.

While enhancing their potential, it is also necessary to have a comprehensive viewpoint and honestly wonder whether other physical or chemico-physical techniques might be sometimes preferred in some respects. As mentioned at the very beginning, the “offer” in this field has greatly increased in recent years, also because the demand of support from science has become more and more widespread, specific and exacting. As a consequence, various technologies, although initially developed for applications in other fields, have been refined and adapted to the peculiar requirements in this domain. Nuclear techniques themselves have benefited from this stimulus, increasing their potential to answer the specific questions raised. We believe that, *e.g.*, compared to other emerging techniques, those based on Ion Beam Analysis with their variants are still on the cutting edge for the study of materials used to produce a work of art, although it may be true that some of their peculiarities are nowadays less “unique” than they were some years ago. Not to mention the extraordinary performance of Accelerator Mass Spectrometry for radiocarbon dating.

We will therefore describe in the following the present, still great, potential of accelerator-based techniques in the field of applications to Cultural Heritage.

2 Particle accelerators for Cultural Heritage

In talking about accelerator-based techniques, we will limit ourselves to those using “small” accelerators, *i.e.* electrostatic machines with a maximum terminal voltage of a few MV, which can be operated even in relatively small laboratories. We will therefore not discuss emerging applications based on the use of very large facilities, such as synchrotron light or neutron facilities, which were recently shown to provide definitely interesting perspectives, although

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perhaps a bit “out of reach” at the moment for a widespread use. It is well possible however that in the future they will be developed to a larger degree of accessibility.

The fields of applications of small accelerators for Cultural Heritage are, as mentioned, compositional analysis through Ion Beam Analysis (IBA), and radiocarbon dating using Accelerator Mass Spectrometry (AMS).

As to the latter, no competitive alternatives are on the horizon: AMS is the only usable technique for high-precision, reliable and almost non-destructive dating of archaeological and historical finds. We will come back to this at the end of the paper, to review the topic and see what is going on in AMS.

Let us start instead from the Ion Beam Analysis techniques for elemental analysis of materials.

2.1 Ion beam analysis

As is well known, to perform IBA, the material under analysis is “bombarded” by particle beams, typically protons or alpha particles produced by an accelerator, and the composition of the material is obtained from the spectroscopy of the particle-induced radiation emitted by the atoms (X-rays) or nuclei (gamma rays or particles) involved in interactions with the impinging beam particles. Among IBA techniques, PIXE (Particle-Induced X-ray Emission), in particular, covers with good efficiency all the elements starting from $Z = 11$ (Na) even using an external beam (*i.e.* without placing the “target” in vacuum, which is an essential prerequisite to ensure no damage in the analysis of Cultural Heritage). Lower- Z elements are not detected by PIXE in the external beam set-up, owing to the severe absorption of their characteristic X-rays, which have very low energy. However, when the experimental set-up also includes detectors for gamma rays and particles, the range of detectable elements further extends to essentially include all the periodic table. Besides, also for those elements that are detectable already by PIXE alone, implementing other IBA techniques allows one to overcome some limitations (see below). IBA is quantitative, very sensitive (the minimum detection limits can reach parts per million), non-invasive and non-damaging (another issue that will be developed below). Compositional mapping, even with high space resolution, is possible, and information can be collected on the layer structure, when present, still keeping the feature of non-destructivity.

Nowadays, other techniques requiring less important instrumentation, or even portable equipment, can compete with Ion Beam Analysis in some cases. It is in particular the portability that makes these new techniques, or refinements of existing techniques, very competitive at least as a first step in a more complete protocol of analysis. Let us take, *e.g.*, LIBS (Laser-Induced Breakdown Spectrometry), sometimes also referred to as LIPS (Laser-Induced Plasma Spectrometry) [1,2]. A plasma is induced from the material by an appropriate laser pulse (typical pulse duration: a few tens of ns, typical energy: some tens of mJ/pulse, typical beam spot: a few hundreds μm) and the composition is obtained through the spectroscopic analysis of the prompt emissions in the visible and UV range due to plasma recombination. LIBS is performed using relatively simple and cheap instrumentation; it is transportable and makes it possible therefore *in situ* analysis. Besides, it can easily yield the depth profile of the detected elements, provided the “drilling” of a micro-hole in the material is tolerated. All considered it is for sure a very interesting technique; however, with respect to IBA — so far at least — there remain a number of limitations that are not always irrelevant to the requirements of art historians or archaeologists. First of all, one is dealing with an anyway invasive and destructive technique (even though at a sub-millimetre level), which can only be accepted for certain categories of works: its use for paintings is, *e.g.*, normally precluded. For the same reason (micro-destructivity) it is clearly unthinkable to perform x - y elemental mapping, which would lead to extend the damage over a larger area than in a single-spot analysis. Besides, the quantitative analysis is definitely less reliable than it is in IBA. The main reasons for that are an insufficiently controlled reproducibility from one pulse to another and the fact that the analytical answer somehow depends on the matrix composition: therefore, relative measurements are required, through the analysis of standards of similar composition (not always easily available). Finally, the minimum detection limits are remarkably worse than those for IBA, which makes therefore LIBS unsuitable to provenance studies based on trace element detection.

