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Nuclear physics for cultural heritage

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Summary. — We report about the expert review, published by the Nuclear Physics
Division of the European Physical Society (NPD EPS), which aims to provide the
public with a popular and accessible account of the latest developments in the field
of nuclear physics application for cultural heritage. The contributions from a range
of leading specialists explain how applied atomic and nuclear techniques can be
used to obtain information that can help us to understand the way of life in ancient
times and how they can be used to conserve cultural heritage treasures. This topical
review draws heavily on European work and is extensively illustrated with important
discoveries and examples from archaeology, pre-history, history, geography, culture,
religion and curation. It outlines key advances in a wide range of cross-disciplinary
techniques and has been written with the minimum of technical detail so as to
be accessible by as wide as possible audience. The large number of groups and
laboratories working in the study and preservation of cultural heritage using mainly
nuclear physics methods across Europe indicates the enormous effort and importance
paid by society to this activity.

1. – Introduction

Precious cultural heritage objects should remain unaltered after they are exposed
to analytical investigation. Therefore, non-destructive and non-invasive methods are of
crucial importance for these investigations. From this point of view, nuclear techniques

are of the highest importance to study objects of cultural heritage. There has been enormous progress in this field in recent decades and our current contribution provides some snippets of the comprehensive topical paper "Nuclear Physics for Cultural Heritage" published by the European Physical Society (EPS) recently [1], which aims for a popular and accessible account showing the broad nuclear physics applications in cultural heritage investigation and preservation.

Nuclear physics contributes to archaeometry mainly by non-invasive investigation of cultural heritage objects with ion and neutron beams. Developments of Ion Beam Analytical methods (IBA) were related to progress in low-energy accelerators, in detectors for particle, X-ray and γ-ray measurements, and in systems for processing experimental data [2], [3]. Ion beams of several MeV penetrate into matter, interact with the atoms and produce X-rays and γ-rays, as well as scattered ions and recoiled matrix atoms among other phenomena, which provide information about the investigated artefacts. Small accelerators can generate a wide range of ion beams, with flexible energy range (and thus adjustable probed depth) and diameter of the beam (from millimetre to micrometer size) [4].

Neutron diffraction or elastic neutron scattering is the application of neutron beams to the determination of the atomic or magnetic structure of a material. Neutrons with a high penetration depth are suited for bulk sample investigation. Neutron activation analysis (NAA) is a multi-elemental analytical technique used for qualitative and quantitative analysis of major, minor, and trace elements. Samples are irradiated with neutrons and the newly formed radioisotopes are created, mostly via the (n,γ) nuclear reaction with thermal neutrons. Nuclear physics contributes significantly to the analytical methods with techniques sensitive to practically all the elements of the periodic table and capable of reconstructing the spatial distribution of the elements present in the sample [2]– [4]. The topical paper [1] gathered experts in nuclear techniques for cultural heritage; in Fig. 1, we report the road map of the research centers and laboratories relevant to nuclear physics studies of cultural heritage with the indicated workplaces which contributed into the topical paper.

Fig. 1. – The road map of laboratories and research centers providing nuclear physics studies of cultural heritage with the distinction of European ion beam facilities (the red squares), neutron sources (the green squares) and accelerator mass spectrometry centers (the yellow squares) and other related facilities (the blue squares). The arrows indicate the laboratories which contributed into the NPD EPS topical paper.

2. – How do ion and neutron beams investigate matter?

