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Nuclear physics for art and archaeology

Studies and treatments for **Cultural Heritage artifacts**

IFIN-HH
Horia Hulubei
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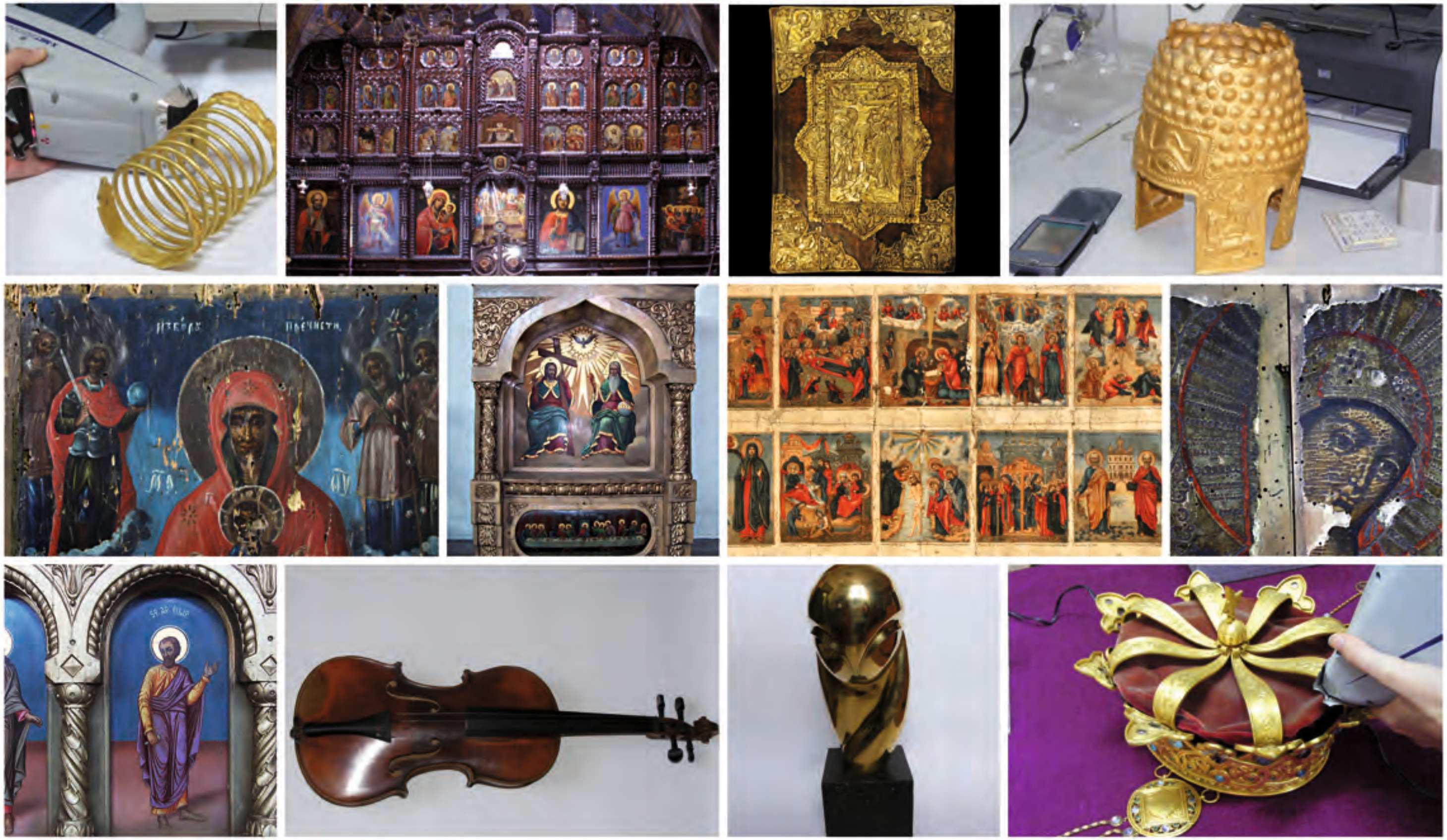
for Research and
Development
in Physics and
Nuclear Engineering



