Technical meeting on "Strategies for Preservation and Consolidation of Cultural Heritage Artefacts through Radiation Processing"

Zagreb, Croatia

4 - 8 June 2018

Organized by

International Atomic Energy Agency (IAEA), Vienna

and

Ruđer Bošković Institute, Zagreb, Croatia

Radiation Chemistry and Dosimetry Laboratory

with the help of

Academy of Fine Arts, Zagreb, Croatia

Croatian Conservation Institute, Zagreb, Croatia

Mimara Museum, Zagreb, Croatia

International Council of Museums Croatia

ORGANIZING COMMITTEE

Mr **Sunil SABHARWAL**
International Atomic Energy Agency
Department of Nuclear Sciences and Applications
Division of Physical and Chemical Sciences
Physics Section
P.O. Box 100, Vienna International Centre
Wagramer Straße 5, 1400 Vienna, Austria
Tel.: +43 1 2600 21744
Fax: +43 1 26007
e-mail: S.Sabharwal@iaea.org
Internet: http://www.iaea.org

Ms **Branka MIHALJEVIĆ**
Ruđer Bošković Institute
Division of Materials Chemistry
Radiation Chemistry and Dosimetry Laboratory
Bijenicka c. 54, 10000 Zagreb, Croatia
Tel.: +385 1 456 1071
e-mail: branka.mihaljević@irb.hr
Internet: http://www.irb.hr

Ms Katarina MARUŠIĆ
Ruđer Bošković Institute
Division of Materials Chemistry
Radiation Chemistry and Dosimetry Laboratory
Bijenicka c. 54, 10000 Zagreb, Croatia
Tel.: +385 1 456 1154
e-mail: kmarusic@irb.hr

IAEA ADMINISTRATIVE SUPPORT

Mr Enrique **NACIF**
International Atomic Energy Agency
Department of Nuclear Sciences and Applications
Division of Physical and Chemical Sciences
P.O. Box 100, Vienna International Centre
Wagramer Straße 5, 1400 Vienna, Austria
Tel.: +43 1 2600 217443
e-mail: E.Nacif@iaea.org

LOCAL ORGANIZING COMMITTEE (LOC)

Ms **Branka MIHALJEVIĆ**
Ms **Katarina MARUŠIĆ**
Ms **Ivana TARTARO BUJAK**
Ms **Željka KNEŽEVIĆ**
Ms **Iva DŽEBA**
Ms **Marijana NODILO**

Ruđer Bošković Institute
Division of Materials Chemistry
Radiation Chemistry and Dosimetry Laboratory

and

Ms **Ana BOŽIČEVIĆ**
Ms **Zvjezdana JEMBRIH**

Academy of Fine Arts
University of Zagreb
Conservation-Restoration Department

TECHNICAL MEETING ON "STRATEGIES FOR PRESERVATION AND CONSOLIDATION OF CULTURAL HERITAGE ARTEFACTS THROUGH RADIATION PROCESSING"

IAEA & Ruđer Bošković Institute, Zagreb, Croatia

View of the sanctuary after conservation and restoration (photo by G. Tomljenović, 2016., photo archive of the CRI)

Purpose: The purpose of the meeting is to share the recent experiences and advances in radiation technology for cultural heritage preservation and consolidation with the stakeholders like conservators, restorers and radiation technologists to expand the application of radiation technology in this area.

When: June 04-08, 2018

Where: Ruđer Bošković Institute, Zagreb, Croatia

Description: The preservation of World Cultural Heritage (WCH) has emerged as a key issue for maintaining national identity, and understanding the influences or exchanges among civilizations throughout history. Cultural heritage artefacts are made up of materials varying from simple mono-components to complex structures integrating inorganic and organic materials. Many of artefacts such as easel and panel paintings, wooden sculptures, library materials, prints, textiles are based on natural organic materials which are prone to biological attack under improper conservation conditions.

Degradation by insects and microorganisms such as fungi and bacteria constitute a major threat against the long-term preservation of WCH.

The success and consolidation of the application of ionizing radiation for inactivation of microbes presents a powerful technique for the disinfection of paper, textiles and wood based cultural heritage artefacts. In recent years, collaboration of radiation processing facilities with cultural heritage institutions such as museums and libraries has opened new vistas for the use of this technology for treating large quantities

of deteriorated products that required emergency intervention or had a complex structure that limited the use of conventional techniques.

The wider use of this technique necessitates a multidisciplinary approach for effectively demonstrating that irradiation does not lead to unacceptable changes in the functional or decorative properties of the artefact as well does not compromise with the authenticity of the artefact.

This Technical Meeting will aim at discussing the recent progress of work towards this goal.

The course will be conducted in English only.

PROGRAMME

Monday, 04th June 2018 - Hall 3

9:00 – 9:30	**Registration**
9:30 – 9:40	**Opening Session** **Branka Mihaljević**, Head of Radiation Chemistry and Dosimetry Laboratory and Organizer of the Meeting
9:40 – 9:55	**Welcoming address** **David Matthew Smith**, RBI Director General: Overview of the Ruđer Bošković Institute Activities and Achievements **Boris Ilijaš**, Head of Sector for Radiological Safety, State Office for Nuclear and Radiological Safety: Welcome address
9:55 – 10:10	**Sunil Sabharwal** International Atomic Agency (IAEA) *Introduction to the IAEA projects related to study and protection of CH objects, future* *Objectives, outcomes of the TM*
10:10 – 10:25	*Radiation Chemistry and Dosimetry Laboratory(RCDL) presentation*
10:25 – 10:30	Election of the Chairperson(s), Adoption of the agenda
10:30 – 11:00	**Coffee break**
SESSION 1: RADIATION SCIENCE AND ART IN HARMONY	
11:00 – 11:20	**Katarina Marušić** - CROATIA *Ionizing radiation for protection of artworks and cultural heritage in Croatia- an overview*
11:20 – 11:40	**Iskra Karniš Vidovič** - CROATIA *Review of the Cooperation between the Croatian Conservation Institute and the Ruder Boskovic Institute*
11:40 – 12:00	**Anđelko Pedišić** - CROATIA *Conservation of Cultural Heritage using Ionizing Radiation in the Context of Wartime Evacuations and Reparing Damages Caused During the War*
12:00-12:20	**Tijana-Annar Trputec Strčić** - CROATIA *Art Residents – Pests and Art*
12:20 – 13:30	**Lunch**
SESSION 2A: IRRADIATON EFFECTS ON COMPONENTS OF CH OBJECTS	
13:30 – 14:10	Introduction lecture 1: **Pablo Antonio Vasquez Salvador** – BRAZIL *From Historical Artifacts to Technology: Ionizing Radiation for Preservation*
14:10 - 14:30	**Zaki Ajji** - SYRIAN ARAB REPUBLIC *Current status of radiation processing in Syria (cellulose materials)*
14:30 – 14:50	**Slobodan Mašić** and **Ivica Vujčić** - SERBIA *The Use of Gamma Radiation for the Treatment of Cultural Heritage in Serbia*
14:50 –15:50	**Coffee**
15:50 –16:10	**Ines Krajcar Bronić –** CROATIA *Brief introduction of C14 method for the cultural heritage dating*
16:10 – 18:00	**Visit to the RBI laboratories** 
~ 18:00	**Welcome Reception** (sponsored by RCDL)

Tuesday, 05th June – Hall 1

SESSION 2B: IRRADIATON EFFECTS ON COMPONENTS OF THE CH OBJECTS		
9:00 – 9:40	Introduction lecture 2: **Maja Šegvić Klarić – CROATIA** *Gamma-irradiation for cultural heritage – could it prevent fungal growth on paper materials?*	
9:40 – 10:00	**Irina Pucić–CROATIA** *Radiation effects on some of the materials constituting CH objects - recent research of the RCDL scientists*	
10:00 – 10:20	**Oleksandr Buhay** – UKRAINE *Application of nuclear techniques for cultural heritage in Ukraine: Problems and perspectives*	
10:20 – 11:00	**POSTERS + Coffee break**	
SESSION 3: SIDE- AND POST-IRRADIATION EFFECTS STUDIES		
11:00 – 11:40	Introduction lecture 3: **Stefania Baccaro - ITALY** *Characterization of radiation processing effects in Cultural Heritage applications*	
11:40 – 12:00	**Petya Kovacheva - BULGARIA** *Some side-effects of gamma-irradiation disinfestation on highly contaminated leathers and librarian materials*	
12:00 – 12:20	**Kumarawadu Ruwan Chandima De Silva - SRI LANKA** *Application of Radiation Surface Modification Techniques for the Preservation of Achieved Materials in Sri Lanka*	
12:20 – 13:30	**Lunch**	
13:30 – 15:00	Introduction on the working group discussions and formation of the working groups	
	Working group on the Recommendations for safe CH components irradiation	Working group on the Analytical tools for safe irradiation of CH
15:00 – 15:30	**Coffee break**	
17:00 – 18:30	**Guided tour of the city center**	

Wednesday, 06th June – Hall 1

SESSION 4A: CURRENT PRACTICES IN RADIATION CONSERVATION OF CH OBJECTS	
9:30 – 10:10	Introduction lecture 4: **Celina Horak - ARGENTINA** *Radiation processing and nuclear techniques capabilities related to cultural heritage in Argentina*
10:10 – 10:30	**Hassan Abd El-Rehim - EGYPT** *Use of Radiation Technology for Preservation of Some Egyptian Cultural Heritage Artifacts*
10:30 – 10:50	**Hae-Jun Park – KOREA** *Application of irradiation technology for conservation of cultural heritage in Korea: Control of fungi and insect in wood cultural heritages*
10:50 – 11:20	**Coffee break**
SESSION 4B: CURRENT PRACTICES IN RADIATION CONSERVATION OF CH OBJECTS	
11:20 – 11:40	**Dagmara Chmielewska-Śmietanko - POLAND** *Electron Beam for Preservation of Biodeteriorated Cultural Heritage Paper-Based Objects*
11:40 – 12:00	**Arbi Mejri - TUNISIA** *Developing of Radiation Treatment Methodologies for Preservation of Tunisian Cultural Heritage: Application in the preservation of women's ceremonial dress in noble textile*
12:00 – 13:00	**Lunch**
13:00	**Visit to chapels in the Sisak region** 
	Conference Dinner (sponsored by IAEA)

Thursday, 07th June

SESSION 5: PROCEDURES FOR IRRADIATION OF CH OBJECTS (incl. dose mapping, dose limit ratio, simulation techniques)		
9:00 – 9:40	Introduction lecture 5: **Constantin Daniel Negut - ROMANIA** *Disinfestation of artefacts by gamma irradiation in Romania*	
9:40 – 10:00	**Volodymyr Morgunov – UKRAINE** *Numerical Simulation of the Radiation Treatment of Cultural Heritage by Bremsstrahlung X-Rays*	
10:00 – 10:20	**Coffee break**	
SESSION 6: CONSOLIDATION: New radiation curable resins		
10:20 – 11:00	Introduction lecture 6: **Laurent Cortella - FRANCE** *Uses and Prospects in Gamma Biocide Treatments and Radiocurable Resin-Based Consolidation Treatments for Cultural Heritage Artefacts*	
11:00 – 11:20	**Luis M. Ferreira - PORTUGAL** *Hybrid materials (gel/solid) by ionizing radiation for conservation of non-metallic inorganic historical materials*	
11:20 – 11:40	**Maria Helena Casimiro - PORTUGAL** *Gels for cleaning artworks*	
11:40 – 12:00	**Alexandra Rodrigues - PORTUGAL** *A case study of consolidation in Conimbriga: The House of Trident and Sword*	
12:00 – 12:45	**Lunch**	
12:45 – 13:45	**Working group discussions**	
	Working group on the Recommendations for safe CH components irradiation	Working group on the Analytical tools for safe irradiation of CH
13:45 – 14:45	Presentations of the discussions and outcomes of the Working groups	
14:45 – 17:00	**Guided tour of the Cathedral and Treasury** 	
~ 18:00	**Joint Dinner (Optional at the participants' expense)**	

Friday, 08th June

9:00 – 10:30	**Drafting the meeting report**
10:30 – 11:00	**Coffee break**
11:00 – 12:00	**Formulation of Action Plan and Recommendations** **Finalization and approval of the meeting report**
12:00 – 12:30	**Conclusions and closing remarks**

Visit to the RBI Laboratories:

1. Radiocarbon Laboratory (C14 dating)
2. Laboratory for Ion Beam Interactions (LIBI, Accelerator)
3. Radiation Chemistry and Dosimetry Laboratory (RCDL)

PRACTICAL INFORMATIONS

WIFI

Free WIFI is availabe in the lecture halls. The network is IRB-Limited.

LOCATION

First day (4th of June) the meeting will take place at RBI, lucture hall in the building 3. All other days the meeting and the poster session will take place in lecture hall building 1.

LUNCH, Coffee break

Lunches and coffee breaks will be served outside the lucture rooms.

VISIT MIMARA MUSEUM

It is our great pleasure to offer you a discounted ticket price of 20 HRK (by showing your accreditation from the TM) for an individual visit to the Mimara Museum during the TM.

Working hours:

Tuesday, Wednesday, Friday, Saturday 10 - 17 h; Thursday 10 - 19 h; Sunday 10 - 14 h.