2˙1. *Ion beam analytical techniques*. – As a result of ion beam irradiation of a material, two types of collisions occur: inelastic collisions and elastic collisions. In inelastic collisions two phases exist. In the first phase particles are emitted (NRA - Nuclear Reaction Analysis). This is followed in the second phase by the emission of gamma rays (PIGE - Particle Induced Gamma-ray Emission spectroscopy) or X-rays (PIXE - Particle Induced X-ray Emission spectroscopy). Nuclear reactions are isotope-specific with no direct relationship between the mass of the target nucleus and the energy of the emitted particles. In elastic collisions, two main phenomena are taking place: (i) the primary ion beam is backscattered and is used in Rutherford Back-Scattering spectrometry (RBS) and (ii) lighter atomic nuclei can be ejected, recoiling from the heavier projectile ions. We will describe some of them in connection to the cultural heritage case studies presented in this review as a taste of the published NPD EPS topical paper [1]. PIXE exploits X-ray emission for elemental analysis [6]– [8]. The energy of a peak in the X-ray spectrum is specific for a particular element, and its intensity is proportional to the elemental concentration. PIXE has a very low detection limit, even down to ppm in the standard practice for thin target. Depending on the sample type and measuring apparatus, the concentration of elements with Z>5 can be determined with PIXE down to about $0.1 - 1\mu g/g^{-1}$. PIGE is a versatile non-destructive analytical and depth profiling technique based on the (p,γ) reaction [9], [10]. The energies and intensities of the γ-ray lines indicate which elements are present and their respective amounts.

A big technological progress was done after the ion microbeam development. In a microbeam, the ion beam from the accelerator passes through a combination of magnetic quadrupoles focusing the high energy ions. The samples are irradiated with an ion beam focused to a spot that can be as small as few hundreds of nm in diameter and standard IBA techniques are used to characterize the irradiated object. By scanning the beam within a defined window across the surface of the sample, a 3D distribution of elements can, in principle, be determined with a nm depth resolution and a lateral resolution limited only by the size of the beam spot. For this purpose, the signals detected are assigned to the x,y coordinates of the beam spot [7].

Some archaeological artefacts cannot be placed in a vacuum chamber because of their large size or the presence of volatile components. Such samples can be analysed using an external ion beam [7], [8]. The beam is extracted from the evacuated beam line into air through a thin window, made of thin metal foils, strong plastic materials like kapton, or Si_3N_4. Practically all setups now allow the scanning measurement mode that produces element concentration maps. The target is encircled by an array of detectors; normally there are at least two X-ray detectors, with a thin window detector for soft X-rays and a detector with a large solid angle but equipped with an additional absorber for hard X-rays. In a standard arrangement, the beam spot at the target is millimeter or less in diameter if the beam is shaped by slits, but it can reach 10 or 30 μm if the beam is focused with suitable magnetic optics [8].

Rutherford backscattering spectrometry (RBS) is the most commonly used non-destructive nuclear method for elemental depth analysis of structures in the nanometer to micrometer thickness range. The method is based on measurements of the energy spectra of several MeV ions (protons, singly charged helium He^+, or heavier ions) elastically scattered from solid samples. The samples are irradiated in an evacuated target chamber and the scattered particles are detected by semiconductor detectors. As a consequence of the scattering kinematics, the energy of the scattered particles increases monotonically

as a function of the element mass. The scattering cross section, i.e. the scattering probability, is proportional to the sample element atomic number squared. Thus the technique is particularly sensitive to heavier elements. The quantity of a particular element in the target is proportional to the number of scattered particles. The incident and scattered particles penetrating through the sample material lose energy progressively and the measured energy loss can be transformed into a depth using the known particle stopping powers in the sample material. In case of RBS, the depth profiling of elements utilizes the defined charged particle energy losses in the investigated material with the depth resolution better than 10 nm. For heavy elements, in a light substrate, the detection limits can be as low as 0.01 atomic % [2], [3]. Standard equipment for IBA methods (PIXE, PIGE, RBS etc.) comprises an electrostatic accelerator, generating ions such as protons, He and heavier ions, with energies from 0.5-50 MeV.