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***Horia Hulubei National Institute of Physics and Nuclear Engineering (NIPNE)**, the largest research institute in Romania, has been involved in activities regarding national cultural heritage studies and preservation for decades. Starting initially from mere individual initiatives, today the institute has expanded its connections with dozens of museums, universities, other research institutes not only from Romania, but also from abroad, elaborating studies and analyses concerning the preservation of material cultural heritage. Covering a wide range of methods, our activities are classified mainly in: compositional analyses, using various nuclear and atomic techniques, gamma radiations treatments, AMS radiocarbon (^{14}C) dating, including different combinations between these. The compositional analyses are not only elemental or isotopic, but also molecular, by means of advanced spectroscopic methods, such as portable XRF (X-Ray Fluorescence), micro-PIXE, micro-SR-XRF (Synchrotron Radiation - X-Ray Fluorescence), AMS (Accelerator Mass Spectrometry), FTIR (Fourier Transform InfraRed) and Raman Spectroscopy, thus determining the artifacts` structure, as well as characterizing or identifying them. The treatments are either for stopping the contamination with some biodegrading agents, or for consolidating the artifacts that are found in various stages of degradation (for example, waterlogged items); furthermore, radiocarbon dating technique can be applied for archaeological samples from organic materials (bones, wood, seeds etc.) that can be up to 60 thousand years old. The techniques are performed using modern equipments, namely either multipurpose facilities (e.g. 3 and 1 MV accelerators, gamma irradiator) that exist within our institute for various research purposes, or exclusively dedicated to studies on cultural heritage (various spectrometers). Through the collaborations that we have, our researchers may expand institute`s activities using advanced equipments from abroad. NIPNE is on a national level the promoter of modern physical and chemical methods concerning cultural heritage, as well as a renowned international leader in such activities. In the present booklet some of the institute`s activities regarding the contributions to the preservation of cultural heritage are presented, describing the mostly used techniques and exemplifying for each of them with a few success stories. The methods, as well as the cases presented are far from covering the multitude of our researches, which are constantly growing in number and importance.*

Dr Livius TRACHE, NIPNE Scientific Director

Radiocarbon dating

The ^{14}C Carbon isotope, also known as radiocarbon, has a vast applicability in the scientific world, being used as a „clock" in estimating the age of certain historic and prehistoric samples, hence its fame. The technique`s potential was referred to for the first time by Willard F. Libby in the „Science" Magazine, May 1947, and the first radiocarbon dating was reported in 1949 by the same Willard F. Libby, who was subsequently rewarded with the Nobel Prize for chemistry, in 1960.

^{14}C is continuously generated in infinitesimal amounts in the superior layers of the atmosphere in the scope of the cosmic radiation flux. Its production is based on the cosmic radiations` reaction with the atmosphere`s most abundent element, namely ^{14}N. The generated radiocarbon chemically reacts with the oxygen, thus producing, through a series of chemical transformations, ^{14}C dioxide, that further enters into the carbon`s global cycle at a planetary scale. During their entire lifetime, plants and animals assimilate ^{14}C from the carbon dioxide present in the atmosphere from water and nutrients, leading to an equilibrium with stable ^{12}C and ^{13}C isotopes ($\sim 1{,}2 * 10^{-12}$ from ^{12}C). After the organism`s death and the cease of radiocarbon intake from nature, the radiocarbon concentration from the organism decreases with a rate determined by the radioactive decay law.

Between 1949 and 1977 radiocarbon dating was performed by means of radiometric measurements. Starting with 1977, AMS (Accelerator Mass Spectrometry) radiocarbon dating technique has gained more and more ground. The main advantages of this method are the efficiency of performing the dating, including the chemical processing of the samples, the highly reduced quantity of sample needed for the dating process (from a few grams to mg in certain cases) and the measurements` precision. The radiocarbon dating laboratory from IFIN-HH uses AMS dating technique, being equipped with a latest generation **1 MV Tandetron accelerator** produced by High Voltage Engineering Europe Company.

AMS radiocarbon dating method is based on measuring the three Carbon isotopes, namely ^{12}C, ^{13}C, ^{14}C, from the given samples in order to determine the $^{13}C/^{12}C$, $^{14}C/^{12}C$ isotopic ratios. The method`s sensitivity rises to the level of 10^{-15} ($^{14}C/^{12}C$), which makes it the most sensitive mass spectrometry technique. Basically, the radiocarbon from the sample is determined by counting every ^{14}C nucleus. Moreover, AMS age determination technique covers a wide variety of samples, from modern ones, with a 10^{-12} ($^{14}C/^{12}C$) concentration, to samples that are at most 60.000 years old, with 10^{-15} ($^{14}C/^{12}C$) concentrations.