The new generations of XRF (X-Ray Fluorescence) spectrometers are also becoming very competitive with IBA. XRF, like PIXE, is based on the detection of characteristic X-rays from the elements in the target, but the inner shell ionization that initiates the process is induced through a photoelectric effect by primary electromagnetic radiation (usually from an X-ray tube), rather than through the interaction of accelerated ions. XRF is one of the first physical techniques that were used for the diagnostics of Cultural Heritage (see, *e.g.* [3]) just because XRF systems can be easily made portable or transportable, although such systems usually show several limitations. However, during the past few years, important improvements have been implemented that significantly reduce these limitations.

For example, in some recent set-ups, the range of detectable elements has been extended to lower Z -values than in traditional portable XRF, thus reducing the handicap towards PIXE under this respect. The reason for the low sensitivity of the XRF to low- Z elements is indeed not only the dependence on Z^5 of the photoelectric interaction cross-section, which of course cannot be overcome. The inverse proportionality of the photoelectric interaction cross-section to $E^{-3.5}$, where E is the energy of the primary photon, also plays a role, and the latter problem can instead be tackled by increasing the intensity of the low-energy component in the primary radiation from the X-ray tube (thinner

exit windows and helium flow from tube to target to increase transmission of low-energy primary X-rays). Using these solutions, certain portable XRF systems [4] can detect even Na, if present in concentrations above a fraction of percent.

Focused primary X-ray beams are now also possible thanks to the use of polycapillary lenses (see, *e.g.*, [5,6]), thus increasing primary radiation intensity and reducing measuring times; not only spot analyses on very small details but even *x-y* elemental mapping [7] can this way be performed in reasonable measuring times.

As a whole, therefore, these new generations of XRF instruments, relatively cheap and capable of *in situ* analysis, are often a valid alternative to PIXE measurements at an accelerator. However, some weak points still remain. The sensitivity to low-*Z* is anyway much lower in XRF, just because of the intrinsic physical properties of the photoelectric interaction. On the contrary, PIXE cross-sections are much higher just for lower-*Z* elements (as an example, X-ray production cross-sections with 3 MeV protons are ~ 1500 , ~ 1300 , ~ 1200 , ~ 1100 , ~ 950 , ~ 850 barns for Na, Mg, Al, Si, P and S, respectively). Also, the “multi-element” character in a single measurement is less extended in XRF with respect to PIXE. In addition, it is very difficult to get by XRF elemental depth profiles, because of the relatively high penetration of the incoming radiation; this is also the reason for the high “background” due to elements from the substrate, and as a consequence for the big problems to correctly quantify the composition, whenever the focus should be on the analysis of thin surface layers laid on a backing support, as is, *e.g.*, the important case of paintings.

Coming back to IBA techniques applied to the analysis of works of art or of great cultural value, an important issue to be stressed is that, when correctly employed, the results are obtained in a totally non-invasive way, with no damage to the analysed materials. This is guaranteed by the possibility of using very weak beam currents (owing, in turn, to the very large cross-sections of the physical processes exploited, see above) in a perfectly controlled way.

Totally unfounded are, *e.g.*, the doubts still raised by somebody about alleged risks of damage to the works, in connection with pigment analysis of paintings; if in some laboratories small visible damages have been produced to paintings, this is only due to the fact that the beam charge density integrated on the analysed spots has been needlessly high. Indeed, with targets of a thickness such as the one of paint layers (a few tens of microns) and using detection systems and geometries that optimize efficiency, more than satisfactory counting statistics are obtained by PIXE with no damage at all, in measurements lasting two-three minutes, with beam currents of the order of 10 pA and a beam size around half a millimetre. It is not a matter of minimizing the significance of the damage problem, as sometimes one happens to hear (“the areas involved are anyway very small”, or “it is anyway less invasive compared to picking up a sample”). When working correctly, the problem does not exist at all with paintings!

Other materials such as glazed ceramics or glass can instead undergo, even by using the ultra-low charge densities quoted above, local chromatic alterations due to the creation of colour centres in the insulating material because of the beam particle implantation. However, even in these cases, such alterations disappear spontaneously after a while, and even more quickly when it is possible — as it is with those materials — to accelerate the annealing process of the “damage” by a local heating. In a few minutes, the chromatic alteration totally disappears [8].

That stated (and it is a basic prerequisite), let us recall recent developments in the use of IBA, which have been particularly important for the applications to the Cultural Heritage.