2˙2. *Analysis using interactions with neutrons*. – Irradiation with neutrons can be used either for elemental analysis using neutron activation analysis (NAA) or using neutron scattering for internal morphology investigation of materials. Samples with mass typically in the range from sub-mg to several hundreds mg, are irradiated with neutrons and the newly formed radioisotopes are created, mostly via the (n,γ) nuclear reaction with thermal neutrons (neutron radiative capture). The irradiation is usually carried out at a nuclear reactor but other neutron sources (radioisotopic or accelerator based) can also be used. In general, the lower the neutron energy, the higher the probability of the neutron radiative capture. When the sample is irradiated, the prompt γ-rays are emitted. Their measurement during irradiation is named prompt gamma activation analysis (PGAA). The objects analyzed by PGAA remain intact, with almost no induced radioactivity, because of a lower neutron flux in the neutron beam lead out of the experimental nuclear reactor compared to the neutron field in the reactor core, which is used for NAA. Since every chemical element, except He, emits prompt γ-rays, the method can in principle detect all elements in the periodic table, but with very different sensitivities. The most sensitive elements include H, B, Cd, Nd, Sm, Eu and Gd, whereas the least sensitive elements are Be, C, N, O, F, Pb and Bi. After transformation of the compound nucleus to a newly formed radionuclide, delayed γ-rays are emitted and measured after the end of irradiation in NAA. The mode, which uses a purely instrumental, nondestructive, approach is commonly called instrumental neutron activation analysis (INAA). In combination with high-resolution HPGe detectors complex γ-spectra from irradiated material in NAA can be disentangled. Although NAA usually requires placing a cultural-heritage object (or a representative sample of it) for neutron irradiation into the reactor, a chemical pre-treatment of the material is not necessary. This procedure therefore preserves the original element composition of the object. Detection limits are primarily determined by neutron capture cross-sections, i.e. the probability of the (n,γ) reaction, neutron flux available, abundance of the target isotope and the measured characteristics of the emitted radiation. INAA can detect up to 74 elements depending on the experimental procedure with very low limits of detection (LOD) ranging from 10^{-7} to 10^{-12} g/g depending on the element and matrix composition. NAA with relative standardisation has recently been recognised as a primary method of measurement, e.g., a method with the highest metrological properties [9]. If a matrix activates well with neutrons, LOD of some elements may not be sufficiently low. In such cases radiochemical NAA (RNAA) can be employed, which uses post-irradiation radiochemical treatment for removing the prevailing activity of matrix or separation of radionuclides of interest. In this way, lower LOD for elements of interest by 1-3 orders of magnitude, can be achieved

compared to INAA (down to sub-ng/g levels).

Small angle neutron scattering (SANS) is a technique for studying nanometer scale structural features in materials. The information obtained, however, is characteristic of the whole irradiated volume of the sample. The SANS technique can determine void sizes in porous media such as cements and marble. SANS can be a proper tool for investigation of structural differences between marble, ceramic, metal objects of different provenance or technologies [11]– [13].

3. – What can we discover?

3˙1. *Ion Beam Analysis - Case studies*. – The example of metal analysis demonstrates identification of gilding techniques. The objects studied were from the Late Antiquity, which favoured gilded silver or bronze jewellery with inlaid garnets. The applied methods were differential PIXE and RBS with an in-air proton beam [8], [14]. Differential PIXE is based on the sequential measurements in the same spot such that protons reach different target depths. This is achieved by the variation of the proton incident angle or by the variation of proton energy. The measurements were made at nine impact energies ranging from 2.78 MeV to 740 keV. The results of the de-convolution procedure are elemental concentration depth profiles, which can reach up few tens of microns below the target surface [14].

The gold layer is found to be about 2.5 μm thick, but the gold is not pure: throughout the profile it is mixed with mercury, which undoubtedly reveals that a fire gilding or amalgamation procedure was used. For this technique, a paste of gold amalgam is applied to the object surface. The object is then heated until the mercury evaporates and a solid gold layer forms at the object surface. The evaporation of mercury is never complete; the gold layer typically contains up to 15% mercury, which then remains as a clear indication of the technique. Gold and mercury layers may also be identified by RBS; however, the mass resolution of the experiment does not allow clear separation of the weak mercury and strong gold signals. The presence of mercury has to be confirmed using X-ray spectra.