Among the samples that can be dated we enumerate: wood, bones, vegetal residues, seeds, carbonates (shells, corals, stalactites/stalagmites, mortar), water, textiles, paper etc. Basically, any sample that was originated in a living organism, and not only, can be dated. The age precision that we ensure is of approximately 1% and the chemical processing associated to AMS measurement can also be performed in our laboratory.

The variety of samples that can be dated within our ***laboratory*** *is extremely wide*

To our potential customers we recommend collaboration in the sampling process in order to avoid any risk of contamination.

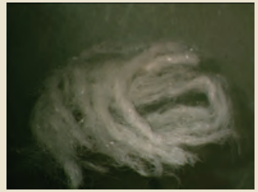
Samples that can be dated at NIPNE, AMS centre:

seeds

bones

wood

textiles



coral

hydraulic mortar

Radiocarbon dating:
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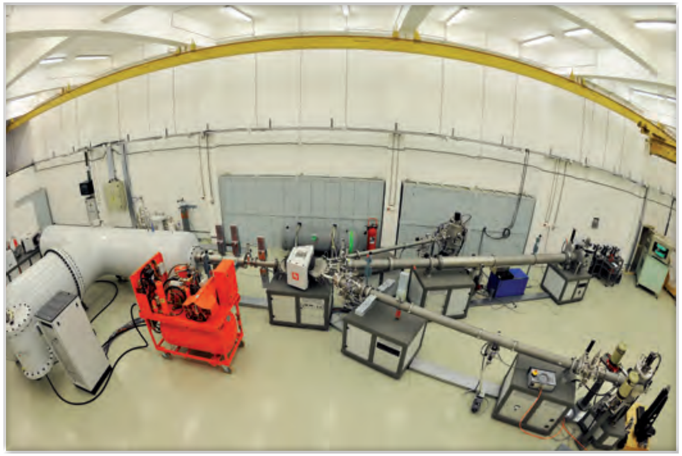
3 MV Tandetron™ accelerator - high sensitivity elemental analyses



The IBA (Ion Beam Analysis) beam line at the 3 MV Tandetron accelerator can be used for high sensitivity elemental analyses for artifacts, art or any other cultural heritage object. The setup allows performing high sensitivity PIXE (Particle Induced X-ray Emission) and PIGE (Particle Induced Gamma-ray Emission) experiments.

The reaction chamber can be used to analyze objects that can be put inside the vacuum chamber (usually small metallic objects such as coins and jewelry). For bigger objects or for objects that cannot be placed in vacuum there is the possibility of beam extraction and measurement outside the reaction chamber, with the detectors in very close geometry.

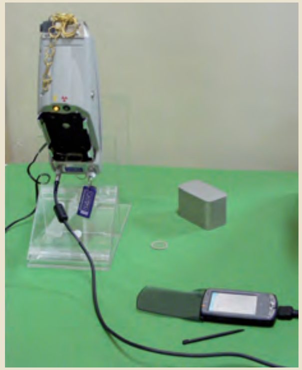
It is important to emphasize that these analyses are nondestructive and of very high precision.

Compositional analyses
on archaeological artifacts and art objects

- golden artifacts: bracelets, hair rings and earrings, diadems, toreutics (ritual vessels), coins (staters, aurei, solidi, hyperperi, ducats)
- silver artifacts: jewelry, toreutics, coins (drachms, denarii, groschen, ducats)
- bronze and copper artifacts: weapons, tools, coins
- paintings and ceramic pigments, inks and ornaments for manuscripts, obsidian (for a more detailed investigation of painting materials, organic binding materials analysis by FTIR and Raman spectroscopy is also presented later in this booklet)

Atomic spectrometric methods (nondestructive):

- **X-Ray Florescence (XRF)** using fixed (elemental analyses in laboratory) and portable spectrometers (*in situ* directly in museums, galleries, collections); detected elements: from potassium to uranium; detection limit: 300-500 ppm (parts per million); analyzed surface: 30 mm diameter; in-depth analysis: 30-60 microns, depending on material
- **PIXE - (Proton Induced X-ray Emission)** - 3 MeV protons; international collaborations: micro-PIXE and micro-SR-XRF (Synchrotron Radiation - X-Ray Fluorescence); detected elements: from magnesium to uranium; detection limit: 5-10 ppm (parts per million); analyzed scanned surface: up to 25x25 mm; in-depth analysis: 30-60 microns, depending on material