The Mimara Museum is an art museum situated at the Roosevelt Square, in Zagreb city centre. Housing a variety of art collections it provides the opportunity to get acquainted with almost all historical artistic periods and styles. The permanent exhibition is made up of the old civilizations collection, European sculptures, ivory collection, Far Eastern artworks, icon collection, collection of drawings and graphics, glass collection, furniture collection, textile collection and oriental carvings. The rich collection of paintings contains works by Italian, Flemish, Dutch, Spanish and French masters dating from the early Medieval Period to the 20th Century.

For more informations on current exhibitions and events please visit website www.mimara.hr

WELCOME RECEPTION

On Monday 4th June at ~ 18:00 Welcome reception sponsored by RCDL will be organized at RBI in front of the lecture hall in building 3.

CONFERENCE DINNER and EXCURSION

On Wednesday June 06th, from 13:00 visit from the Ruder Boskovic Institute to wood chapels in the Sisak region wil be organized. After the excursion the Conference Dinner is planned at the restaurant in the Old Town Sisak, (sponsored by IAEA and RCDL) around 17:30.

Wooden churches and chapels are the greatest achievement of traditional architecture in northern Croatia, especially in the area of Lucerne oak (Quercus robur), growing in lowland forests along the rivers Sava, Drava, Danube, Kupa and their tributaries. From a large number of original churches, today there are only forty left in the mentioned area dating from the period of the 17th to the late 19th century.

Method of building wooden churches in Turopolje - joining wooden beams

Saint Barbara's chapel in Velika Mlaka

Near Zagreb, in the urban area of the city, there is the former village of Velika Mlaka with the wooden chapel of St. Barbara in the middle - a baroque jewel of wooden architecture in Turopolje. The first written trace dates back from 1642 and the history of the construction is followed up until 1912 when the porch was upgraded. The oldest part of the chapel is the 17th century shrine with an apse which is particularly emphasized by the beautiful wing altar with portraits of life and martyrdom of St. Barbara on one side of Christ's Passion on the other side, while the main

altarpiece displays the standing figure of the saint and is dedicated to St Barbara. Right beside the chapel, we find a one-story wooden cardak (čardak) carved wooden porch that serves as a rectory and together with the chapel makes a harmonious unity. Attention is also drawn to the small wooden chamber used to store wheat, a remnant of the old church manor. In 1976, when the parish of Velika Mlaka was founded, Saint Barbara's chapel becames aparish church.

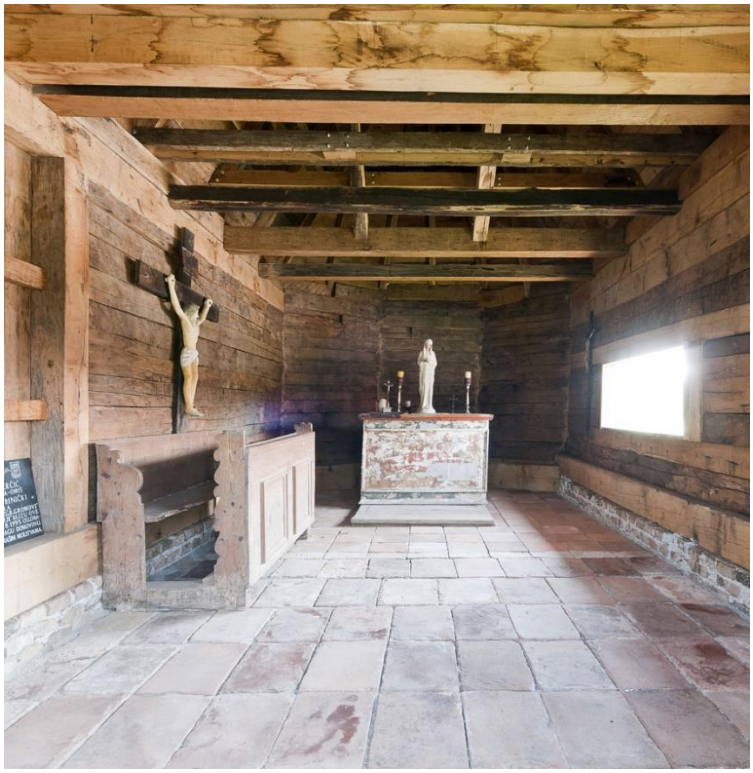
(Source: http://www.touropolje.com/barbara.html)

Saint Martin's chapel in Stari Brod

Apart from being an important cultural monument of the Republic of Croatia, Saint Martin's chapel in Stari Brod has a special significance for the local community as it symbolizes the centuries-long survival of the village along the river Kupa, which has survived more than four centuries of frequent flooding and three wars only in the 20th century. The chapel is first mentioned in archive documents in 1699. It was built of oak planks at the base of the brick. Walls, ceiling of the nave, vestibul and sanctuary were covered with 88 shallow wooden cassettes of unequal dimensions and bordered with decorative laths. Before the conservation and restoration work, the chapel was

neglected, its roof dampened and in some places there were no roof tiles, so part of the rainwater slipped inside the chapel. This caused the movement and deformation of architectural elements and separation of the joints of painted wooden planks. Ceilings of painted wooden moldings were partially torn, due to the long exposure to high humidity, twisted and cracked, and on their unguarded backs were deposited slippery layers of dust mixed with faeces, stalk and remains of dead animals. It also weakened the bonding of layers deposited on a wooden carrier, resulting in their separation and occasional falling off.

The project of conservation and restoration of the chapel began in 2001 with historical-artistic research, producing images of the current situation and assessment of the state of timber and damage of the painted wooden paneling. After stripping of the plaster in 2002, the renovation of the chapel and the replacement of the roof had begun. At the same time, the dirt on the back of the wooden panel was removed, a gamma-radiation disinfection was performed at the Ruđer Bošković Institute in Zagreb, separated parts of the painted layer were fixed, wooden support was consolidated and carved and the removal of impurities was completed. By 2015, the reconstruction of the substrate layer damage By 2015, reconstruction of the substrate layer damage and the final retouch of the painted layer on all panels and decorative laths were installed in the chapel in the same year. After completing of the assembly painted wooden paneling, the restored altar is returned to the chapel.



This conservation and restoration project was rewarded with the European Union Prize for Cultural Heritage of Europe Nostra 2017.

(Source:http://www.h-r-z.hr/index.php/djelatnosti/konzerviranje-restauriranje/drvena-polikromna-skulptura/2187-drvena-kapela-sv-martina-u-starom-brodu)

Chapel of St. John the Baptist, Stara Drenčina

Chapel of St. John the Baptist in Stara Drenčina is an example of the historically layered sacral wooden traditional architecture of Pokuplje area. It is mentioned as far back as 1696. The most valuable is a baroque phase of the chapel from 1748. Extensive conservation and restoration works on the construction of the church and in its interior were successfully completed by the Croatian Restoration Institute in 2006.

(source: http://dizbi.hazu.hr/object/26939)

Sisak, the Old Town

Nowadays, the Sisak Fortress is a monument of the highest category and of a cultural value of national importance. It represents one of the few almost completely preserved specimens of fortification architecture from the time of Croatian-Turkish wars. Construction started in 1544, at the very confluence of the river Kupa in Sava and in 1550 it was completed for its basic purpose. The building material used was mainly from the remains of Roman town Siscia. Ottoman army leader Hasan Pasha Predojević besieged the fortress three times until the final defeat on June 22,

1593 in the crucial battle for the defense of Sisak and the entire Croatian kingdom. The fortress has been damaged and repaired several times during the following centuries. During the Second World War it was hit by shells and one of its parts was heavily damaged, especially the northwest tower. After the war, the damaged parts were restored. New damage occurred during the Homeland War, but they have been repaired in the meantime. The Sisak Old Town's premises have recently been used to accommodate the Sisak City Museum and a restaurant where dinner is planned is situated there.

GUIDED TOUR

On Tuesday 5th June from 17:00 to 18:30 guided tour (sponsored by touristic office Zagreb) of the historical part of Zagreb will be organized. The meeting point will be at 17:00 in front of the Manduševac Fountain at Ban Jelačić Square (main square).

On Thursday 7th of June a guided tour (free of charge) of the Cathedral and Treasury, will be organized. We will travel by cars directly from the RBI to Kaptol at 14:45. Afterwards the joint dinner will be organized around 18:00 in a nearby restaurant.

ABSTRACTS

(IN ORDER OF PRESENTATION)

S 1.1

IONIZING RADIATION FOR PROTECTION OF ARTWORKS AND CULTURAL HERITAGE IN CROATIA- AN OVERVIEW

KATARINA MARUŠIĆ,[1] IRINA PUCIĆ,[1] TANJA JURKIN,[1] BRANKA MIHALJEVIĆ,[1] BRANKA KATUŠIN RAŽEM,[1] DUŠAN RAŽEM,[1] MARIO BRAUN[2]

[1]Ruđer Bošković Institute, Department for Material Chemistry, Radiation Chemistry and Dosimetry Laboratory, Bijenička c. 54, 10000 Zagreb

[2]Croatian Conservation Institute, Gršković eva 23, 10000 Zagreb

Background. The Ruđer Bošković Institute (RBI) is the largest Croatian research centre in sciences and science applications. The Radiation Chemistry and Dosimetry Laboratory (RCDL) has remained until the present day the only unit in the country pursuing both basic and applied scientific research in the fields of radiation chemistry, dosimetry and radiation processing.

The effects of ionizing radiation are studied mainly in liquid model systems, in an effort to understand the nature and fate of the reactive short-lived species: ions, electrons, excited molecules and free radicals. Gamma-irradiation and time-resolved technique (laser flash photolysis) are essential for the fulfilment of the research mission. The study of some radiation-induced effects in suitably tailored materials has led to the development and use of various dosimetry systems, which found their applications in radiation protection and radiation processing practices. The high-dose liquid chemical dosimetry system, based on the ethanol-chlorobenzene, has been accepted as a joint ISO/ASTM 51538 standard.

Radiation technique also became a necessary tool in many areas of scientific research especially in radiation synthesis and modifications of advanced materials and nanotechnology. An important part of our mission remains the research of potential applications of irradiation for sterilization, pasteurization, disinfection and decontamination of medical, pharmaceutical, food and other products [1], and finally for protection and conservation of cultural heritage objects. The group of the RCDL researchers works on research and development of dosimetry systems suitable for wide ranging applications over many orders of magnitude, from environmental dosimetry to radiation processing dosimetry. Integral parts of this research are characterization of dosimetry systems and radiation fields, dosimetry of various electromagnetic and particle radiations (neutrons and charged particles) and evaluation of dosimetry techniques.

Methodology. The equipment is a batch type panoramic gamma irradiator (activity about 70 kCi ^{60}Co) which has been designed by the RCDL staff, its periodical upgrading having been assisted by the IAEA. It is the only facility of its kind in Croatia and the region. The irradiator is suitable for a variety of applications, from medium dose range used in radiobiology to high doses used in radiation processing and radiation chemistry. The capacity of the irradiator chamber is 4 - 6 m^3 of material per batch. There is no conveyor to transport goods into and out of irradiation chamber giving maximum flexibility with respect to the dimensions and weight of objects.

Fig. 1. Irradiation facility at the RBI

Results. As the radiation technique has a lot of advantages in the conservation treatment of cultural artefacts the interest for irradiation conservation treatment has been extremely increased in recent years.

The doses applied for irradiation treatment at the RCDL have been as generally accepted in the professional literature: for disinsection (insect control in wooden objects, textiles, paper, parchment) 0.5 to 2.0 kGy, for desinfestation (control of fungi in wooden objects, paper, leather) 5 to 10 kGy, and for control of bacteria 5 - 20 kGy. The dose is fine-tuned depending on the materials that constitute the object and its state. The decision is made by irradiation facility staff in cooperation with restorers and other specialists.

The RCDL has a long lasting experience in the application of irradiation in the preservation of cultural heritage (CH) objects. Since 2005. it intensified their activities, including both international and national cooperation in the field. RCDL and the Croatian Conservation Institute (CCI) have formal Cooperation Agreement from April 2006. The cooperation with the CCI in that field grew in time to become most intense during the actions for the salvation of numerous polychromic sculptures and other objects damaged during the War in Croatia (1991-1995) [2]. It is estimated that over the past 30 years in cooperation with the CCI almost 95% of all treated objects (wooden sculptures, parts of altars, furniture pieces, tools, musical instruments and other objects made of wood, paper, straw, textile and leather) were subject to desinsection. Most often single CH objects would be treated, but irradiation has been proved an especially appropriate method when a complete dismantled altar, iconostas or an entire museum collection had to be treated simultaneously to avoid cross-contamination. Presently about 20 m^3 comprising mainly wooden heritage objects, are treated annually at the RBI facility.

Except of the CCI, very lively cooperation with the other interested parties (museums, archives, libraries) also exists. These institutions are: Central Laboratory for Conservation and Restoration of Archives, Croatian State Archives; Conservation and Restoration Department of the Museum of Contemporary Art (MSU); Museum of Arts and Crafts; Croatian History Museum; Etnographic Museum, Zagreb; Technical Museum, Zagreb; Mimara Museum; Museum of the Serbian Orthodox Church in Croatia, Zagreb; Museum of Cetinska Krajina, Sinj, National and University Library in Zagreb, and many museums and galleries out of Zagreb. Recently the scientific cooperation between the RBI and the Department of Restoration of the Academy of Fine Arts and the Faculty of Pharmacy and Biochemistry, University of Zagreb, has been very essential.