Another interesting application is the study of the origin of Lapis lazuli. Lapis lazuli is a semi-precious blue stone widely used for different purposes since the antiquity, but, at present, there are still some lacking pieces of information about both its trade in ancient times [15]– [17]. External proton microprobe was used as the external beam allows non-invasive, multi-technique (PIXE and PIGE) study of objects of almost any shape and dimension, see Fig. 2 Left. Historical sources of lapis lazuli are located in hardly accessible places, such as the Afghan and Pamir Mountains and stones were transported for thousands of kilometres. Unfortunately, these trade routes are largely incomplete and unknown. Only a few sources exist in the world because of the restricted compositional and physical constraints in which lapis lazuli can form. Therefore assigning sources of raw material to man-made objects can help historians and archaeologists reconstruct ancient trade routes.

A systematic study of this fascinating stone compared the physico-chemical properties of rocks from four different sources (Afghanistan, Tajikistan, the Lake Baikal region and Chile) see Fig. 2. Many analysed lapis lazuli rocks and objects come from the collections of the Museo di Storia Naturale (University of Florence, Italy).

Ion microbeam analyses using Ion Beam Induced Luminescence (IBIL) and PIXE were performed on selected stones. IBIL allowed a Chilean origin to be excluded because of the absence of wollastonite, a mineralogical phase typical of Chilean provenance. Wollastonite is characterised by a particular luminescence pattern which was not observed in
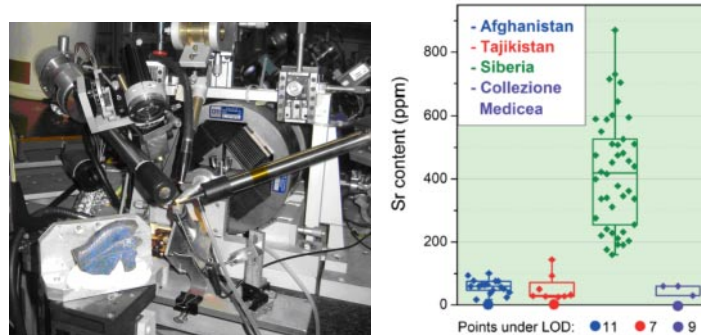
Fig. 2. – **(Left)** An artwork from the "Collezione Medicea" during IBA analysis carried out at the external microbeam at INFN-LABEC in Florence. **(Right)** Sr content in diopside minerals from various sources. The boxes contain the central 50% of measurement, while the vertical bars indicate the full range of the measured data. The horizontal lines in the boxes divide the data in two identically sized groups. The large dots at zero content indicate points with Sr content below the detection limit.

IBIL measurements on the artworks. The rocks from the three Asian provenances are all characterized by the presence of diopside, a luminescent mineralogical phase commonly present in lapis lazuli. For the provenance discrimination, the study focused on markers, such as for example the presence or absence of the trace elements in the stone of a specific mineral phase. After this study, some of the markers found on rocks have been successfully used to characterise six precious artworks of the Collezione Medicea in Florence [18]. Among the detected elements, Sr has the sharpest capability to discriminate between different provenances: a quantity higher than 150 ppm has only been detected in Siberian samples. In the Collezione Medicea artworks, the Sr content is always below 100 ppm, so the Siberian provenance can be excluded (Fig. 2 Right).

3ʹ2. *NAA and PGAA-case studies*. – Nuclear analytical techniques played a pivotal role in helping to solve a high-profile historical forensics "cold case". The famous Danish astronomer Tycho Brahe died in Prague on the 24th October 1601, after a short, 11-day lasting illness, following a banquet held by the Count of Rosenberg. In 2010, Brahe's tomb was reopened and new remains (hair, beard hair, bones) were procured for analysis, which was conducted by a Czech-Danish consortium. Hairs with identifiable root were selected for the determination of time-course of mercury concentrations. The hairs were cut in 5-mm long sections, each corresponding to around 15 days of growth. The section closest to the root is newly grown hair. The length of hairs available was around 2 cm, enough to determine a time-resolved mercury intake in the two months period before Brahe's death. The hair sections were cleaned with the IAEA standardized procedure [22] and analyzed with RNAA at the Nuclear Physics Institute in Řež, the Czech Republic [19], [20], [23].