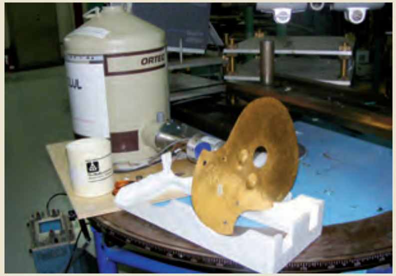
XRF Portable Spectrometer X-MET 3000TXR+ (Rhodium anode)

XRF Portable Spectrometer X-MET 3000TX+ (Silver anode)

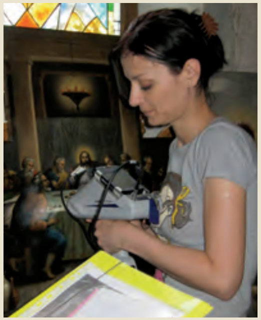
XRF Portable Spectrometer ;
Queen Mary's crown - Alba Iulia Coronation ceremony - October 15th, 1922
(made by "Falize" Jewelry House, Paris)

Au=85%
Ag=11.1%
Cu=2.9%
Red garnets, not rubies, as stated by the Jewelry House

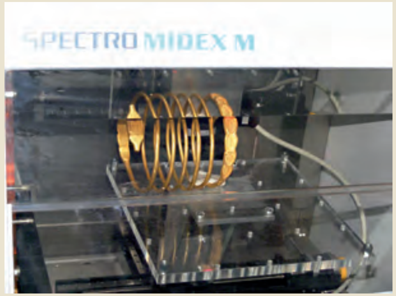
XRF Portable Spectrometer; Getic helmet from Coţofeneşti
Au=76%
Ag=22.5%
Cu=1%



XRF Fixed Spectrometer with 241Am source; The Big Idol from Moigrad (Neolithic)
Au=91%
Ag=8%
Cu=0.2%



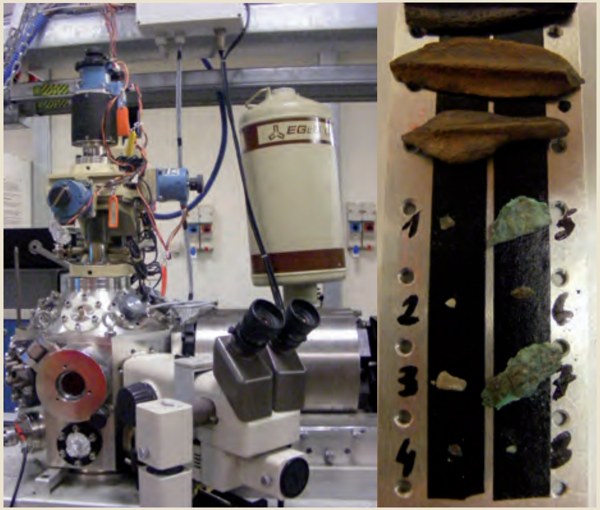
XRF Portable Spectrometer; pigments of mural painting and iconostasis of Măgurele Church - Ilfov County; painted by Gh. Tăttărescu, 1853: red-cinnabar, lead white with white zinc from a XXth century repainting, ochre, iron blue, chrome-yellow, gold-powder mixed with "bolos" - a special type of ochre



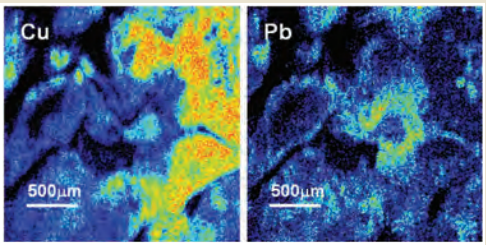
XRF Fixed Spectrometer: SPECTRO MIDEX M (Rhodium anode); Dacian gold spiraled bracelet - 13 bracelets: Au=8 4.2-92.9% ; Ag=6.3-16.2%; Cu=0.4-2.1% Alluvial gold (Valea Pianului - Alba County) mixed with surface vein gold (Valea Morii - Apuseni Mountains)

XRF Portable Spectrometer; pigments and varnish of a presumed Stradivarius violin: a lead-based pigment (XVIIth - XVIIIth centuries) and in some areas a chromium-based pigment (XXth century) from a repainting