For instance, the idea of differential PIXE [9–11] has provided significant progress, because it allows us to obtain information on the depth distribution of elements — still preserving the no-damage feature. In differential PIXE, the measurement is repeated on the same spot with different beam energies. Thinking, *e.g.*, of paintings on wood or canvas, with a sequence of layers of typical thickness of tens of microns (starting from the surface: protective varnish, paint layer(s), *imprimitura*, preparation), the range of protons in the typical materials employed is just appropriate to sample — by analyzing the same spot at different energies up to some MeV — the protective varnish only, or, as energy increases, also the painting layers until reaching the *imprimitura* and the preparation layer. As a consequence, comparing the X-ray spectra obtained at different energies is very useful to discriminate the composition of the different layers. It is obviously required to take many factors into account, such as: the change of X-ray production cross-section while the beam penetrates into the layers, progressively losing energy; the self-absorption of X-rays in the material itself; and, last but not least, the variability of the paint layer thickness from point to point, so that in the case of paintings the concept itself of thickness is something not perfectly defined *per se*. Common sense must be therefore used, and before drawing “absolute” conclusions about layer thickness from differential PIXE results, it is important to check the variability from point to point within a given colour area.

Differential PIXE has been used for the analysis of paintings of great masters like Leonardo [12], Antonello da Messina [13], Vasari [14], Mantegna. It has been possible not only to reconstruct the colour palette used by the artists, but also to answer more difficult and detailed questions asked by the art historians and restorers.

For instance, in the measurements on the painting by Leonardo examined at the Florence accelerator (“Madonna dei Fusi”, ex-Reford version), information on the layer structure of the painting was obtained from differential PIXE in a fully non-destructive way [12], verifying a sophisticated technique to render colour shades with very thin paint layers. It was also possible to get an estimate for the layers thickness, which came out to be little more than ten microns in some cases. At INFN-LABEC in Florence, another useful application of differential PIXE has been performed on a work by Vasari [14], a small painting on wood, part of the great complex known as “Pala Albergotti”; differential PIXE



Fig. 1. Mantegna's *Madonna col Bambino* (oil on canvas, 1460, kept at Accademia Carrara, Bergamo) during PIXE analysis at the scanning external microbeam set-up at INFN-LABEC in Florence.

measurements, performed prior to restoration, verified the presence of surface deposits or alterations to be removed, thus contributing to the restorers' decisions.

An important step forward for IBA applied to Cultural Heritage has been the implementation of scanning external microbeam facilities. Using list-mode acquisition systems where the beam position coordinates are acquired together with the energy signals from the detectors, it is possible to reconstruct elemental maps with high space resolution, reaching $10\ \mu\text{m}$ or even somewhat less [15]. Much better resolutions cannot be achieved when using external beams: the effect on the beam size of the exit window (although being ultra-thin Si_3N_4 , of even only 100 nm thickness), and of the beam path in atmosphere (although the target is placed only 2–3 mm after the exit window), limits the ultimate space resolution to that size. However, this is more than sufficient in problems dealing with Cultural Heritage, and compositional information can be safely collected from tiny details of a work.

Here again, the great analytical potential arising from such developments can be exploited to answer specific questions of real interest to the art historians and restorers. An example is given by the results obtained using the external scanning microbeam set-up on the so-called “*Ritratto Trivulzio*”, a portrait of a gentleman by Antonello da Messina [13]. “Imaging” measurements by the microbeam significantly contributed to understand the technique used by Antonello to achieve particular shadowing effects, and to take conscious and cool-headed decisions on how to proceed with the surface cleaning of the painting. Also a painting by Mantegna (shown in fig. 1 during the measurements) was analysed by PIXE at LABEC, using the scanning external microbeam set-up. Examples of elemental maps collected from some details of the figure of the Madonna are given in fig. 2.

When space resolution is required to be pushed to ultimate levels, the drawback is that the investigated area cannot be very large, unless a very long measuring time is possible. With a beam of 10 microns, collecting sufficient statistics per pixel over the scanned surface requires maybe a few tens of minutes to scan a few square mm. And not always indeed, a very high space resolution is strictly necessary in problems related to Cultural Heritage. Instead, it may be very useful to map composition over larger size areas (some square cm) but with lower resolution, of the order of a few hundred microns [16]. To this purpose, external millibeam set-ups have been developed where the beam size is defined by simple collimation (easily achieved down to two-three hundred microns), still keeping the scanning feature and list-mode acquisition. This kind of set-up does not provide beam scanning like the microbeam systems, but mapping is anyway obtained by displacing the target in front of a fixed beam thanks to x - y motion stages.