The acceptance of the irradiation method and its correct application depend on the understanding of conservators and restorers of its advantages and limitations. The need to disseminate this kind of knowledge and to provide basic information on the irradiation method to potential users in a systematic manner has led the RCDL to take active part in conservators' restores' education at all levels.

Ongoing research in the RCDL on cultural heritage irradiation through the Coordinated Research Project of IAEA: *Developing Radiation Treatment Methodologies and New Resin Formulations for Consolidation and Preservation of Archived Materials and Cultural Heritage Artefacts*, is aimed on a systematic overview of the required minimal doses for radiation treatment of the most common and specific microorganisms found on CH artefacts, accompanied by a database of the microorganisms common for that type of CH. We consider that radiation specialists could use all results obtained from this project as a valuable guideline for appropriate irradiation treatment and conservators when they meet problems of biologically contaminated cultural or art artefacts.

Recently the International Atomic Energy Agency (IAEA) published a book on the use of ionizing radiation for the protection and conservation of cultural heritage objects, entitled "Uses of Ionizing Radiation for Tangible Cultural Heritage Conservation" [3]. This valuable edition, the first of its kind in the area, contains joint contributions by the members of the RCDL. This publication provides the most up-to-date knowledge of radiation technology applied to conservation and consolidation of cultural heritage objects in European member states, and is a valuable source of information for curators, conservators, restorers, art historians,

archaeologists and scientists active in various areas of cultural heritage conservation in museums, libraries, archives, archaeological institutions, historic buildings and conservation workshops. Croatia is one of the initiators of organizing IAEA regional projects on this topic, thanks to the fact that the RBI has been already applying radiation techniques for the preservation of cultural heritage objects for many years. This is one of the reasons why our country has been ranked among the few European countries, such as France, Poland and Romania, where there is experience of using radiation for the protection of cultural heritage objects.

References:

[1] Ražem, D. Twenty years of radiation processing in Croatia. *Radiation Physics and Chemistry,* 71 (2004) 597 - 602.

[2] Katušin-Ražem, B, Ražem, D., Braun, M. Irradiation treatment for the protection and conservation of cultural heritage artefacts in Croatia. *Radiation physics and chemistry* 78 (2009), 729-731.

[3] Uses of Ionizing Radiation for Tangible Cultural Heritage Conservation / Sabharwal, Sunil (ur.).
Vienna: International Atomic Energy Agency, 2017.

S 1.2

OVERVIEW OF THE COOPERATION BETWEEN THE CROATIAN CONSERVATION INSTITUTE AND THE RUĐER BOŠKOVIĆ INSTITUTE

ISKRA KARNIŠ VIDOVIČ

Senior conservator / art historian

Head of Section for Training, Professional Development and International Cooperation

Grškovićeva 23, 10000 Zagreb

The Croatian Conservation Institute and the Ruđer Bošković Institute have been cooperating for many years on various projects. Although the institutes have been cooperating intensely for some time, a crucial moment was when the contract between the Ruđer Bošković Institute and the Ministry of Science, Education and Sports of the Republic of Croatia, on the one hand, and the Croatian Conservation Institute with the Ministry of Culture of the Republic of Croatia, on the other, was signed in 2006. This contract established the cooperation on scientific research of cultural goods and materials from which they were made. This collaboration involved the preparation and realization of joint science research and development research projects, the joint use of equipment, presentation and publication of research results, etc.

A special element of the cooperation between the Croatian Conservation Institute and the Ruđer Bošković Institute is using gamma radiation for conservation and rescue of cultural heritage affected by the damage caused during the war (1991-1995), which continued after the war was over in cases of emergency. Today, conservation and restoration use more and more interdisciplinary research and diagnostics. Research on individual projects, such as the extremely valuable underwater find - a bronze statue of an athlete (the so-called *Apoxyomenos*) from the 2nd or 1st century BC, and education of conservators and conservator-restorers through joint organization of more scientific conferences, seminars and workshops were particularly emphasised.

S 1.3

WARTIME RESCUE OF CULTURAL GOODS USING RADIATION - EXAMPLE OF WARTIME EVACUATION AND PROTECTION OF FURNISHINGS FROM THE CHURCH OF ST. LADISLAUS IN POKUPSKO

BRANKA KATUŠIN-RAŽEM, PHD
Ruđer Bošković Institute
Division for Materials Chemistry
Radiation Chemistry and Dosimetry Laboratory
Bijenička c. 54, 10000 Zagreb
ANĐELKO PEDIŠIĆ, MA
Croatian Conservation Institute
Department for Polychrome Wooden Sculpture
Zmajevac 8, 10000 Zagreb

Background of the study. Wartime conditions, maintenance and preservation without continuity, relocations, and inadequate temporary storage facilities cause major deteriorations of cultural heritage. The war in Croatia (1991-1995) seriously jeopardized Croatia's cultural heritage. During the autumn of 1991, due to war destructions, conservation and restoration institutes began an extensive operation to save cultural heritage. Museum and gallery collections, church, library and archive inventories were stored in the provided, often improvised spaces. Around 5000 objects, mostly wooden polychrome sculptures, paintings and parts of altars, were evacuated. In order to reduce the problem of large-scale biodegradation, the Croatian Conservation Institute decided to apply the radiation method on works of art using the irradiation device at the Ruđer Bošković Institute.

Methodology. The presentation will lay out the general principles and procedure of using radiation for conservation, and years of experience in the field of cultural heritage protection, with a special place that belongs to the rescue of cultural goods threatened by war. A typical example of rescuing cultural heritage from areas affected by war is the evacuation of furnishings from the parish church of St. Ladislaus in Pokupsko, and all subsequent applied protection procedures carried out at the workshops of the Croatian Conservation Institute, including irradiation at the Ruđer Bošković Institute.

Results. Rescue, evacuation and protection of cultural heritage affected by the war in Croatia was a serious challenge for many experts from various fields, as well as volunteers, involved in the protection of cultural goods.

The radiation method was particularly suitable and effective for the prevention of large-scale biological degradation of works of art endangered by the war since a large number of objects needed to be processed in a short period.

The use of the radiation method at the Ruđer Bošković Institute to rescue cultural heritage endangered by the war in Croatia (1991-1995) was recognized by international experts as a particularly successful example of applying this method

S 1.4

ART RESIDENTS – PESTS AND ART

TIJANA-ANNAR TRPUTEC STRČIĆ
Senior conservator - restorer
Croatian Conservation Institute
Grškovićeva 23, 10000 Zagreb

The presentation is an overview of biological damage on works of art that conservators encounter in their practice, particularly on wooden objects such as furniture, sculptures, altars and paintings on wooden supports.

The growth of bacteria, mould and fungi, as well as insect infestations, cause serious and continuous problems in art preservation.

Treatments such as radiation processing help prevent further damage and enable the process of consolidation of material before further conservation-restoration interventions.

S 2A.1

FROM HISTORICAL ARTIFACTS TO TECHNOLOGY: IONIZING RADIATION FOR PRESERVATION

PABLO A.S. VASQUEZ

Nuclear and Energy Research Institute – IPEN/CNEN/SP
Av. Prof. Lineu Prestes, 2242, Cidade Universitaria,
CEP:05508-000, Sao Paulo, SP, Brazil

Keywords: cultural heritage preservation, ionizing irradiation, radiation processing, disinfection,

Degradation have been affecting Brazilian cultural heritage artifacts and archived materials of organic origin. Local weather conditions, as temperature and humidity, added to the action of insects and microorganisms has let in total evidence the biodegradation phenomena. Natural disasters, particularly floods also have affected many collections within the country. In this scenario, ionizing radiation processing arises as an alternative to traditional disinfection methods of cultural heritage artifacts and archived materials. Over the past years, the Nuclear and Energy Research Institute–IPEN through the Multipurpose Gamma Irradiation Facility located inside the University of São Paulo campus has started a strong collaboration program with conservation and preservation institutions and the conservative community to disclose the irradiation technique benefits. Gamma irradiation has several advantages when compared with conventional preservation methods mainly related to the safety, efficiency, reliability, capacity, process time and safe for environment. Several materials have been irradiated for disinfection purposes successfully such as works of art, museum collections artifacts, books, manuscripts, drawings, archive documents, musical instruments, ethnographic objects, archaeological findings, natural history collections among others from various regions of the country. To ensure the safety of the irradiation process on tangible materials, some research is being developed regarding to the possible long term effects or post-effects by studying the kinetics of free radical decay reactions in cellulose based objects using electron paramagnetic resonance. No significant modifications were observed in the irradiated material after the cellulose radical decay time, the material will stay stable for its remaining lifetime. Photographic and cinematographic films were also disinfected by ionizing radiation and characterized using FTIR spectroscopy, UV-Visible spectroscopy and electron microscopy techniques. Results shown that disinfection by ionizing radiation can be successfully achieved and safely applied with no significant changes or modifications of main properties of the constitutive materials of the processed objects.

S 2A.2

CURRENT STATUS OF RADIATION PROCESSING IN SYRIA (CELLULOSE MATERIALS)

Z. AJJI[1], I. OTHMAN[1], A. ALI[2]

[1]Department of Chemistry, Atomic Energy Commission, P. O. Box 6091, Damascus, Syria

[2] Tishreen University, Faculty of Technical Sciences

Cotton fibres were grafted with two monomers using gamma radiation, acrylic acid methyl methacrylate, and also viscose fibres were grafted with acrylonitrile. The influence of different parameters on the grafting yield was investigated as: solvent composition, comonomer composition, and irradiation dose. Some properties were investigated with respect to the grafting yield as optical and mechanical properties. Whiteness, lightness, reflective, and yellowness indexes were determined with respect to the increasing grafting yield. Also tensile strength and strain% of the grafted f fibres were studied.

S 2A.3

THE USE OF GAMMA RADIATION FOR THE TREATMENT OF CULTURAL HERITAGE IN SERBIA

SLOBODAN MASIC, IVICA VUJCIC

University of Belgrade, Vinča Institute of Nuclear Sciences, P.O. Box 522, 11001 Belgrade, Serbia

Background of the study. Serbian folk costume occupies a prominent place in the culture and tradition of the Serbian people. Its role in history is very important as a symbol of ethnic identity, and it is emphasized in visual and aesthetic values. Textile materials of wool, linen, hemp, silk and cotton were mostly used for making folk costumes. These materials can be contaminated with keratinolytic bacteria (B. Mesenthericus, B. subtilis, P. vulgaris), fungi (Trichophyton, Fusarium, Chaetomium, Aspergillus) or insects (Dermestidae, Oecophoridae (brown house moth), Tineidae (cloth moth), Tinea pellionella, T bisselliella Hofmannophila pseudospretella). The use of gamma irradiation in order to decontaminate the textile material of cultural heritage is a well-known technique. The literature describes the radiosensitivity of all known organisms that can contaminate textiles. Different doses are needed for the destruction of each of these microorganisms. So, for example, for the destruction of the insect, a dose of 0.5-2 kGy is required, for fungi 4-10 kGy and for complete decontamination of 5-20 kGy. In order to analyze the effects of gamma radiation on the change in the color of the fabric, the structure and the mechanical properties of the fibers, the patterns of wool, flax, hemp, silk and cotton are irradiated in gamma facility with doses of 1, 2, 3, 5, 7, 10, 15, 20 and 25 kGy. By spectrometric analysis, we examined the color change of undyed samples, as well as samples dyed with natural colors, and unnatural aniline colors. Using the SEM microscopy, a change in the structure of textile materials after exposure to gamma radiation was examined. The mechanical properties of the materials after exposure were tested by mechanical methods of analysis.

The second phase of our activities related to the protection of cultural heritage is the conversation of old wooden objects of the Serbian Orthodox Church. For this purpose, the method of lyophilization and subsequent polymerization by ionizing radiation is used. First, the characteristics of three different monomers (styrene, methyl methacrylate and butyl methacrylate) after polymerization were tested. The solutions of these monomers in methanol were made. We used solutions with concentrations of 30%, 50%, and 70% of monomer. Thereafter, the previously lyophilized wood samples were dipped into these solutions, and after 24 h wood samples were removed from the solution, dried and irradiated. In this way, the solution is polymerized and the wood is permanently protected. Based on the analysis of the polymer loading into the material, the best monomer and the most optimal concentration of the solution were selected. After that, the selected solution is used for treating wooden objects which belong to the Serbian Orthodox Church.

Methodology. The examination of the change in the colors of the fabric after the irradiation were performed with Spectrophotometer Shimadzu UV–Visible UV-2600 (Shimadzu Corporation, Tokyo, Japan) equipped with an integrated sphere (ISR-2600 Plus (for UV-2600)) in the 220 780 nm range and 1 nm step. Microstructural characterization of fiber samples was done using a Mira3 Tescan field emission scanning electron microscope (FE-SEM), operated at 20 keV, at a different magnification in order to analyze the morphology of the samples.

The wood samples were put into lyophilizator for 30 min. After that, the samples were wiped with textile fabrics and put into polyethylene bags and sealed to prevent the impregnated monomer from evaporating. They were then irradiated by a ^{60}Co gamma source at a dose rate of 10 kGy/h. Then, the polymer loading (PL) was calculated according to the following equation:

$$PL\% = \frac{W_{pol} - W_{wood}}{W_{wood}}$$

where W_{Wood} and W_{pol} are the mass of untreated wood and wood with polymer, respectively.
The lyophilization is carried out using the device Freeze dryer , HarvestRight.