XRF Portable Spectrometer; alloy of a Mlle Pogany III statuette type presumably belonging to Brâncuși: brass (Cu=75%, Zn=19%, Sn=3%, Pb=1.7%); used by Susse Fonderie, Paris, around 1960. The brass used at Valsuani Fonderie, Paris, by Brâncuși during his life is different from this one (Cu=82%, Zn=12.5%, Sn=4%, Pb=0.4%)

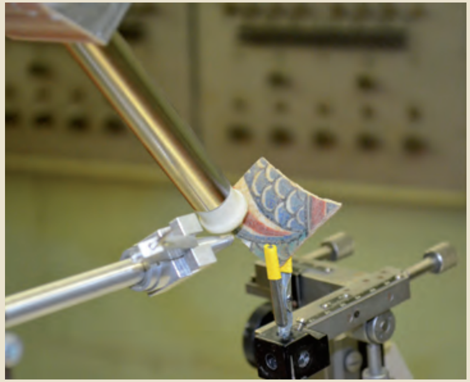


Micro-PIXE: collaboration with LNL INFN Legnaro, 3MeV protons - AN2000 accelerator;



premonetary signs such as arrowheads, Histria, VI-V century BC; lead segregation against copper - primitive bronze metallurgy

Milli-PIXE: collaboration with Wigner Research Centre for Physiscs of the Hungarian Academy of Sciences, Budapest, 5 MV Van de Graaff accelerator; Iznik glazed ceramics fragment excavated (2010-2011) from Suceava`s



archaeological site (the ruins of Prince Vasile Lupu`s Palace, Suceava); Cobalt-blue pigments from Saxony (Erzgebirge Mountains) with Ni and As as minor elements and from Kashan (Iran) with only traces of Ni

Main collaborators: *National History Museum of Romania, "Vasile Parvan" Archaeological Institute, National History Museum of Transylvania, National History and Archaeology Museum Constanța, Faculty of History – University of Bucharest*

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FTIR and FT-Raman molecular spectroscopic methods

FTIR and Raman vibrational spectroscopic methods are complementary techniques used for identifying and characterizing materials and organic/inorganic substances by applying non-destructive or minimal destructive tests.

Applications:

- identifying painting materials using FTIR and FT-Raman spectral databases;

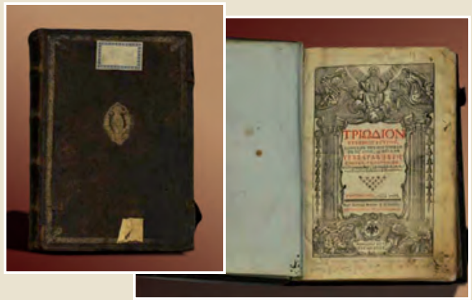
"Car cu boi", Nicolae Grigorescu (Private Collection - originated from Maiorescu Collection) - oil painting on canvas; identified pigments: lead white, cinnabar, chrome-yellow and iron blue

Saint Nicholas Icon - "Dintr-un lemn" Monastery - Râmnicu-Vâlcea; Russian School (Suzdal region) XIXth century; egg tempera on wood; XRF and FT-Raman analyses; identified pigments: lead white, silver foil on a lead white layer, chrome-yellow, ultramarine

Infrared Spectroscopy provides more information on the organic component of the painting layer, and Raman spectroscopy is a nondestructive and non-contact analysis method used mainly for the study of pigments.

- characterising the molecular structure and the chemical modifications generated by the gamma irradiation treatment of polychromatic wood, archives, textile and leather goods;

Ancient book with leather cover, XVIIIth century, Brăila Museum (after the irradiation, the molecular structural modifications are insignifiant)



- investigating molecular properties in order to characterize the degradation stage of leather samples and to identify the pigments used in human skin tattoos (provided by the National Institute of Legal Medicine).

Tattooed human skin sample

Other physical methods of analysis

Color tests - the reflected colour can be measured, as well as other colour parameters, such as the amount of white or of yellowing. Analysed matrices: painting materials, paper, ceramics.

Thermal analysis tests (TG/DSC) - the determination of oxidation and thermal decomposition temperatures through **thermogravimetry** (TG) and **Differential Scanning Calorimetry** (**DSC**). Analysed matrices: fossil resins, painting materials, paper, wood, leather, parchment, wool, textiles etc.