Another very useful feature for Cultural Heritage is the possibility of integration of more IBA techniques, simultaneously exploited during a beam run. For instance, including a gamma detector for PIGE (Particle Induced Gamma ray Emission) has proven to often significantly enrich the overall information, making it possible to unveil the presence of low- Z elements even below surface layers of a few tens of μm . X-rays from these elements have too low an energy

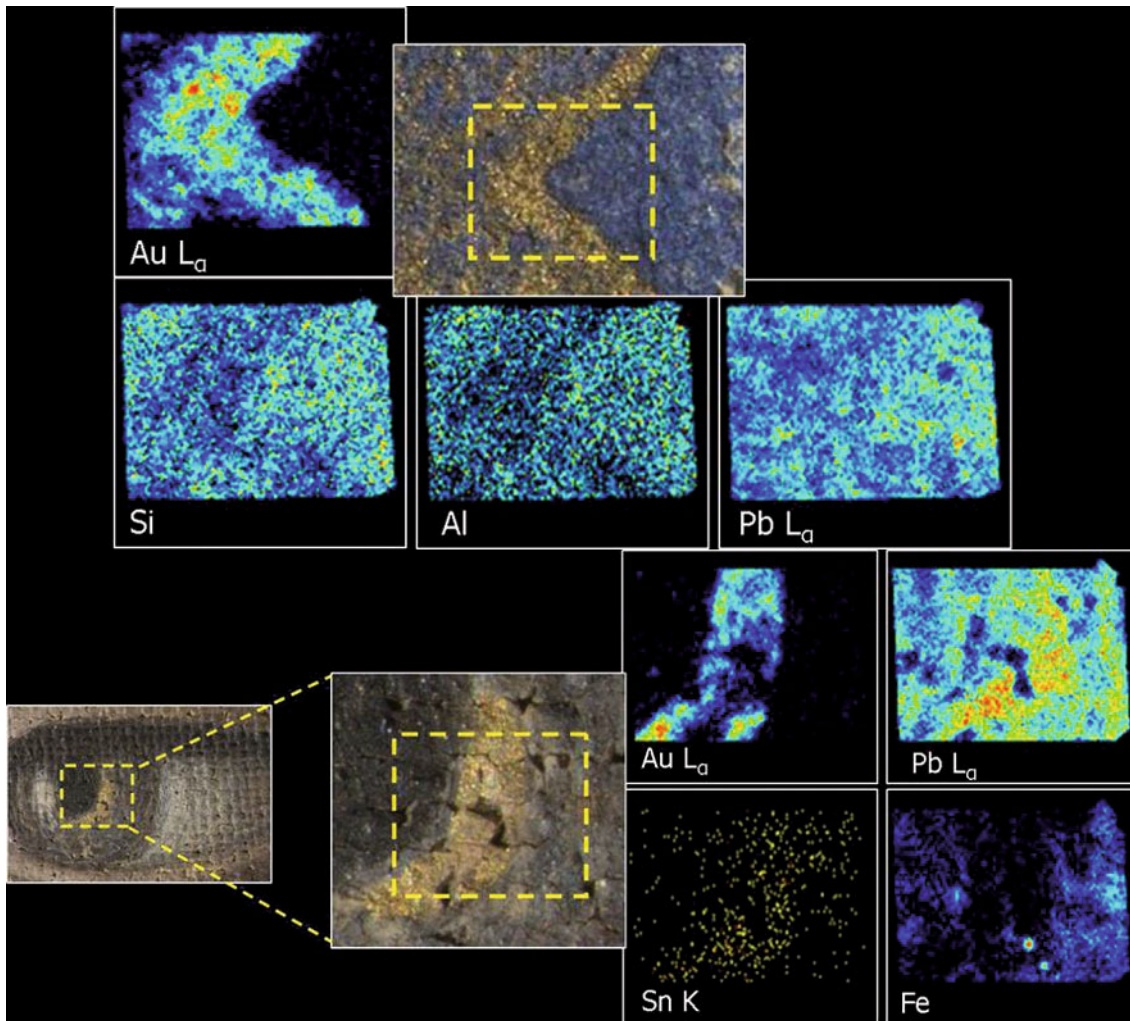


Fig. 2. Details of the painting by Mantegna (above, part of the veil of the Virgin; below, the eye of the Virgin), and corresponding X-ray distribution maps obtained by PIXE at the external scanning microbeam set-up at INFN-LABEC. The size of the dotted yellow areas shown in both cases are $1.6 \times 1.8 \text{ mm}^2$. As usual, in the maps a colour scale corresponds to X-ray counts per pixel (from black-blue to yellow-orange-red \rightarrow from low counts to higher counts).

to be transmitted through the surface layer, while gamma rays, having much higher energies, do not undergo absorption at all. On the other hand, it is just from low- Z elements that it is more probable to induce gamma emission, because the Coulomb repulsion between beam particles and target nuclei is smaller; beam particles can get closer to the nucleus and the probability of nuclear interactions is therefore higher. Using PIGE has, *e.g.*, allowed us — through the detection of the 440 keV gamma rays from the $^{23}\text{Na}(p, p'\gamma)$ reaction — to identify with certainty the use of the ultramarine pigment to paint the sky in the painting by Leonardo mentioned above [17], and several applications in the study of ancient glasses have also been reported, where the detection of gamma rays from ^{23}Na was important in many respects [18].