Control and measurement of the absorbed radiation dose were performed using the Ethanol-chlorobenzene dosimetry system (ECB).

S 2B.1

GAMMA-IRRADIATION FOR CULTURAL HERITAGE – REDUCTION OF FUNGAL GROWTH ON PAPER MATERIALS

MAJA ŠEGVIĆ KLARIĆ[1], KATARINA MARUŠIĆ[2], LUCIJA SINČIĆ[1], SILVIJA MARIJANOVIĆ[1], IRINA PUCIĆ,[2] ANA BOŽIČEVIĆ,[3] BRANKA MIHALJEVIĆ[2]

[1]Department of Microbiology, Faculty of Pharmacy and Biochemsitry, University of Zagreb, HR-10000 Zagreb, Croatia
[2]Radiation Chemistry and Dosimetry Laboratory, Ruđer Bošković Institute, HR-10000 Zagreb, Croatia
[3]Conservation-restoration of cultural heritage, Academy of Fine Arts, Zagreb, Croatia

Background of the study. A number of cultural heritage (CH) objects e.g. paintings contain paper as base material which is vulnerable to biodeterioration due to fungal growth. Gamma-irradiation has been proposed as one of the physical methods for control of fungal contamination of CH but it can have unwanted side effects on natural and synthetic organic polymers in paper-based material when applied in high and repeated irradiation doses.

Objectives. This study was aimed to assess gamma irradiation dose and dose rate necessary for reduction of fungal contamination to acceptable level on paper. Specific aims were: 1) to determine composition of mycobiota commonly occurring on paper; 2) to assess antifungal effect of irradiation doses (2, 7, 20 and 50 kGy, at dose rates 0.1 and 8,6 Gy/s) against commonly occurring mycobiota; 3) as well as artificially inoculated secondary colonizer *Cladosporium spaherospermum* that can be found on cellulose materials.

Methodology. Paper (Verge 120 g) was cut in squares 3.5 x 3.5 cm (0.15 g) and fungal composition of paper squares was analysed by plate count method. Briefly, to determine the concentration of naturally occurring mycobiota samples were homogenised and serially diluted (up to 10^{-4}) in peptone water and plated onto Malt Extract Agar (MEA). First group of paper squares containing naturally occurring mycobiota were incubated at 25°C and 70% of relative humidity (Rv) for 7 days. The second group of paper squares were sterilised by autoclave (15 min, 121°C, 1.2 Bar), then inoculated with *Cladosporium spaherospermum* at concentration 100 CFU/g and incubated in the same manner. Upon 7 days of incubation naturally occurring mycobiota and Cladosporia concentration in positive control samples was determined as previously described. All other tubes with paper samples containing natural mycobiota or artificially inoculated Cladosporia were irradiated with 60-Co gamma source at RCDL to doses 2, 7, 20 and 50 kGy, and dose rates 0.1 and 8.6 Gy/s. Upon irradiation samples were incubated for 0, 7, 14, 28 and 56 days at 25°C. After each incubation period samples were serially diluted (up to 10^4) and plated onto MEA to determine the number of viable fungi.

Results. *Alternaria* spp., *Aspergillus* spp., *Cladosporium* spp.., *Penicillium* spp. white mycelia and yeasts comprised naturally occurring mycobiota, with initial concentrations of 200 CFU/g. These fungi were inhomogeneously dispersed on paper showing „hot-spot" contamination. After 7 days of incubation at 25°C and 70 of Rv the concentration of paper mycobiota and artificially inoculated Cladosporia was 10 and 100 folds higher, respectively, comparing to their initial level.
Fungicidal effect of gamma radiation on naturally occurring mycobiota was dose and dose rate-dependent. Lower doses 2 and 7 kGy were not effective when applied at 0.1 Gy/s; species of paper natural mycobiota recovered in concentrations 100-2000 CFU/g (Fig.1.). Reduced concentration of white mycelia (40 CFU/g) was recovered on 0^{th} and 14^{th} day upon exposure to 7 kGy at dose rate 8.6 Gy/s. Dose of 2 kGy (8.6 Gy/s) was less effective than 7 kGy but returned concentration of natural mycobiota to the initial level (200 CFU/g). High doses 20 and 50 kGy applied at both dose rates inhibited recovery of the majority of the fungi except yeasts and white mycelia; yeasts were recovered on 14^{th} day (200 CFU/g) and 90 CFU/g of white mycelia was viable on 0^{th} day.

Artificially inoculated Cladosporia were resistant to 2 kGy applied at both dose rates, while doses 7, 20 and 50 kGy were not effective when applied at lower dose rate; upon irradiation Cladosporia recovered in concentration range 10^3-$3x10^4$ CFU/g. When these doses were applied at dose rate 8.6 Gy/s almost completely inhibited recovery of Cladosporia; the only exception was obtained on 14^{th} day after radiation with 20 kGy but concentration was 1000 fold reduced from the initial level (Fig. 2.).

Conclusion. Taken together, fungicidal effect of gamma radiation was dose and dose rate-dependent. Lowest dose of 2 kGy at higher dose rate reduced majority of fungal growth (except Cladosporia) to the initial level that was recorded before incubation in humid conditions. Doses 7, 20, and 50 kGy were effective against mycobiota including Cladosporia, only when applied at higher dose rate. Species of *Cladosporium*, yeasts and white mycelia were the most resistant fungi to gamma-irradiation particularly when doses were applied at 0.1 Gy/s.

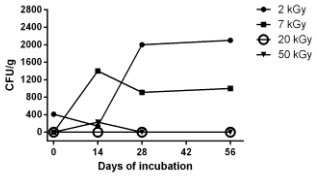


Figure 1. Effect of gamma irradiation doses (0.1 Gy/s) on naturally occurring fungi

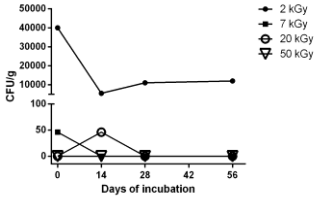


Figure 2. Effect of gamma irradiation doses (8.6 Gy/s) on *Cladosporium sphaerospermum*

Acknowledgement

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S 2B.2

RADIATION EFFECTS ON SOME OF THE MATERIALS CONSTITUTING CH OBJECTS-RECENT RESEARCH OF THE RCDL SCIENTISTS

IRINA PUCIĆ, senior scientific associate

Radiation Chemistry and Dosimetry Laboratory
Division of Materials Chemistry
Ruđer Bošković Institute, Zagreb, Croatia

During more than 25 years of CH treatment at irradiation facility of the Radiation Chemistry and Dosimetry Laboratory objects made of various perishable materials were irradiated. While general guidelines for treatment ensure that there will be no unwanted side effects to the materials of the objects occasionally we are confronted with combination of materials with different response to gamma-irradiation what may particularly be a problem if higher absorbed doses have to be applied for fungal contamination treatment. Other frequently asked questions are how the treatment would affect an already damaged material and whether its post-irradiation aging would be influenced. Since we strive to avoid any irreversible side effects to CH objects that prompted us to initiate several studies. Additionally we compare sensitivity of various experimental methods to radiation induced changes and assess significance of detected effects if any.

Nacre or mother-of-pearl, a is a common ornamenting material on CH objects and in most cases it cannot be removed prior to irradiation. Nacre is a natural biocomposite based on crystalline calcium carbonate. Natural nacre colors are white, yellowish or gray. We studied the impact of gamma-radiation on optical properties of two nacre types obtained from the Museum of Arts and Crafts, Zagreb. One was white and the other yellowish. Both were irradiated under the same conditions to different absorbed doses. Colorimetry in CIE Lab space revealed that at high doses the lightness of both nacres shifted to darker grey hues while the color component's (red, green, yellow and blue) behavior depended on the nacre type. Observable changes in color of the studied nacres occurred at doses much above the dose range needed for radiation treatment of CH objects [1]. To assess the cause of color change UV-Vis reflectance spectra and thermoluminescence glow curves were analyzed. UV-Vis spectra of samples irradiated to high doses revealed carbonate radical anion absorption as a possible color center. TL glow curves of non-irradiated nacres were significantly different. TL response of yellow nacre to irradiation was anomalous, its signal did not increase with dose indicating that it was previously heated to enhance its color. The TL response of white nacre to irradiation was more regular with some changes in the shape of spectra at the doses over 6 kGy. In white nacre glow curves indicated presence Mn^{2+} and formation of several defect types on irradiation.

The finding of heavily damaged historic silks from 17th century prompted the study of possible unwanted effects of fungal decontamination by gamma-irradiation. Contemporary silk was used as a model and a part of the samples was artificially aged. Some of the unaged and aged samples were irradiated to 6 kGy and other to a much higher dose of 120 kGy to identify radiation-specific damage, if any. To achieve detectable damage selected irradiated and non-irradiated model samples were subjected to further artificial aging. None of the assessment methods used (ATR-FTIR, SEM thermal analysis) revealed any radiation-specific change. Provided that the conformations of fibroin, protein that constitutes slik fiber, are identified and analyzed separately, FTIR is the method of choice for monitoring the effects caused by any treatment of silk. An increase in the amide I/II absorption intensity ratio is a sensitive though ambiguous indicator of silk degradation. Transformation of more stable beta-sheet to alpha/random coil fibroin conformation is a definite proof of degradation. It occurred exclusively on artificial aging of model silks and was accompanied by pronounced morphology changes confirming the role of conformation on silk stability. In non-treated historic silks

the fraction of more stable beta-sheet conformation was unexpectedly high as was the iron content that likely protected silk structure. Since irradiation produced insignificant and likely partially reversible effects radiation treatment of silk textile is deemed safe beyond the absorbed dose proposed as an upper limit for fungal decontamination, 8 ± 2 kGy. [2]

Further research focuses on how interactions of chosen components affect overall radiation sensitivity of model objects, particularly in absorbed dose range needed for treatment of fungal contamination. Preliminary studies on selected dyes in combination with different grounding materials gave confusing results. The effect of irradiation treatment on paper and canvas used in painting treated with common coatings is ongoing.

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S 2B.3

APPLICATION OF NUCLEAR TECHNIQUES FOR CULTURAL HERITAGE IN UKRAINE: PROBLEMS AND PERSPECTIVES

OLEKSANDR BUHAY

Institute of Applied Physics NAS of Ukraine, Sumy, Ukraine

Preservation and multiplication of cultural heritage belong to priority areas of the state policy in culture sphere. According to the ratified international conventions, protection of cultural heritage is an international-legal responsibility of our country to world community.

Many of the cultural heritage objects in Ukraine requires scientifically correct characterization preservation and restoration, which demands the consolidation of efforts from the Ministry of Education and Science of Ukraine, the Ministry of Culture of Ukraine and the National Academy of Sciences of Ukraine. According to information gathered within the IAEA technical cooperation, near 14 million museum objects of the state part of the Museum Fund of Ukraine are kept in museums of Ukraine, and their number is being annually increased by 200 thousand due to archaeological excavations. Number of immovable objects of cultural heritage (pieces of architecture) is more than 120 thousand. Advanced experience shows that the application of nuclear physics methods and techniques is an effective means for preservation, characterization and restoration of objects of cultural heritage. In Ukraine, however, there is no access to modern techniques because of insufficient funding and sometimes of lack of information in the end-users involved in attribution, preservation and restoration. All this leads to the fact that the opportunities available in our country are not used to its full.

In some cases, the absence or non-use of nuclear techniques makes it impossible to implement necessary conservation measures, and the state loses its non-reproducible cultural heritage. Sometimes the experts have to address to foreign laboratories because the facilities available in Ukraine that could be used for solving the tasks of monument protection require slight upgrade. All this involves budget funds which could be spent on this modernization and could considerably reduce the price of such tasks fulfillment.

The problem of disinsection of wooden sculptures by Pinzel may serve as an example. There were also problems with selection and realization of approaches for conservation of large archeological wooden objects of the the Kievan Rus era which have recently been excavated on Poshtova Square in Kyiv. Only about 2 thousand objects per year are subject to the preservation procedure in Ukraine.

Institute of Applied Physics of Ukraine (IAP NAS of Ukraine) takes an active part in characterization of these objects with non-destructive methods, that is very crucial for the valuable artifacts. Institute works closely with the archeologists of the Berlin University, the Warsaw University, the German-Slavonic Expedition of the V. N. Karazin Kharkiv National University and Institute of Archeology of Naitonal Academy of Sciences of Ukraine. There is also an established collaboration with the National research restoration center of Ukraine. However, it cannot make things better. In order to solve the problem, it is advisable to develop a conception on implementation of modern nuclear and physical techniques for attribution, dating, restoration and preservation of cultural heritage in Ukraine and a schedule of measures to realize it. Together with experts from the Ministry of Culture of Ukraine and the Ministry of Education and Science of Ukraine we have developed the concept projects and the schedule of measures of the concept implementation. This concept will allow raising additional non-budgetary financing.