Chromatographic tests (GC-MS and HPLC - Gas Chromatography - Mass Spectrometry and High Performance Liquid Chromatography) - fatty acids profiling from microbial, biological and organic matrices which contain fats by using MIDI method (Microbial IDentification Inc.); identifying volatile organic compounds by thermal desorption from the materials. Analysed matrices: fossil resins and paper.

Amber of Baltic origin, Germany

Elemental and isotopic analysis by Induced Coupled Plasma Mass Spectrometry (ICP-MS) - elemental and isotopic structural characterisation of materials by minimal destructive analysis: approx. 70 elements and 130 isotopes detection limit at ppb level (ng/g). Analysed matrices: fossil resins, marble, ceramics, alloys, sediments etc.

EPR (ESR) spectroscopy - Electron Paramagnetic Resonance (Electron Spin Resonance) - identification and characterization of free radicals generated by the irradiation of various substances and paramagnetic centres containing transition elements (Fe^{3+}, Cu^{2+}, Mn^{2+}, V^{4+}). Analysed matrices: ceramics, wood, paper, textiles etc.

Thermo-luminescence - Optically Stimulated Luminescence (TL-OSL) - authentication of ceramic matrices (clay and ceramic pots, tiles, bricks etc.).

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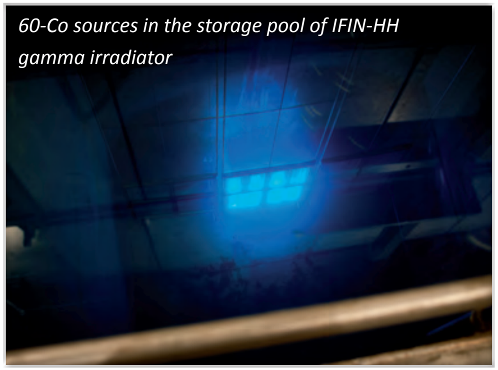
IRASM gamma radiation treatments

Many cultural heritage items are threatened by biological attacks, the organic constituents (cellulose, collagen or proteins) being food for microorganisms and insects. Improper storage conditions lead to massive biologic attacks in museums, archives or libraries, which are difficult to stop or eliminate because of the large quantities of items involved. Compared to other techniques, gamma radiation treatment has a major advantage: the biocide effect is ensured by the radiation`s high penetration power. At a molecular level, the photons or electrons break the molecular bonds initiating further chemical reactions. The scission of the DNA double coil is the major cause for the biocide effect and the basis of the applications related to "killing" the pests (bacteria, fungi or insects). The physical measure which best describes the gamma radiation effects is the absorbed dose - Gy (Gray) unit. In order to reduce the risk of degrading the treated item, establishing the correct irradiation dose for a particular class of materials is of major importance.


60-Co sources in the storage pool of IFIN-HH gamma irradiator

Disinfection and disinsection of wooden items

What mostly affects wood are woodworms or wood-boring beetles. Insects have a relatively low resistance to irradiation, thus pests are easily eliminated, regardless of the development stage (larvae, eggs). Fungi are inactivated at higher irradiation doses, which are well supported by wood. Despite the fact that cellulose is known to be degraded by ionizing radiation, the lignin-cellulose assembly shows no changes on a large dose interval.

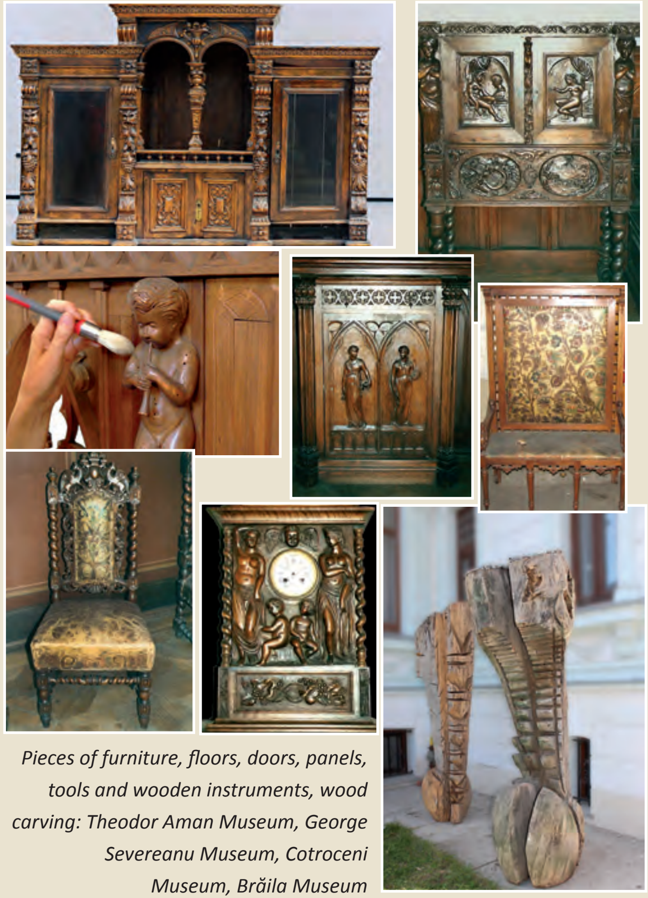
In the case of painted wood the issue on how pigments or varnish are affected is raised. In literature there are reports on dose response for over 30 pigments and varnishes and it is accepted that a dose of 10 kGy will not cause painting degradation, while insects and most of the fungi are killed.