Talking about the simultaneous use of more IBA techniques for Cultural Heritage analysis, it is worthwhile mentioning the development of IBIL (Ion Beam Induced Luminescence), even in external scanning microbeam set-up, to extend the information provided beyond elemental analysis [19,20]. IBIL exploits the emission of photons in the IR/VIS/UV range (200–900 nm in the set-up at LABEC), which can take place from a material excited by ions in the usual energy range of a few MeV. For some materials, it may allow us, in principle, to determine: the nature of molecular bonds, the valence state of the ions, the characteristics of the crystal lattices, and even the presence of trace elements, impurities, structural defects. With extremely weak-intensity (sub-pA) beams, IBIL from some materials is still characterised by very high yields, and can therefore be useful also to prevent the possible onset of beam-induced damage, since a decrease of the IBIL signal occurs well before any visible damage.

Finally, although this is no more a conventional IBA technique, and larger accelerators are needed to produce higher-energy beams, the DPAA (Deep Proton Activation Analysis) techniques should also be mentioned. DPAA [21]

is in a sense a development of IBA and to some extent has opened a new field of applications: it makes it possible to investigate material composition at a “quasi bulk” level exploiting proton beams at some tens of MeV and the cross-section behaviour of some nuclear reactions, which has a maximum in depth within the bombarded materials.

In summary, therefore, we believe that using IBA in the field of Cultural Heritage problems can still achieve — in a totally non-destructive way — information of an unsurpassed quality and variety.

Obviously, this great potential is not always strictly necessary; thus, it is a wise attitude (as with any other technique) to make a sensible use of IBA, case by case, taking into consideration the specific problem of the art historians or restorers, and the possible external constraints (*e.g.*, difficulties in handling or moving the work to be analysed). It is important to create protocols that may include first *in situ* analysis with other techniques and ion beam techniques to follow, in order to complete and/or better understand some results.

2.2 Radiocarbon dating and Accelerator Mass Spectrometry

Radiocarbon dating is based on the measurement of the residual concentration of ^{14}C in finds of organic nature, *i.e.* once belonging to a living organism. We will not even recall the principle, assuming it as very well known. Reference texts are, *e.g.*, [22,23].

The challenge of radiocarbon dating is that the concentration to be measured is very small; in atmosphere — therefore also in the living organisms — it is roughly 10^{-12} , and the older the find, the smaller the residual concentration (for instance, since ^{14}C half-life is ~ 5700 years, after 50 thousand years the concentration drops to $\sim 10^{-15}$). The requirement of such a huge measurement sensitivity adds to another fundamental requirement, namely measurement precision. Indeed, the relationship linking the age t and the residual radiocarbon concentration $^{14}R(t)$ is

$$t = \tau \ln \frac{^{14}R(0)}{^{14}R(t)}, \quad (1)$$

where τ is the lifetime (~ 8200 years) and $^{14}R(0)$ the concentration when the organism was still living. The propagated uncertainty on the age t is therefore

$$\delta t = \tau \frac{\delta^{14}R(t)}{^{14}R(t)}, \quad (2)$$

which means, *e.g.*, that a $\pm 1\%$ on the measurement of $^{14}R(t)$ results already into ± 80 years on t .

Combining high sensitivity and high precision is in itself not easy. But there is a further requirement: ideally, the measurement should be non-destructive, or destructivity should be limited to low levels. In fact, materials to be dated are often historically or archaeologically precious and they should not be destroyed; but even when this is not the case, very often they are intrinsically of very low mass, so that large quantities are not available for dating at all.

As is by now well known, sensitivity, precision and quasi-non-destructivity are all three features of Accelerator Mass Spectrometry at a Tandem accelerator (see, *e.g.*, [24,25]). The sample — properly prepared — is used as the ion source material and what is mass-analysed is the ion beam after acceleration.

The limit of the alternative methodology (β -counting), *i.e.* requiring to destroy for the measurement relatively large masses of the sample (grams or tens of grams, which are often unavailable at all, or anyway unconceivable to destroy) is fully overcome: few milligrams only (sometimes even less) of a sample are required by AMS. The key points in AMS are the complete suppression of molecular isobars $^{12}\text{CH}_2$ and ^{13}CH , which are destroyed during electron stripping at the high voltage terminal, and the high efficiency of the ion extraction at the source and of the beam transmission until the detector. Statistics of several ten thousands of counts (therefore well below percent precision) are by now standard in times as short as about 30 minutes overall for recent samples, starting from few mg of the material to be dated. The huge advantage in terms of the tiny masses needed with respect to β -counting has been decisive to extend the range of radiocarbon-datable finds, and nowadays maybe ten to twenty thousand dates are produced per year in the world. Once in a while, some of these results hit the headlines in the media, especially when traditions or beliefs strongly entrenched in the culture or in the religions are disproven, as was the case of the Turin Shroud [26], or others [27–30]; but the largest part of radiocarbon dates remain unknown outside the specialists’ field. Still, they represent a crucial tool for the advancement of archaeological knowledge (more and more frequently now, also in support of art-historical hypotheses). It is a great help that Nuclear Physics and associated technologies offer to archaeologists and historians.