S 3.1

CHARACTERIZATION OF RADIATION PROCESSING EFFECTS IN CULTURAL HERITAGE APPLICATIONS

STEFANIA BACCARO, ALESSIA CEMMI, ILARIA DI SARCINA

ENEA – FSN Department for Fusion and Nuclear Safety Technologies
CASACCIA R.C., 301, Via Anguillarese - 00123 Rome (Italy)

Background of the study. The present paper is related to the activities performed at the ENEA Calliope gamma irradiation facility (Casaccia R.C., Rome, Italy- Fig.1) in the framework of the IAEA Coordinated Research Project 'F23032'- Research Agreement No. 18922/R0. In order to increase knowledge on the advantages and limitations of nuclear technology for Cultural Heritage applications, it is very important to define suitable irradiation conditions (in terms of irradiation dose, dose rate and environmental atmosphere) and to evaluate some irreversible physical-chemical modification induced by ionizing radiation on treated materials, namely "side-effects". Furthermore, several information about the prediction of paper behavior and the synergic radiation-temperature effect can be achieved by accelerated ageing process, performed at various temperature, humidity and environmental conditions.

Methodology. Radiation and temperature effects as well as side-effects on irradiated paper were investigated by using chemical and spectroscopic techniques (Viscosity, PL, FTIR, ESR).

Results. The results obtained at the Calliope facility were summarized as in the following [1, 2]:

- *microbiological investigations to study the effect of dose rate and environmental irradiation conditions on typical bio-deteriogens present on archived materials:* experimental results provide confirmation that chewing insects are potentially harmful bio-deterioration agents due to their ability to feed on papery materials. The different vulnerability of irradiated papers vary according to the applied absorbed dose, dose rate and environmental atmosphere. The doses used in our experiments (less than 5 kGy), enough for disinfesting and considerably reducing microbial load, do not cause appreciable negative effects since all erosion percentages are negligible and extremely acceptable.

- *study of the instantaneous and post-irradiation effect on paper irradiated by gamma radiation using chemical and spectroscopic techniques:* the evaluation of the gamma induced side-effects and on the accelerating ageing effects on cellulose-based materials indicates that at low doses no differences in term of cellulose oxidation are shown as a function of the irradiation atmosphere, while with the increase of the absorbed dose (10 kGy) the oxidation in air becomes more severe, as confirmed by the decrease of the viscosity (proportional to the cellulose polymerization degree). No significant dose rate effect was evident. The investigation of the paramagnetic species induced by radiation indicates that the irradiation process is more effective if performed under inert atmosphere and the free radicals produced are also more stable during time.

Figure 1. *Left*: view of the Calliope irradiation cell (as seen through the yellow lead-glass window of the Control Room,). *Right*: dosimetric set-ups and lead walls for tests at lower dose rates.

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S 3.2

SOME SIDE-EFFECTS OF GAMMA-IRRADIATION DISINFESTATION ON HIGHLY CONTAMINATED LEATHERS AND LIBRARIAN MATERIALS

PETYA KOVACHEVA[1)], NELI BOSHNAKOVA[2)]

[1]University of Sofia "St. Kliment Ohridski", Faculty of Chemistry and Pharmacy, Sofia, Bulgaria
[2] BULGAMMA, Sopharma JSC, Sofia, Bulgaria

Background of the study. Gamma-irradiation is recognized to be among the most efficient methods for preservation of biodeteriorated artefacts, due to its biocide effect with high effectiveness, reliabilty and lack of toxic residues in the treated materials. Although there are often hesitations on its use due to the possible degradation effects on the irradiated materials, especially at doses, aimed to inactivate bacterial contaminations. This presentation describes side-effects of gamma-irradiation on leather and paper materials with 20 kGy and 25 kGy, applied when highly contaminated samples are to be preserved.

Methodology. Calf leather, calf suede and pig skin patterns were selected and analysed by: SEM, EPR, DSC, FTIR and TG/DTG before and after the gamma-irradiation treatment with 25 kGy at two different dose rates. Long-term side-effects on scientific books and journals were studied by EPR, DSC and TG/DTG, 4.5 years after their gamma-irradiation with 20 kGy. The selected paper samples were taken from six different issues, published in Germany, Russia and USA in the period from 1896 to 1962 years.

The irradiation of the leather and paper materials was performed in the gamma-irradiation facility BULGAMMA based on JS-850 ^{60}Co type gamma irradiator at Sopharma, Bulgaria. The absorbed dose distributions were measured with Ethanol Chlorobenzene routing dosimeters.

Results. No influence on the morphology and the molecular structure of the three leather samples was detected, as revealed by the SEM and FTIR analysis. Higher side-effects were noticed in the leathers, irradiated at low dose rate, as compared to those, irradiated at standard dose rate. Increase of the spin concentration after irradiation with 25 kGy absorbed dose in the calf leather and pig skin samples at low dose rate was registered. No change of the spin concentration was found in the pig skin samples, irradiated at standard dose rate with 25 kGy. The DSC analysis showed that gamma-irradiation of calf leather with 25 kGy led to increase of the enthalpy of the collagen softening (melting) with 26 % at low dose range and 31 % at standard dose rate. The changes of the enthalpy of this process after irradiation of calf suede and pig skin were found to be negligible at both dose rates. TG/DTG analysis showed 5 to 7 % decrease of the weight loss in the calf leather and calf suede as a result of gamma irradiation with 25 kGy at low dose rate. Slight increase of the weight loss in the calf suede and in the pig skin as a result of gamma-irradiation with 25 kGy at standard dose rate was determined. The long-term side-effects on the gamma-irradiated librarian books were found to be highest in the oldest or in the most contaminated book.

Acknowledgements. The financial support of the International Atomic Energy Agency, Coordinated Research Project F23032, Research Contract № 20567 "Studying Side-Effects of Gamma Irradiation Treatment for Disinfestation of Cultural Heritage Artefacts" is gratefully acknowledged.

S 3.3

APPLICATION OF RADIATION SURFACE MODIFICATION TECHNIQUES FOR THE PRESERVATION OF ARCHIVED MATERIALS IN SRI LANKA

K. R. C. DE SILVA[1]*, A. K. RATNAYAKE[1], S. Y. RATNAYAKE[1], C. D. R. PATHIRANA[1], H. A. A. N. ALWIS[1], M. KATUGAMPOLA[2], A. H. M. H. ABAYARATHNA[2], S. D. M. CHINTHAKA[3]

[1]Sri Lanka Atomic Energy Board
[2]University of Kelaniya
[3]University of Sri Jayewardenepura
[1]No. 60/460, Baseline Road, Orugodawatta, Wellampitiya, Sri Lanka.
[2]Dalugama, Kelaniya 11600, Sri Lanka.
[3]Gangodawila, Nugegoda, Sri Lanka.

Background of the study

Since Sri Lanka's civilized history had been dated back to centuries before Christ, the country is abundant with broad range of cultural heritage artefacts from statues to pebbles. Majority of the history and the exquisite knowledge on religion, traditional medicine, astrology, architecture and technology was written on ola-leaf manuscripts (writings on palm leaves), which had been susceptible to deterioration by microbial attacks and environmental conditions over centuries. Along with the ola-leaf manuscripts, ancient paintings, fabrics and wooden artefacts had been experienced similar circumstances and there is growing concern for development of novel conservation techniques to preserve these artefacts. The current study is focussed on the development of radiation curable surface coating for such artefacts, which could mitigate the effects of microbes, humidity, temperature and other environmental phenomenon. In addition, transparency and the flexibility of the coating, enhancement of dimensional stability and water repellence are the other properties of interest. Monomers of methyl methacrylate and styrene and polymers of polystyrene and alkyd resin, were subjected to radiation induced polymerization, cross-linking and grafting by Co-60 gamma radiation to achieve the desired properties, as available in the published literature for conservation of cellulosic (paper and wooden) artefacts.

Methodology

Two independent solutions containing 2% polystyrene in styrene and methyl methacrylate (MMA) monomers and poly ethylene glycol – 400 (1%) and industrial microbicide concentrate (0.3%) as additives, were applied on paper based material (3 – 6 decades old) by immersion and spraying methods and exposed to gamma radiation dose of 15 kGy at a dose rate of approximately 0.33 kGy/hr. In a separate experiment, paper based materials were immersed in solutions of alkyd resin (with variable concentrations from 5% to 40%) in styrene and methyl methacrylate monomers containing same additives, and were subjected to similar irradiation treatment. Irradiated samples were evaluated for their water repellence properties in both experiments.

Results

All samples exhibited a significant increase in weight per unit area, which is the evidence for the radiation induced polymerization, cross-linking and grafting during the aforementioned experiments. In the first experiment, highest weight increase per unit area (7 – 15%) was recorded for the samples treated with 2% polystyrene in methyl methacrylate by immersion method and in all cases, higher weight increases were observed for immersed samples than their sprayed counterparts. However no significant improvement in water repellence properties was observed for any samples treated with 2% polystyrene. Weight increase per unit area progressively increased with the concentration for paper samples immersed in alkyd resin solutions as indicated in the figure 1. Alteration to the appearance of the treated paper samples (imprinting of the text from the opposite page) was observed for higher alkyd resin concentrations (30% and 40%) in both monomer solutions. Also, samples treated with alkyd resin concentrations of 20% and higher (in both monomers), exhibited significant improvement in water repellence properties, in contrast with their low concentration counterparts.

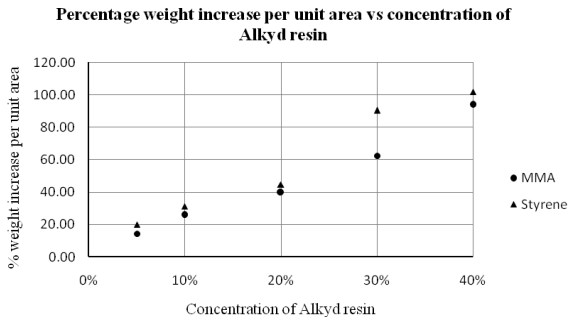

Figure 1: Variation of percentage weight increase per unit area with alkyd resin concentration in methyl methacrylate and styrene monomer solutions

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S 4A.1

CAPABILITIES OF CNEA FOR THE PRESERVATION AND STUDY OF THE CULTURAL HERITAGE

CELINA I. HORAK

Radiation Technology and Application Management,
National Atomic Energy Commission
Argentina

In the National Atomic Energy Commission of Argentina, there is a network of laboratories that are working in the application of nuclear or related techniques, to solve specific needs for the maintenance and valorization of cultural heritage. Museums, archaeological sites, Institutions possessing cultural assets, Libraries, Historical archives, are some of the users of these techniques, either for the characterization, preservation and authentication of cultural heritage and other valuable goods.

Most of the laboratories has been working on these fields for many years. They are distributed along the three Atomic Centers of CNEA and have the following techniques that allow:

- Characterization and dating of objects from the analysis of the composition and type of materials: diagnostic techniques for images; Analysis by neutron activation; X-ray fluorescence; X-ray diffraction; Raman microscopy; Micro-Infrared Spectroscopy by Fourier Transform (micro-FT-IR)
- Preservation through Gamma Radiation Treatment for arthropod or fungi disinfestations of historical objects or cultural value, furniture, and other archaeological items; Restoration and enhancement of bibliographic material.

Regarding to the preservation of cultural heritage artifacts through the application of gamma irradiation treatment for insect eradication and disinfection, this is conducted as an interdisciplinary approach, determining the minimum and maximum irradiation dose depending on the artifact and the objective, followed by the dose mapping in the irradiation facility, to assure the determined dose range. Along the last decades, furniture from the XIX century, a Christ statue, pictures, embalmed animals, documentary files and books were evaluated and treated by irradiation, obtaining satisfactory results and a good dissemination of the knowledge on this technique.

S 4A.2

USE OF RADIATION TECHNOLOGY FOR PRESERVATION OF SOME EGYPTIAN CULTURAL HERITAGE ARTEFACTS

H.A. ABD EL-REHIM

National Centre for Radiation Research and Technology (NCRRT Address
Atomic Energy Authority, Cairo,
Egypt

Background of the study. An important part of the cultural heritage inventory is preserved in objects made of bio-degradable materials, including wood, leather, textile, and paper. To lose them means to lose a part of humankind's identity. Biodegradation is due to the insects and microorganisms like bacteria or fungi. For them natural polymers are nutrients. Different fighting methods against bio-deterioration have been established and used, included radiation technique.

Methodology. Reactivation of polymers method was chosen as a practical way of implementation for the synthesis of the polymer nano-composite Silkscreen supports have been used as an incipient support filled with the used polymer dissolved in solvent dried at room temperature. Then, the shroud was placed facedown. The previously treated silkscreen support was laid over them back of the shroud, making sure that the warp is correctly aligned. Paper pulp poultices of diluted acetic acid was used to reactivate the synthesized polymer so as to the adhering force be limited between the support and the behind surface of the shroud, thus, there is no penetration of the adhesive into the upper surface of the ancient linen. The method gave excellent results without suffering any penetration of the polymer onto the fabric and thus achieving a successful consolidation process.

Results. Research on modified consolidant for ancient artifacts containing cellulose compound such as wood, textiles and manuscripts has been investigating. The work aims to consider a rescue for ancient carbonized materials such as papyri and textile wrappings as it could retain their lost cellulosic formation and increase their durability to survive using organic materials prepared by radiation. Enhancement of mechanical properties and radiation resistance of some natural materials using Graphene nano-sheet was investigated. Using Graphene oxide, mechanical properties of Cellulosic materials like Papyrus were improved as well as their radiation resistance.