Three different hairs, both from the first (TB77) and second opening (TB38, TB39) of Brahe's tomb were analyzed, with results that consistently showed that the mercury concentration decreased in Brahe's last two months of life [19], [23] (see Fig. 3 Left). Two months before his death, the mercury concentration had been higher than the median found in populations nowadays. In any case, the values found (16 μg/g), are well below levels seen in moderate mercury intoxication (200 to 800 μg/g) and therefore toxicologically insignificant. The researchers at Řež, Czech Republic also analyzed two
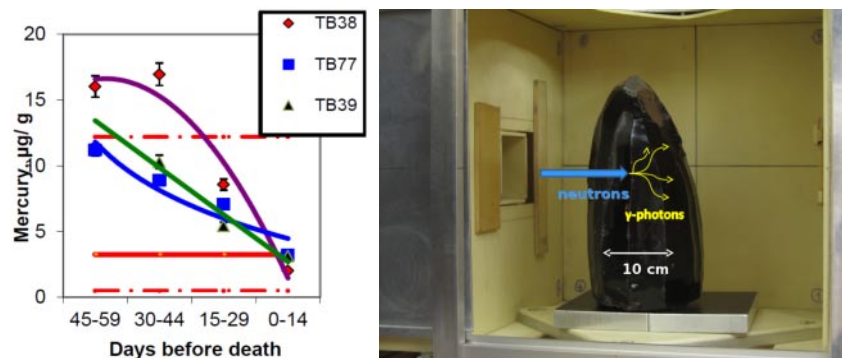
Fig. 3. – **(Left)** Mercury concentrations as a function of the days before Tycho Brahe's death measured by RNAA in three different beard-hairs.**(Right)** An obsidian core from Nyirlugos, Hungary, held in the sample holder of the PGAA station of the Budapest Neutron Centre. The object is from collection of the Hungarian National Museum.

hair samples with μ-PIXE, in a quantitative manner. The results matched those achieved with RNAA, so that it could be concluded that Tycho Brahe did not die from acute mercury poisoning. Analyses of Brahe's bones carried out by Danish researchers proved that Brahe was not exposed to lethal doses of mercury several years before his death, i.e., he did not suffer from chronical mercury poisoning either.

In prehistoric times people knew where good quality materials could be quarried to make everyday tools. Sometimes, final or semi-final products were carried hundreds of kilometres from the localities, where the raw materials were mined. If we can analyse the composition of tools and fingerprint chemical components characteristic of the material's provenance, this can enormously help archaeologists to reconstruct prehistoric trade and migration routes. Non-destructive studies can also help distinguish between different basic types of raw materials (e.g. obsidian, flint, silex, felsitic porphyry) which are sometimes easy to confuse on the basis of visual examination [5]. The easiest task is to determine the provenance of obsidian - a volcanic glass which was popular as a raw material from the early Palaeolithic period, see Fig. 3 Right.

The geological sources are quite well known and their compositions are distinctive of the geological formation and thus define the locality. Besides trace elements of Rb, Nb, Yb, etc. that can be measured by destructive INAA. B and Cl, as well as some major components (Ti, Fe) were precisely quantified by PGAA , and found to be fingerprints of the main raw material sources. In particular a border zone between the distribution areas of the so-called Carpathian and Lipari obsidians has been identified. This border falls in the inland part of modern Croatia [21], [13].

4. – Conclusions

The application of atomic and nuclear techniques to the study of archaeological objects gives the historian or archaeologist material information that can help them to understand life during ancient times. This knowledge is necessary to test the authenticity and provenance of artefacts and to prepare and carry out necessary restorations. All these objectives are common to a very large community of people working in the field of archaeometry, i.e. the application of science to art and archaeology. For all these re-

search activities, a multi-disciplinary approach is essential, bringing together physicists, chemists, archaeologists, numismatists, historians, geologists and conservators from different laboratories, institutions and museums. This paper brings to you some case studies demonstrating the importance of nuclear physics and the exciting role for many scientific branches and provides a useful opportunity to show the public, and also the professional community, just how broad and important the field of application of nuclear techniques has become in the study of cultural heritage, its characterisation and preservation.

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