The possibility offered by AMS to date samples of few mg has been also decisive to construct the calibration curve, through which one corrects the “radiocarbon ages” t_{rC} , derived from eq. (1) using conventional values for the starting concentration $R(0)$ and for the lifetime τ itself. Calibration is the second fundamental step to achieve reliable absolute ages, and is based on a curve that has been constructed through the radiocarbon measurement of samples of independently known age. Such a curve (t_{rC} *vs.* real calendar age) is periodically updated on the basis of new data. Obviously, the more samples of independently and safely known age are measured, the more reliable becomes the calibration curve. On the other hand, the mass of the available safe samples is often small; thus it is only thanks to

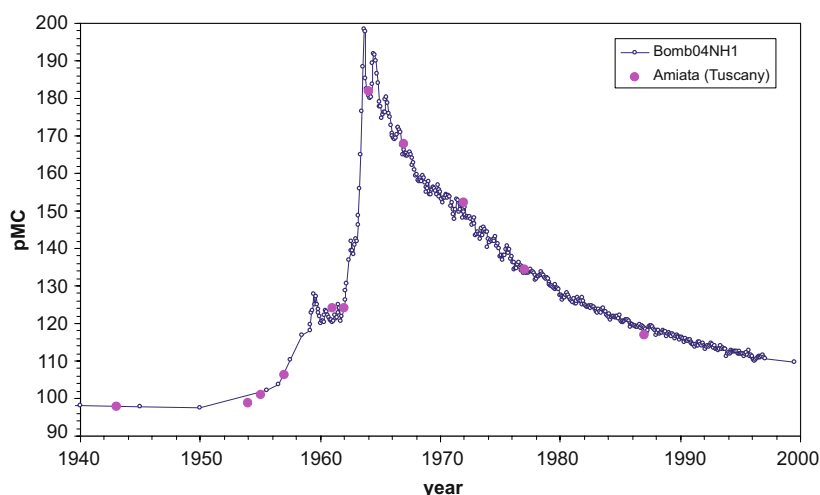


Fig. 3. Relative variation of ^{14}C concentration in the atmosphere in recent decades. Concentrations are expressed in pMC, *i.e.* percent of Modern Carbon. Bomb04NH1 is the published bomb curve [35] as compiled from the data available in the northern hemisphere, above 40° latitude; also shown as full dots are the results of measurements performed at LABEC on tree rings samples collected from an oak trunk at Monte Amiata, in southern Tuscany (Italy).

AMS that we can count on a calibration curve that accurately covers — exploiting dendrochronology — ages until ~ 10000 years ago and by now extends, although with lower and lower time detail for more and more remote periods, to about 50000 years [31], which is anyway the present limit of sensitivity of the technique.

In conclusion, although it is not a novel technique, having been introduced about thirty years ago, AMS still remains today the only reasonably possible technique for radiocarbon dating, and no alternatives are on the horizon. There is anyway a great deal of progress in procedures and technologies within AMS itself.

As to procedures, a relatively recent progress, again AMS-related since it requires dating small mass samples, is the so-called “wigggle-matching” [32,33]. In the measurement of a single find, were it not for the need to recalibrate, one might think of making t_{rC} uncertainty small at will, by simply increasing counting statistics to reduce the uncertainty in the residual concentration of ^{14}C . However, because of the need of recalibrating (with the additional uncertainty it implies in the determination of the true age) it makes no sense to push counting statistics beyond a level corresponding to, say, few per mil uncertainty. But in case more samples are available, among which the age difference is *a priori* known (this is the case, *e.g.*, of different tree rings fragments from the same tree), just the oscillations of the calibration curve can be exploited to improve the precision of dating. Indeed, the known information about the age difference is a constraint to the independent radiocarbon dates of the single samples when fitting the whole set of data to the oscillations of the calibration curve. The uncertainty of the age obtained can be remarkably reduced, even to few years.

A case where such a technique has been successfully applied is the accurate chronological placement of the famous eruption of the volcano in the Greek island Thera [34]. Trapped within the lava a tree trunk was found, where the growth rings were still clearly discernible. A sequence of samples with known age difference was thus obtained and they were radiocarbon dated with AMS. The calibration of this sequence keeping wigggle matching into account allowed the archaeologists to restrict the time interval of the eruption to a period between 1627 and 1600 BC (95% probability). This period is about a hundred years older than believed on the basis of historical sources, which has caused an interesting debate having a vast echo and still under way.

Clearly, wigggle matching is not always applicable, and even when this is the case, the experimental effort required is remarkable, because several measurements are needed to significantly improve the accuracy of the date. In most cases, either no finds are available with known age difference, or the effort is not worthwhile because the accuracy obtained by a single measurement, after recalibration, is sufficient. It should be emphasized, anyway, that even when a set of associated samples of known age difference is available, they are invariably low-mass samples. Thus, it is only the capability of AMS to date such samples that makes the application of wigggle matching possible.