Radiation synthesized of polymer composite with, anti-microbial properties was used for Consolidation of the 18th Dynasty Funeral Shroud.The ancient linen shroud dated to Hatnofer (Senenmut's -chief minister at Queen Hatshepsut's era- mother) about 1850 B.C. from plain texture linen(1/1) , having carbonic and metallic inked inscription from Book of the Dead. Chitosan nano-composite; as an excellent, stable non-staining adhering polymer can be safely used in consolidation of ancient Egyptian linen textiles.

S 4A.3

Application of irradiation technology for conservation of cultural heritages in Korea: Control of fungi and insect in wood cultural heritages.

MINCHUL YOON, HAE-JUN PARK

Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, Jeongeup 580-185, Republic of Korea

Background of the study. We investigated the use of radiation techniques for development of alternative technologies in accordance with regulations of chemicals fumigants and ensure the practical applicability and R&D projects for organic cultural heritage for long-term conservation. Methyl bromide was previously used as a fumigation agent for controlling the biodegradation of organic cultural heritages. However, it was banned in 1997 based on the Montreal Protocol because of its toxicity to humans and the environment. It cannot use the Methyl bromide from 2018 in Korea. For disinfection of decay fungi and insects, irradiation technology has been applied for preservation of cultural heritages in the world including the France, Croatia, Czech, UK, Italia, and Brazil. Korea has high level radiation technology, human resource, and instrumental infra in radiation industry. Our investigated results show that radiation treatment of Korean traditional cultural heritages is extremely efficient and could be used to preserve organic cultural heritages from being damaged by decay fungi and insects. We expected that radiation techniques contribute reduction in administrative costs through advanced processing technology and expansion of retention period of cultural property. Methyl bromide was previously used as a fumigation agent for controlling the biodegradation of organic cultural heritages. Gamma rays are electromagnetic waves radiated from radio-active isotopes like cobalt-60 and cesium-137, and have a high penetration power. Although irradiation is effective for destroying microorganisms and insects inside the target object, the irradiation dose should be applied in accordance with the object's geometric shape and penetration depth. If the absorbed dose is not sufficient, the target cannot be completely disinfected. Therefore, calculating the optimal irradiation dose is necessary for field application. In this study, it has been investigated the disinfection of Korean cultural heritages by gamma irradiation.

Methodology. The samples were irradiated in a cobalt-60 irradiator (point source, AECL, IR-79, Nordion, Canada) with various absorbed doses (from 0.2 to 4 kGy). Dosimetry was performed using 5 mm diameter alanine dosimeters (Bruker Instruments, Rheinstetten, Germany).

Results. In these researches, 25 species of wood decay fungi were inactivated by less than 5 kGy gamma irradiation, timber pests were fully inactivated by less than 1 kGy gamma irradiation. In addition, radiation stability of major components of Korean cultural heritages against gamma radiation was evaluated. Moreover, this study was conducted to investigate the effect of gamma radiation on cell wall degradation, cellulose crystallinity, and flexural strength of *Pinus densiflrora*, *Zelkova serrenata*, and *Paulownia tomentosa*. Fungal contamination was identified on three traditional Korean agricultural tools, Hongdukkae, Holtae, and Gimjeotgae which had been stored in a museum. Nine primary species were identified from these items: *Bjerkandera adusta*, *Dothideomycetes* sp., *Penicillium* sp., *Cladosporium tenuissimum*, *Aspergillus versicolor*, *Penicillium* sp., *Entrophospora* sp., *Aspergillus sydowii*, and *Corynascus sepedonium*. By the gamma radiation at the dose up to 100 kGy, the cell wall degradation was not detected with scanning electron microscope (SEM) observation from all samples, and the flexural strength was not significantly changed. Cellulose crystallinity was neither changed by the gamma irradiation. These results confirmed that radiation treatment of Korean traditional cultural heritages is extremely efficient and could be used to preserve organic cultural heritages from being damaged by decay fungi and insects.

This technical results reported (1)2013 International Symposium on Conservation of Cultural Heritage in East Asia

S 4B.1

ELECTRON BEAM FOR PRESERVATION OF BIODETERIORATED CULTURAL HERITAGE PAPER-BASED OBJECTS

DAGMARA CHMIELEWSKA-ŚMIETANKO[1], URSZULA GRYCZKA[1], WOJCIECH MIGDAŁ[1], JAROSŁAW SADŁO[1], KAMIL KOPEĆ[2]

[1] Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland, e-mail:d.chmielewska@ichtj.waw.pl

[2] Faculty of Chemical and Process Engineering, Warsaw University of Technology, Ludwika Waryńskiego 1, 00-645 Warsaw, Poland

Background of the study. Library and archival collections can be affected by bioburden because of improper storage conditions or accidents such as floods. Therefore, libraries, museums and archives are still looking for optimum decontamination methods because the commonly used EtO gas fumigation has many disadvantages. EtO fumigation is a time-consuming process and the possibility of toxic residues in disinfected material after the decontamination results in the fact that more and more countries to limit its use. Moreover, resistance of some microorganisms (e. g. Pyronema domesticum) to ethylene oxide has been observed.

A promising alternative to this technique can be ionizing radiation. Radiation technologies are successfully applied to the sterilization of medical devices, to the hygienization of food products, to the synthesis and modification of polymers and in the protection of the environment.

Mostly gamma irradiation has already been applied in the treatment of cultural heritage (CH) objects. However, the possibility of application pathogenic microorganisms as biological weapons has predetermined experimental testing of electron beam (EB) technology for commercial sterilization of mail by radiation methods. Electron beam irradiation can be effectively applied for decontamination of biodeteriorated archives as well as for preventive conservation of large volumes of books in short time. Electron beam processing is a much faster process than treatment with gamma rays what can limit post oxidation related effects of paper degradation.

To gain public acceptance for radiation methods in large-scale applications many analytical techniques must be used in order to determine possible changes of mechanical, chemical and physical properties of treated objects. Complex study of material properties before and after radiation decontamination should ensure degradation monitoring and process validation. Moreover, paper is complex material which properties depends on the manufacturing process, fillers present and further paper application. Because of paper complexity different methods should be used in order to carry out investigation of mechanism of paper degradation. Some of the research methods appears very suitable for this aim others don't provide information we are looking for.

Advanced study on the influence of electron beam irradiation on the properties of different paper-based object and elaboration of irradiation procedures suitable for their treatment will help to develop and to implemet this technology.

Methodology. Three different kinds of paper (Whatman CHR1, office paper and newsprint paper), which varied in their manufacture process and composition were investigated. Samples of different papers were irradiated with electron beam using 10 MeV, 10 kW linear electron accelerator ''Elektronika''. Sheets of each type of paper enclosed in envelopes were treated with doses of 0.4, 1, 2, 5, 10 and 25 kGy. Control (non-irradiated) samples of each paper were also prepared for comparative studies. Delivered doses were confirmed using Gammachrome Harwell dosimeter for lower doses, and the calorimetric method involving graphite calorimeters was applied to measure absorbed radiation doses in a range from 5 to 25 kGy.

Different methods were applied for the investigation of optical, mechanical, thermal and chemical properties of the samples before and after irradiation. The morphology of samples was evaluated using scanning electron microscopy (SEM) coupled with

Energy-dispersive X-ray spectroscopy (EDX) that enabled to determine paper samples composition. The influence of electron beam irradiation on cellulose was observed by pH measurements of paper, thermogravimetric analysis (TGA) and electron paramagnetic resonance (EPR). Paper colour, the most prone to changes paper parameter were studied with colour spectrophotometer. Moreover mechanical properties of paper were examined before and after irradiation as well. Electron beam radiation inactivation patterns of different microorganisms present in different paper materials were studied as well.
Changes in all samples properties were determined according to the relevant ISO and TAPPI standards. Moreover, changes of the selected parameters of the samples in time after irradiation have being monitored in order to evaluate post-irradiation effect.

Results. SEM analysis revealed difference in the structure of the different papers samples resulted from the different manufacturing methods. Additionally, elemental analysis of the samples gave information on different fillers and residues present in the different papers. Measurements of tensile strength in cross machine direction (CD) and in machine direction (MD) for different kind of paper EB irradiated with different doses showed that changes of tensile strength of paper samples under ionizing radiation are not significant. Microbiological investigation confirmed that dose of 5 kGy completely eliminate all studied kinds of bacteria (gram-positive and gram-negative) as well as fungi (fig.1) in Whatman CHR 1 paper, newsprint paper and office paper. Optical parameters for all studied papers are stable for materials irradiated with doses not higher than 5 kGy, however colour coordinates are still changing with time after irradiation and the effect is being evaluated. Investigation of optical parameters of the paper after irradiation confirmed that coordinate b* is the optical parameter the most sensitive to electron beam irradiation, what means that paper samples irradiated with high doses became more yellowish.

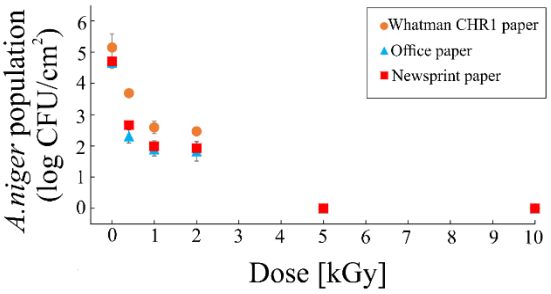

Fig. 1. *A. niger* population on the different kinds of paper as a function of EB radiation dose.

The control samples and the irradiated samples show similar thermal stability in air on heating.
The unirradiated Whatman and office papers samples showed no radicals. All irradiated samples have shown the specific spectrum of irradiated cellulose. The quantity of radicals induced by irradiation has increased with the dose, however gradual decrease of radicals intensity is observed in time. The depletion of trapped free radicals showed a stabilization after 4 weeks after EB irradiation. Significant pH change is visible only for office paper irradiated with the highest applied dose. Investigation of changes of the colour parameters of the different papers in time after irradiation revealed the different colour coordinates change in different way in time, what is connected with different composition of the samples and presence of the different fillers.
To sum up the results, taking into account even high levels of the microbiological contamination (in the order of 10^5 CFU/cm^2) of paper-based objects electron beam irradiation with doses of 5 kGy ensures elimination of harmful microorganisms and simultaneously prevents paper materials degradation.

S 4B.2

DEVELOPING OF RADIATION TREATMENT METHODOLOGIES FOR PRESERVATION OF TUNISIAN CULTURAL HERITAGE: *APPLICATION IN THE PRESERVATION OF WOMEN'S CEREMONIAL DRESS IN NOBLE TEXTILE.*

[1]ARBI MEJRI, [3]SONIA MEJRI, [1]JALEL CHATTI, [2]ZIED TRABELSI,

[1]High Dose Dosimetry Laboratory . National Center for Nuclear Sciences and Technologies. Sidi Thabet, 2020 Ariana, Tunisia.

[2]Radiotreatment Laboratory. National Center for Nuclear Sciences and Technologies. Sidi Thabet, 2020 Ariana, Tunisia.

[3]Laboratory of Biotechnology and Nuclear techniques, National Centre for Technology and Nuclear Sciences. Sidi Thabet, 2020 Tunis.National Center for Nuclear Sciences and Technologies. Sidi Thabet, 2020 Ariana, Tunisia.

Background of the study. The cultural heritage is a unique and irreplaceable witness of our past. Despite its moral and material value, our heritage is unfortunately exposed to environmental factors such as UV light, Humidity, moisture, insects and bacteria, which accelerate the aging phenomena of our cultural heritage, and in some cases cause deterioration of the object. In recent years conservators have begun to recognize that preventive conservation is important as well as curative conservation. Conservation treatments may play a greet role against the acceleration of deterioration phenomena of museum artefacts object.

In this paper we illustrate the use of Gamma irradiation technology to assist in the conservation of Tunisian textile cultural heritage artefacts. In particular, the paper will describe the gamma irradiation dose effects on textile artefacts during decontamination or desensitization process. Three textile samples were selected from familial patrimonial objects and treated with different gamma irradiation doses (0.5 to 7 kGy). A mechanical, Colorimetric and microbiological characterization of the artefacts were done. The results showed that all treated samples are decontaminated after irradiation at 7 kGy dose and showed progressive losses in tensile strength with dose increasing.

Microbiological results show that the survival rate of bacteria and fungi was significantly reduced function of the dose increase compared to untreated samples. Results obtained by colorimetric test show a small change hardly discernible to the naked eye in the color properties of sample I after irradiation at 7kGy.

Thus, Gamma irradiation technique with appropriate dose can be an effective method in the field of conservation of artefacts objects, and it do not promote meaningful alterations on the evaluated properties.

Keywords: Textile Artefacts, Gamma radiation, Color changes, mechanical behavior.

Methodology

1. Description of textile artefacts studied

Women's outfits in noble textile, which belong to a family patrimony, are used as part of this research work. The choice of outfit is justified by the fact that is not admissible scarify objects from national heritage. The outfits selected have undergone for a long time (5-70 years), storage conditions (humidity, temperature, and insects) more severe than the conditions of storage of the Artifacts objects in the museums or the appropriate storage rooms. This may help us later in assessing the effectiveness of gamma radiation treatments of textile-based artifacts. A Sept Textile samples were cut into 120*2 mm (length*width) warp test specimens. The warp strips were produced by raveling away yarns on each side forming 15 mm wide strips with a 2.5 mm fringe down each side. Five samples were used for each test.