One of IRASM`s remarkable achievements was the irradiation of the iconostases from two Romanian historical churches. For transport and irradiation, the large iconostases (6x4 meters) were dismantled in pieces of up to 2.5 meters. Several collections of icons (more than 400 icons), of sizes varying from 30x40 cm to 150x200 cm, were also treated.

Disinfection treatments for film archives

Photographic films can also be seriously damaged by fungi attacks. Having entirely a synthetic composition, magnetic tapes are less exposed to microbiological attack, but contamination starts when they are stored along with photographic films (beta tapes) or cartons (audio tapes).

Iconostases, pieces of iconostases and wood painted icons: Izvoarele Parish (Prahova), Eparchy of Brăila, "Moldova" National Museum Complex (Iaşi), Tismana Monastery (Gorj), Robeşti Parish (Vâlcea)



Pieces of furniture, floors, doors, panels, tools and wooden instruments, wood carving: Theodor Aman Museum, George Severeanu Museum, Cotroceni Museum, Brăila Museum

Decontamination of large quantities of documents

The major threat for paper items are fungi, which rapidly spread due to increased humidity, which can easily activate the fungal growth. Paper is made of cellulose fibers, but with low lignin content or none, in which case the risk of degradation is higher. At low irradiation doses cellulose`s degree of polymerization is reduced, but this is not reflected in paper`s macroscopic properties. A number of reports showed no changes in the properties of paper (mechanical, colour, pH, water sorption etc.) for doses in the range of 5 to 10 kGy. This is explained through a behavior similar to reticulation for the cellulose irradiated at low doses (new hydrogen bonds are created that strengthen fiber`s tridimensional structure).

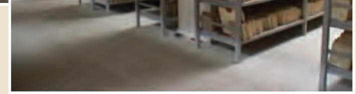
Textiles, leather and parchment

Textiles can be equally affected by insects, fungi or bacteria. Microorganisms (fungi) are the main threat for historical leather and sometimes insects as well (woodworms, in the case of ancient book covers). Due to reduced water retention, parchment is more resistant to pest attacks, but it is more exposed because of its age.

The lack of information concerning the irradiation effects on textile, leather or parchment artifacts is caused by the smaller quantities in which such items are found. The proper irradiation dose is selected according to each type of material (cotton, wool, silk, leather etc.), as well as to the artifact`s degradation stage.

Books, magazines, ancient religious books, lithography, archives: National History Museum, Brăila Museum, Eparchy of Brăila, Silvestru Parish, Romanian Literature Museum, Sports Museum, Library of Electrotechnic Research Institute, Romanian Parliament Archive, private collections and archives


Tapestry furniture, carpets and rugs, traditional costumes and other articles of clothing: Theodor Aman Museum, George Severeanu Museum, "Brancovan Palaces" Cultural Center, "Moldova" National Museum Complex (Iaşi)

Photographic films and magnetic tapes: National Film Archive, TVR Archive, Radio Archive

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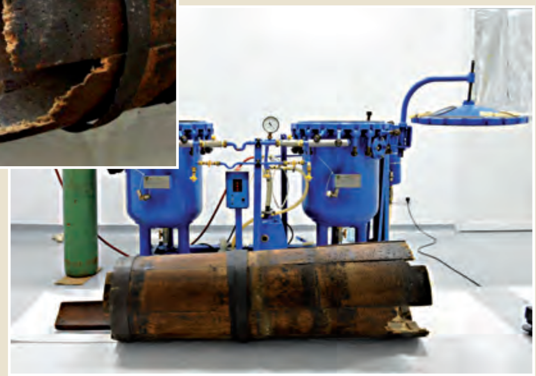
Consolidation of cultural heritage wooden artifacts by impregnation with resin and radio polymerisation