Talking about “anomalies” in the equilibrium concentration of ^{14}C in the past, there is a peculiar one not yet exploited in applications to Cultural Heritage. It is the “bomb peak”, *i.e.* the sudden relevant increase in atmospheric concentration of ^{14}C in the cold-war period because of the nuclear tests in atmosphere by the world powers, until the non-proliferation Treaty of 1963. The fission neutrons released by these explosions, after thermalising produced a huge extra quantity of ^{14}C (reaction $^{14}\text{N}(n_{\text{th}}, p)^{14}\text{C}$), which in few years, between 1955 and 1964, almost doubled its atmospheric concentration. Subsequently, after the tests ceased, the concentration progressively decreased, as the excess of $^{14}\text{CO}_2$ molecules was reabsorbed in the natural carbon cycle, diluting in particular in the great reservoir of the ocean waters. An example of the behaviour of ^{14}C concentration in the recent decades is shown in fig. 3.

Such fast and large variations in atmospheric concentrations also affected all organisms living during those years. This circumstance now offers an obvious opportunity of discriminating between “before” and “during” the considered period, or even from year to year within it. Many interesting applications have been performed in forensics and in the field of biology already [36,37]. An intriguing possibility in the field of Cultural Heritage would be, *e.g.*, to exploit the bomb peak to discover possible fakes, performed recently, of drawings on paper or paintings on canvas attributed to authors of the first half of the XX century.

From the point of view of instrumental developments of ^{14}C AMS, recently the interest in lower voltage accelerators has considerably grown. The first Tandems to be used for AMS were “inherited” from the measurements of basic nuclear physics, therefore having maximum terminal voltages of several MV; subsequently, dedicated machines started to be built, with maximum terminal voltage around 2.5–3 MV, which was found to be sufficient. Recently, the use of even smaller machines for radiocarbon measurements has been attempted and dedicated lower voltage accelerators have also been commercialised; experimental systems with even only 200 kV have been successfully tested [38]. They are obviously much more compact, but this does not imply that they are necessarily easier to use. Indeed, the stripping efficiency in the Tandem terminal, after a first acceleration stage to very low energies, is negligible to obtain multiply charged positive ions; therefore, what is analysed after the second acceleration are the ^{14}C 1^+ ions, and the molecular isobar suppression is lower. In addition, the much lower energy makes final counting much more critical, with high energy losses in the dead layers at the entrance of the final counters, as well as a large straggling. All this makes further discriminations based on the measurement of small energy differences, or ΔE - E detectors, very difficult if not impossible. In any case, a lot of progress has been made to overcome these problems, and the achievable precision and sensitivity can approach the one obtained with larger machines. Paradoxically however, just for the sophisticated devices adopted to bypass or overcome these problems, these systems — even more than the larger ones — must be left in the hands of physicists. The hope to give archaeologists a *do-it-yourself* dating machine is for the moment far from being realised.

3 Conclusions

We believe that we can express the firm conviction that nuclear techniques with small accelerators have a long future in the field of Cultural Heritage; it may be stimulating for us, nuclear physicists, and still really useful to the community of scholars and conservators. Obviously, one has to use these techniques at their best and a judicious choice must be done in order to use them appropriately — *i.e.*, when they really are useful. When necessary, they must be integrated or sided by complementary techniques, both within physics and in other scientific disciplines. A message emerges indeed from a careful analysis of the field of “Science for Cultural Heritage”, *i.e.* that more and more often it is sensible to employ a wide range of techniques to satisfactorily and fully answer the more and more demanding and complex questions proposed by scholars and restorers. This observation on the one hand demonstrates the vitality of the whole sector of scientific applications for the study of the patrimony, on the other witnesses that human and hard sciences connect and look for each other with increasing frequency, with great benefit for the growth of both.

The significance of applications of Science to Cultural Heritage is increasingly perceived at all levels, starting from the general public to the high spheres of politics. It should not be forgotten however that any hope of feeding these applications, improving them and anyway maintaining them updated and effective is closely connected here — as in all fields of applied Science — to also maintaining alive the fundamental research from which applications originate.