Figure 1: *Photographic image of the three studied artifacts models.*

Table 1: *Description of the artifacts and their physical state*

Object	**description**
Samples I: Towel and blouse, model 1940-1950	Sate: Relatively degraded. Composition : Silk and pearls Condition of storage: HR 70-90%, T: 15-40°C Age: 50-60 years
Samples II: Towel blouse, model 1940-1950	Sate: Extremely degraded, discolored and some tears. NB : Towel is wasted Composition : Cotton and Silk Condition of storage: HR 70-90%, T: 15-40°C Age: 50-60 years
Samples III: Dress of festivity, model 1960	Sate: Relatively degraded. Composition : Cotton and Silk Condition of storage: HR 70-90%, T: 15-40°C

2. Irradiation conditions

The textile samples were irradiated at 0.5; 1; 3 and 7 kGy under room conditions (60-70 HR, 23°C) using Tunisian Gamma irradiation Facility at a dose rate of 13, 48 Gy/min (12-04-2017).

Figure 2 *Gamma Irradiation conditions of the three studied artifacts models.*

3. Microbiological analyses

Total aerobic, yeast and mould colony forming units (CFU) were determined by standard spread plate methodology using plate count agar (PCA) and Sabouraud. PCA plates were incubated at 30°C for 48h and Sabouraud plates were incubated at 25°C for 3-5 days.

Results.

1 Characterization of the artefacts

In order to understand the effect of gamma irradiation doses origin of the differences in the susceptibility to degradation of the samples, a number of characterisation tests were performed on each of the artefacts model samples (Model I, Model II and Model III) , these included: Colour and Mechanical proprieties degradation. The aerobic bacterial population decrease against irradiation dose was studied to allow comparison between the samples and to help in the identification of the appropriate irradiation procedure for each Model.

1.1. Color properties

The color intensity ΔE (color difference between the non-irradiated and irradiated) was calculated and are illustrated in Figure 3 as an irradiation dose function. The figure shows that ΔE increased with dose increasing, and accompanied by a significant augmentation of yellow color components (+b*). This indicates that Gamma irradiation dose can induce color variation the textile artifact sample. These color changes can be

attributed to the trapping of the excited free radicals formed by ionization radiation in the irradiated material.

The results represented in figure 3 show a noticeable color change in samples treated with gamma irradiation as most of the treated samples became darker than untreated ones. The totalities of the samples treated with the highest dose (7 kGy) have a significant color changes.

The degree of coloration of textile samples treated and untreated with gamma irradiation was estimated as a variation in optical density at a corresponding wavelength, where the absorbance is measured. The results suggest that the degree of discoloration (%) is the highest at the lowest dose 0.5 kGy.

Abutalib MM (2015) [19] showed that gamma irradiation of polycarbonate was accompanied by a net increase in the darkness of the samples.

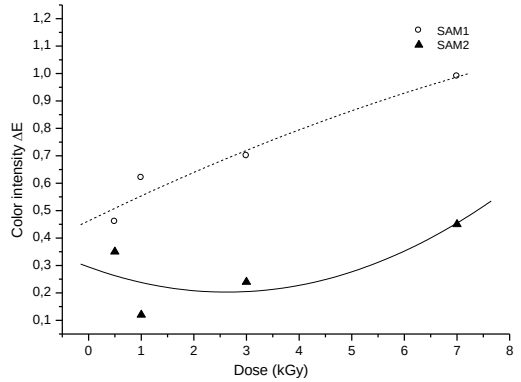

Figure 3*: Curve of the variation of the color intensity ΔE with the gamma irradiation dose For Model I and II)*

1.2. Tensile strength properties

Maintenance of mechanical integrity and achievement of decontamination are both important when choosing the irradiation preservation procedure for artefacts.

Tensile strength and elongation of untreated and treated samples before and after being aged by different doses were measured. The percentage losses in tensile strength and elongation compared with untreated un-aged samples are presented in figure 4 and 5 (Model I). The results of initial characterization show that the treatments increased the tensile strength and elongation of samples. The effect of gamma irradiation on the mechanical properties of textile shows a dose dependent in studied samples. The same results are observed in case of Model II and III.

As illustrated in Figure 4 and 5 the Broking force associated with strength at break decrease with the increasing of irradiation. The result showed a significant decrease in mechanical performance and noticeable changes in appearance color of the parts with absorbed dose of 3 kGy and higher. However, for dosages below 3 kGy, samples showed no significant decrease in mechanical performance or change in appearance.

The results show that after gamma irradiation ageing has a significant role in degradation rate of tensile properties for either low dose treated textile samples or those treated with high different doses. This finding is similar to the results of studies on other polymers which suggest that polymers accelerate the deterioration by light [20]. This may be due to the nature of the different polymers types which were used in that evaluation.

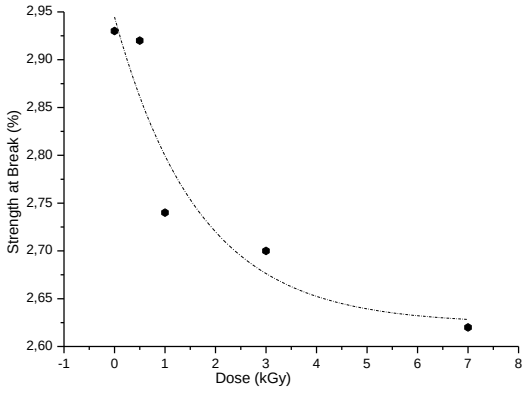

Figure 4: *Strength on brook function of dose variation*

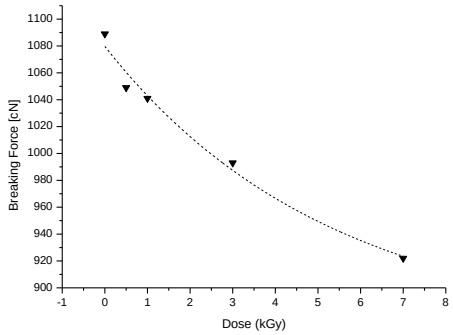

Figure 5: *Brooking force function of dose variation*

1.3. Microbiological quality

The microbiological quality of irradiated and un-irradiated textile artefacts was assessed by counting the number of total aerobic mesophilic bacteria and yeast and molds. The effects of gamma irradiation and the changes in counts of aerobic mesophilic bacteria and yeast and molds are depicted in figures 5 and 6. Microbial loads showed differences ($P<0.05$) between germs and between radiation doses. The aerobic bacterial population decrease and inhibited significantly with the enhancement of radiation dose. Gamma ray irradiation at 7 kGy resulted in significant reduction in total aerobic and yeast and molds microorganism content (2 log), while the irradiated samples at 0.5 and 1 kGy still sparingly contaminated when compared to controls receiving no irradiation treatment. Complete sterilization was obtained at 7 kGy.

The D-values (decimal reduction dose, is the dose of radiation needed to reduce the number of viable organisms by 1 log (10 fold, 90%)) are respectively 2 and 3.4 kGy respectively for total aerobic mesophilic bacteria and yeast and molds. As shown, the D- values differs significantly for each organism.

The differences in sensitivity to irradiation among microorganisms might be due to the differences in their chemical and physical structure, antiseptic properties and their ability to recover from the radiation injury [21]. The actual dose employed is a balance between what is needed and that what can be tolerated by the product without objectionable changes.

This study indicates that gamma irradiation is an effective treatment for microbial decontamination of textile artefacts.

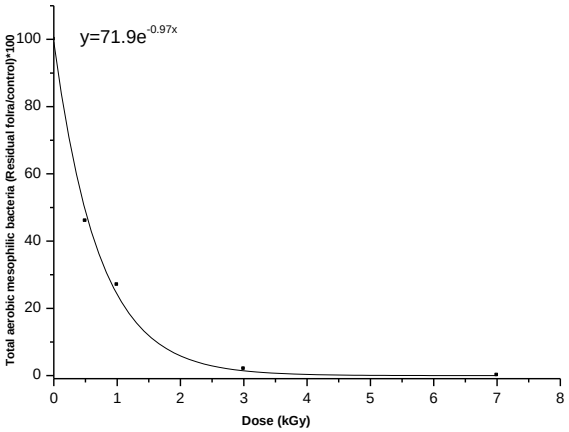

Figure 6: *Survival Curve of the residual aerobic contamination germs (relative variation compared to the untreated control test) function of gamma irradiation dose (0.5; 1; 3 and 7 kGy).*

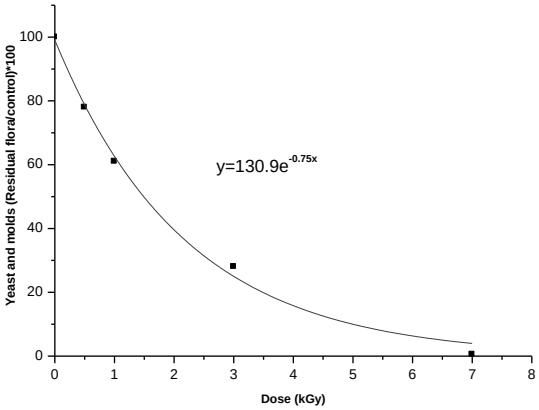

Figure 7: *Survival Curve of the residual yeast and mould contamination germs (relative variation compared to the untreated control test) function of gamma irradiation dose (0, 0.5,1, 3 and 7 kGy).*

Initial studies suggested that losses of material might be occurring due to the high microbiological contamination [22]. To overcome this problem, gamma irradiation was applied to the different textile artefacts, to slow down and reduce maximally the deterioration and degradation process. A connection between the durability of the artefacts and the contamination of the original synthetic textile quality is identified, indicating the influence of inherent biological factors on stability. The major contributory factors determining

degradation appear to be the fungi and aerobic bacteria content [23]. Conservators find themselves faced with the challenge of preserving these ageing artefacts which are showing evidence of significant degradation and to decrease maximally contamination charge.

As reported by many study, the preventive conservation of cultural artefacts strictly depends on environmental conditions and their variations in time [24-26]. Inappropriate variations in the air humidity and temperature could enhance the risk of damage to works of artefacts and other cultural heritage articles being displayed in museums [27, 28].

Conclusion

Based on the microbiological quality, color properties and tensile strength analysis, it is possible to conclude that there were no meaningful alterations on the textile samples submitted to irradiation at the selected dose range from 0.5 to 7 kGy. Therefore, the use of gamma rays from a 60-cobalt source was shown to be efficient when subsequent treatments for disinfection and decontamination of textile-made cultural heritage are required, once it does not damage the textile structure nor generate sub-products that could harm people in physical contact to the artifacts.

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S 5.1

DISINFESTATION OF ARTEFACTS BY GAMMA IRRADIATION IN ROMANIA

CONSTANTIN DANIEL NEGUT, IOAN VALENTIN MOISE, MIHAELA ENE, MARIA MIHAELA MANEA, ION BOGDAN LUNGU, MIHALIS CUTRUBINIS, IOANA RODICA STANCULESCU, CORNELIU CATALIN PONTA

HORIA HULUBEI National Institute of Physics and Nuclear Engineering (IFIN-HH), IRASM Radiation Processing Department, 30 Reactorului Street, Magurele - Ilfov, PO-Box MG-6, RO-077125, Romania

Background of the study. IRASM Radiation Processing Department of Horia Hulubei National Institute of Physics and Nuclear engineering is the result of IAEA TC Project ROM 8011 which was finalized in 2000, when the first industrial irradiator was commissioned in Romania. The main goal of the project was the promotion of radiation processing for industry, agriculture, and preservation of cultural heritage artefacts. Later, the irradiation facility evolved into a radiation processing centre by adding a Microbiological Laboratory and a Physical-Chemical Testing Laboratory. Besides the industrial irradiator (SVST Co-60/B), a research irradiator (GC-5000) was installed in IRASM in 2012, under the IAEA TC Project ROM 8015.

Large scale treatment of artefacts started in 2001 with disinfestation of furniture from Cotroceni National Museum. Since then, different types or artefacts have been treated in IRASM facility: furniture, wooden sculptures, paintings, books, carpets, clothes, film reels. In the same time, IRASM was involved in national R&D projects in which side-effects of gamma irradiation were evaluated for painted wood, paper, leather and textiles. We are currently involved in IAEA CRP F23032 regarding the development of ionizing radiation technology for consolidation and preservation of artefacts with a project focused on the modern painting materials and post-irradiation effects on the properties of paper.

Methodology. Complex studies were performed to evaluate the side-effects of gamma irradiation on the structural and functional-decorative properties of artefacts. Different non-destructive and destructive methods were involved such as spectroscopic techniques (Reflectance Spectroscopy -Colorimetry, FT-IR/Raman, and Electron Paramagnetic Resonance), thermal analysis, and mechanical tests.

Irradiation of samples was performed in air, at room temperature, in conditions similar to those used in the treatment of artefacts. Applied doses were higher than 10 kGy (the usual maximum dose that we use for artefacts) in order to put into evidence small changes. In these experiments, dose rate was ranging from 0.5 to 5 kGy/h.

Results. The colour of a painting is mainly given by pigments which are particulate inorganic or organic solids usually incorporated in a binder. Pigments retain their crystal or particulate structure, so there is a small probability that they could be chemically affected during irradiation. However, their colour can be affected by formation of irradiation colour centres which are electrons trapped in crystal defects. We have investigated the colour changes induced by irradiation (26 kGy) in 22 historical pigments. Only marble dust (calcium carbonate) showed stable, significant colour changes upon irradiation. It becomes darker and its greenish-yellow colour turns into a reddish-blue shade. The saturation of colour with the dose appears at 7 kGy. However, marble dust is mainly used for the ground layer of the painting, thus it will not influence the colour of the painting layer except this is extremely thin. Measurements on a white spot of lead white in mixture with calcium carbonate from a Gospel (Sourkhat - Armenia, 1354) irradiated at 5 kGy showed no colour changes upon irradiation.