The physical, chemical and biological agents act on cultural heritage items, causing aspect modifications (size, shape or color), loss of resistance, partial or total structural damage due to chemical changes (degree of polymerization, molecular structure, oxidation state etc.). The use of radio polymerization *in situ* in order to restore the properties of the damaged wood is yet another application of the gamma irradiation process, with the purpose of preserving the cultural heritage. The technique implies the insertion in the item`s pores of a polymer solution (the resin) which is able to reticulate, thus creating a tridimensional structure that would fill the pores, hence consolidating fragile objects. The consolidation is performed in special tanks and takes place in four stages:

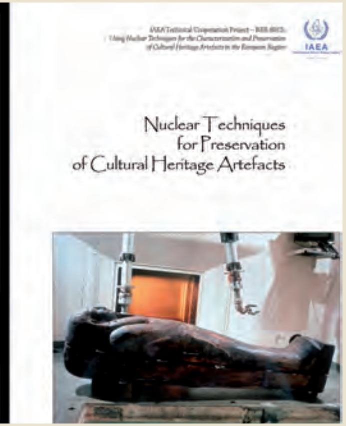
- the item is introduced in the impregnation tank, under vacuum, for 8-16 hours;
- the resin solution is inserted in the tank, completely sinking the item;
- the resin propagates into the object`s pores in nitrogen atmosphere at 2-5 bars for 16-24 hours;
- the excess of resin is removed and the item is exposed to gamma radiations, which determine the occurence of the consolidation process by radio polymerisation - reticulation; hence, the tridimensional structure in the item`s pores is generated.

In 2014 two ethnographic objects from Golești Viticulture and Pomiculture Museum were consolidated at NIPNE, IRASM in collaboration with Nucleart, Grenoble: a wooden butter churn and an old wooden stool, both in critical stages of degradation.

Wooden butter churn, XIXth century, Goleşti National Museum Complex, Argeş



International acknowledgements



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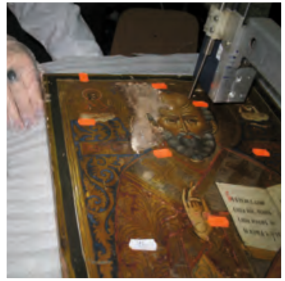
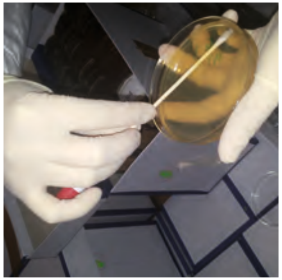
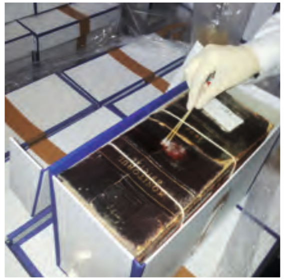
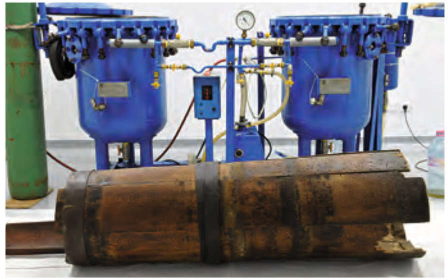
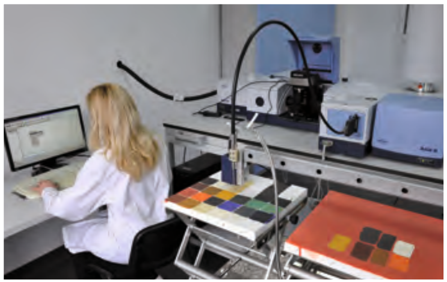
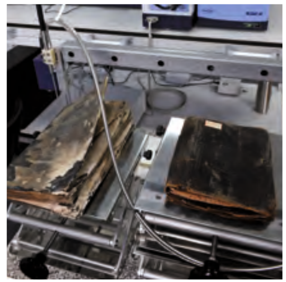
For additional updated information, as well as forms for analyses of samples please visit:
http://www.nipne.ro/patrimoniu and *http://ifin-hh.radiocarbon.ro*



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