References

1. A. Giakoumaki, K. Melessanaki, D. Anglos, *Anal. Bioanal. Chem.* **387**, 749 (2007).
2. J. Agresti, A.A. Mencaglia, S. Siano, *Anal. Bioanal. Chem.* **395**, 2255 (2009).
3. S. Sciuti, G. Suber, *Riv. Nuovo Cimento* **14**, 7 (1991).
4. A. Migliori, P. Bonanni, L. Carraresi, N. Grassi, P.A. Mandò, *X-Ray Spectrom.* **40**, 107 (2011).
5. M.A. Kumakhov, *X-Ray Spectrom.* **29**, 343 (2000).
6. C. Fiorini, A. Longoni, A. Bjeoumikhov, *IEEE Trans. Nucl. Sci.* **48**, 268 (2001).
7. A. Longoni, C. Fiorini, C. Guazzoni, S. Buzzetti, M. Bellini, L. Strüder, P. Lechner, A. Bjeoumikhov, J. Kemmer, *X-Ray Spectrom.* **34**, 439 (2005).
8. M. Chiari, A. Migliori, P.A. Mandò, *Nucl. Instrum. Methods B* **188**, 151 (2002).
9. I. Brissaud, A. Guillò, G. Lagarde, P. Midy, T. Calligaro, J. Salomon, *Nucl. Instrum. Methods B* **155**, 447 (1999).
10. C. Neelmeijer, I. Brissaud, T. Calligaro, G. Demortier, A. Hautojärvi, M. Mäder, L. Martinot, M. Schreiner, T. Tuurnala, G. Weber, *X-Ray Spectrom.* **29**, 101 (2000).
11. P.A. Mandò, M.E. Fedi, N. Grassi, A. Migliori, *Nucl. Instrum. Methods B* **239**, 71 (2005).
12. N. Grassi, A. Migliori, P.A. Mandò, H. Calvo del Castillo, *X-ray Spectrom.* **34**, 306 (2005).
13. N. Grassi, *Nucl. Instrum. Methods B* **267**, 825 (2009).

14. N. Grassi, P. Bonanni, C. Mazzotta, A. Migliori, P.A. Mandò, *X-Ray Spectrom.* **38**, 301 (2009).
15. L. Giuntini, M. Massi, S. Calusi, *Nucl. Instrum. Methods A* **576**, 266 (2007).
16. N. Grassi, L. Giuntini, P.A. Mandò, M. Massi, *Nucl. Instrum. Methods B* **256**, 712 (2007).
17. N. Grassi, A. Migliori, P.A. Mandò, H. Calvo del Castillo, *Nucl. Instrum. Methods B* **219-220**, 48 (2004).
18. G. Weber, Y. Vanden Bemden, M. Pirotte, B. Gilbert, *Nucl. Instrum. Methods B* **240**, 512 (2005).
19. S. Calusi, E. Colombo, L. Giuntini, A. Lo Giudice, C. Manfredotti, M. Massi, G. Pratesi, E. Vittone, *Nucl. Instrum. Methods B* **266**, 2306 (2008).
20. A. Quaranta, J.C. Dran, J. Salomon, M. Tonezzer, C. Scian, L. Beck, S. Carturan, G. Maggioni, G. Della Mea, *Nucl. Instrum. Methods B* **266**, 2301 (2008).
21. G. Pappalardo, A. Esposito, G.A. Cirrone, G. Cuttone, S. Garraffo, L. Pappalardo, F. Rizzo, F.P. Romano, S. Russo, *Nucl. Instrum. Methods B* **266**, 2286 (2008).
22. S. Bowman, *Radiocarbon Dating* (University of California Press/British Museum, 1990).
23. R.E. Taylor, *Evol. Anthropology* **4**, 169 (1995).
24. C. Tuniz, J.R. Bird, D. Fink, G.F. Herzog, *Accelerator Mass Spectrometry: ultrasensitive analysis for global science* (CRC Press, Boca Raton, 1998).
25. M.E. Fedi, *Accelerator Mass Spectrometry for ¹⁴C dating*, in M.P. Colombini and F. Modugno (Editors) *Organic Mass Spectrometry in Art and Archaeology* (Wiley, Chichester, UK, 2009) p. 459.
26. P.E. Damon *et al.*, *Nature* **337**, 611 (1989).
27. W. Kutschera, W. Müller, *Nucl. Instrum. Methods B* **204**, 705 (2003).
28. M.E. Fedi, A. Cartocci, F. Taccetti, P.A. Mandò, *Nucl. Instrum. Methods B* **266**, 2251 (2008).
29. D. Penny, Q. Hua, C. Pottier, R. Fletcher M. Barbetti, *Nucl. Instrum. Methods B* **259**, 388 (2007).
30. M.E. Fedi, L. Carraresi, N. Grassi, A. Migliori, F. Taccetti, F. Terrasi, P.A. Mandò, *Radiocarbon* **52**, 356 (2010).
31. P.J. Reimer *et al.*, *Radiocarbon* **51**, 1111 (2009).
32. G.W. Pearson, *Radiocarbon* **28**, 292 (1986).
33. C. Bronk Ramsey *et al.*, *Radiocarbon* **43**, 381 (2001).
34. W.L. Friedrich, B. Kromer, M. Friedrich, J. Heinemeier, T. Pfeiffer, S. Talamo, *Science* **312**, 548 (2006).
35. Q. Hua, M. Barbetti, *Radiocarbon* **46**, 1273 (2004).
36. E.M. Wild, R. Golser, P. Hille, W. Kutschera, A. Priller, S. Puchegger, W. Rom, P. Steier, *Radiocarbon* **40**, 273 (1998).
37. S. Bernard, J. Frisén, K.L. Spalding, *Nucl. Instrum. Methods B* **268**, 1295 (2010).
38. H.-A. Synal, M. Stocker, M. Suter, *Nucl. Instrum. Methods B* **259**, 7 (2007).