Although there is a significant decrease in the degree of polymerization of irradiated paper, this effect does not correlate with changes in mechanical properties or colour. A dose of 10 kGy can be regarded as a threshold dose

below which mechanical and optical properties of paper are not significantly affected. However, the post-irradiation effect of free radicals induced by irradiation in paper is still under debate. Previous studies used thermal annealing of free radicals. This method can enhance their effect because at lower temperature most of them combine locally, thus producing no effect. We are currently studying the kinetic of free radicals at room temperature by EPR spectroscopy and their effect on the colour of paper by reflectance spectrometry. The results obtained so far on the reference material (Whatman paper) and naturally aged paper (book from 1898) show that the post-irradiation effect of free radicals is significant only on fresh paper. The depletion of free radicals in Whatman paper does not correlate with the yellowing effect suggesting that in the degradation of paper are involved complex, chain reactions.

S 5.2

NUMERICAL SIMULATION OF THE RADIATION TREATMENT OF CULTURAL HERITAGE BY BREMSSTRAHLUNG X-RAYS

V. MORGUNOV

Ukrainian Engineering Pedagogics Academy, Kharkiv, Ukraine.

Radiation treatment is a modern well established technology for cultural heritage restoration. The treatment by gamma rays is most usually used for radiation treatment. But there are a lot of countries that haven't gamma irradiators. There are only 200 gamma ray irradiators in 45 countries in whole world, in Europe only 18 from 56 countries have gamma ray irradiators [1].

Moving cultural heritage through the borders even in EU is a big bureaucratic trouble. But there a lot of electron beam accelerators. There are about 24,000 electron accelerators around the world. In most cases the use of electron accelerators for cultural heritage treatment is unacceptable because of high dose rates. In such cases, bremsstrahlung can be used, which can be received in electron accelerators.

X-rays are more penetrating than electron beam, but less penetrating than gamma rays. They are more costly than gamma processes but will decrease exposure times, require less shielding and shorten turnaround times. In spite of that efficiency of electron X-ray conversion is low (not more than 10%), when we are talking about invaluable cultural heritage, the cost of processing is negligible with the cost of cultural heritage.

One of the main tasks in the radiation treatment of cultural heritage is to determine the absorbed dose and dose rate in treated objects. In the case of cultural heritage, it is impossible to determine the absorbed dose and dose rate on dummy objects because of the cultural heritage are unique ones. In such cases, it is possible to use numerical simulation of radiation treatment using Monte Carlo methods.

It was used the open-source object-oriented software toolkit GEANT4 [2, 3]. All the relevant physical processes were included into the calculations: Compton scattering, photoelectric effect, Rayleigh scattering, bremsstrahlung and ionization.

At first the code was validated when considering the characteristic radiation. Results show very good agreement of the bremsstrahlung intensity for the spectra with tube voltages 40 kV and a reasonable accordance for 100 kV and 150 kV. A higher bremsstrahlung intensity was noticed for the simulated spectra with 25 kV and 30 kV. Characteristic peaks are lower in the simulated spectra for all the simulations where they are present. These results point to a low than expected proportion between the characteristic photons and the bremsstrahlung photons.

Then the simulation of X-rays treatment of wooden sculpture was carried out. A map of absorbed doses for this sculpture was obtained.

It is shown that numerical simulation can be used for prediction of absorbed doses and dose rates when X-rays are using to treat various cultural heritage with complex geometry after the validation with the real experiments.

The author would like to acknowledge support from IAEA.

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S 6.1

USES AND PROSPECTS IN GAMMA BIOCIDE TREATMENTS AND RADIOCURABLE RESIN-BASED CONSOLIDATION TREATMENTS FOR CULTURAL HERITAGE ARTEFACTS

QUOC-KHOI TRAN, CLAUDIA SALVAN, MELISSA POLONI, CHRISTOPHE ALBINO, LAURENT CORTELLA

ARC-Nucléart
CEA Grenoble - 17, rue des Martyrs - 38054 Grenoble cedex 9 - France

Gamma radiation experience in cultural heritage and new need.

Gamma radiation-based treatment for cultural heritage has been proposed more than 50 years ago. At ARC-Nucléart, both gamma biocide treatments and radiocurable styrene-polyester resin consolidations have been implemented since the 1970s. This last process in known in France as the "Nucléart" process. But, despite some resounding success and a demonstrated real efficiency, these techniques are still of limited uses for heritage conservation. Indeed, if such denoted "nuclear" process can scare the less scientific public, more rational reluctance due for instance to fear of negative effects induced by ionization in irradiated material have been expressed. Such secondary effects are usually low, far away from strong and irreversible degradation, as often understood by many curators by comparison to well-known ultraviolet exposure. However, it is impossible to prove the absolute safety of these treatments on the whole constituent materials of the cultural heritage. So that one have always to try to characterize the possible effects on the new materials that he is facing. This was for instance the case with "exotic" materials likely to be encountered during mass processing for the French national archives. Another issue is the probable toxicity of styrene as recently more and more expressed, making us looking for new radiocurable styrene-free resins that could replace styrene polyester in our consolidation process.

Investigation

Concerning "exotic" archive materials behaviour after gamma radiation treatment for biocide treatment, two parallel investigations were conducted by two independent teams. The first one was conducted on samples included in boxes that have all undergone the fungicidal dose irradiation process in an industrial plant. Morphological macro and micro observation, colorimetry and UV artificial aging were implemented by the scientific team of Bibliothèque nationale de France to study the potential effect on many samples of photographic process and other reproduction process documents. The other one was conducted in ARC-Nucléart on argentic photography, tracing paper and architect blueprint, using colorimetry and FTIR, at doses from 2 to 15 kGy.

Concerning styrene-free resin, acrylic monomers such as hydroxy-propyl methacrylates, alkyl methacrylates and available styrene-free resins were tested, before on modern wooden samples before to available degraded wooden samples "for science". Spectroscopic analysis (FTIR, NMR), dimensional changes, mechanical testing, colorimetry, SEM observations were carried out.

Results

No strong effect were observed in both studies about "exotic" archival materials behaviors under gamma radiation. Only the transparent parts of some x-rays radiography and whites zone on photographic albumen prints have highlighted color changes in the order of $\Delta E = 5$ to 6.

Acrylic monomers added of polymers such as well-known Paraloid® in order to increase the viscosity are retained to be the best candidates in order to replace the styrene polyester resin in the so-called "Nucléart" consolidation.

S 6.2

HYBRID MATERIALS (GEL/SOLID) BY IONIZING RADIATION FOR CONSERVATION OF NON-METALLIC INORGANIC HISTORICAL MATERIALS

LUÍS M. FERREIRA[1], ALEXANDRA P. RODRIGUES[1,2], FERNANDA M.A. MARGAÇA[1], M. HELENA CASIMIRO[1]

[1] C2TN, Instituto Superior Técnico, Univ. de Lisboa, 2695-066 Bobadela LRS, Portugal

[2] Dep. Conservação e Restauro, FCT, Univ. NOVA de Lisboa, 2829-516 Caparica, Portugal

Background of the study. Non-metallic inorganic materials are the base composition of a large and important group of cultural heritage artefacts. Pottery and decorative artefacts, statues, mosaics, tiles, roof tiles and ancient monuments are examples of this vast group.

Due to their importance as a testimony of our past and evolution, a special attention and demanding effort has been done for the development of new materials and methods for an effective and sustainable conservation and preservation of this important historical legacy. The challenge is even more demanding for artefacts exposed to environmental conditions, with the consequent effect of biodegradation, and to general public fruition, as it is the case of ancient roman mosaics.

Ormosils have been showing a singular tailorable association of properties with a wide range of applications (e.g.: improving the robustness of limestone's and enhancing water-repellent properties; environment-resistant and crack-free thick antireflective coatings), which, together with its chemical nature (silica-based materials) may clearly benefit the conservation of non-metallic artefacts. Ionizing radiation techniques have been proving to be an efficient technique for the preparation and functionalization of this type of hybrid materials, which are now being tested for conservation purposes.

Methodology. These studies are being developed taking roman mosaics as reference target. The guidelines are: *i)* Preparation and functionalization of new polydimethylsiloxane (PDMS) based hybrid materials through ionizing radiation techniques, in two different final forms, gel (standalone use) and solid state (additive to materials already in use). Adjusting experimental conditions like reactants' concentrations, irradiation method and atmosphere, dose rate and samples' absorbed dose, etc, allows tailoring the final material's properties, making them suitable for the different intended applications; *ii)* Assessment of hybrids behaviour applied on mosaic replicas and consequent readjustments and optimisation. Biocide efficiency of the obtained materials will be tested *in vitro* against microorganisms identified *in situ*. Their application on the original substrates will also be evaluated; *iii)* Development of efficient and expeditious methods for the application of hybrids in the conservation of roman mosaics. Special emphasis must be given to their compatibility with native materials and retreatability concerning future conservation interventions; *iv)* Transfer and adjustments of developed materials and methods for the conservation of other non-metallic historical artefacts.

Results. First batches of hybrid materials, prepared from PDMS, tetraethylorthosilicate (TEOS) and zirconium propoxide (ZrPO) as precursors, are homogeneous, transparent, monolithic and amorphous. The increment of ZrPO content has lead to a decrease in the flexibility of the samples. They also present structural organisation at nano scale and high thermal and physico-chemical stability. Their biocide properties against native microbiota showed a decrease of the growth of some important microorganisms (Gram + bacteria, bacilli and fungi) when in contact with hybrids. Biocide activity showed to be a function of the ZrPO content.

By controlling the MW of PDMS, the absorbed dose and atmosphere of irradiation it is possible to control and access the gelification point of the new hybrids in a reliable way.

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S 6.3

GELS FOR CLEANING ARTWORKS

M.HELENA CASIMIRO[1], L.M. FERREIRA[1], T.G. PAIVA[2], R.V. BARRULAS[2], M.C. CORVO[2], S.O. SEQUEIRA[3,4], C. CASANOVA[3], H. PAIVA DE CARVALHO[5], N. MESQUITA[5], A. PORTUGAL[5], A. CANNAS[6], C. ALFARO[7], P. APARÍCIO[7], M.F. MACEDO[3,4]

[1] C2TN, Instituto Superior Técnico, Universidade de Lisboa, 2695-066 Bobadela LRS, Portugal

[2] i3N Cenimat, Departamento de Ciência dos Materiais, FCT, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

[3] Departamento de Conservação e Restauro, FCT, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

[4] VICARTE, FCT, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

[5] Centro de Ecologia Funcional, Departamento de Ciências da Vida, FCT, Universidade de Coimbra, 3000-456 Coimbra, Portugal

[6] Direcção-Geral do Livro, dos Arquivos e das Bibliotecas, Arquivo Histórico Ultramarino,1300-095 Lisboa, Portugal

[7] Fundação D. Luís, Casa das Histórias Paula Rego, 2750-800 Cascais, Portugal

Background of the study. Books, prints, drawings, watercolours, engravings as well as all other works of art based on paper are very susceptible to fungal biodeterioration processes due to their organic composition and hygroscopicity. Biodeterioration caused by mould is a major problem that affects paper based collections in museum, archives and libraries all over the world.

Cleaning fungal stains from paper artefacts is currently performed either by the use of bleaching agents, solvents, enzymes or laser ablation. However, all these methods have major drawbacks, such as: lack of effectiveness on melanized stains (bleaching, solvents, enzymes); causing physicochemical damages on cellulose (bleaching, laser ablation); high toxicity (bleaching, solvents); or high costs (laser ablation). Therefore, parallel to the development of efficient and safe decontamination methods, there is an urgent need of a solution that is effective in removing the fungal stains without causing any additional damage to the paper document or artwork. It should simultaneously be non-toxic, environmentally friendly and easy to apply.

Methodology. In CleanART project, team envisioned a new methodology for cleaning fungal stains on paper that intends to be a major breakthrough in this area and is being targeted to meet all the above requirements. The project activities encompass four phases: identification of the paper stains and the respective fungal flora, synthesis of dedicated cleaning gels, testing the effectiveness and secondary effects of the developed compounds on paper materials. Synthesis of cleaning gels will compare traditional chemical synthesis and alternative radiation induced polymerization techniques. To benefit from mechanical strength and hydrophilicity, vinylpyrrolidone and 2-hydroxyethyl methacrylate (single or combined) will be used to form stable polymeric networks.

Results. Preliminary results for the development of gel materials to be used in cleaning of artworks are very promising.

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S 6.4

A CASE STUDY OF CONSOLIDATION IN CONIMBRIGA: THE HOUSE OF TRIDENT AND SWORD

ALEXANDRA P. RODRIGUES[1,2], SANDRA CABO-VERDE[1], M. HELENA CASIMIRO[1], VIRGÍLIO H. CORREIA[3], JOÃO COROADO[4], LUÍS M. FERREIRA[1]

[1] C2TN, Instituto Superior Técnico, Univ. de Lisboa, 2695-066 Bobadela, Portugal

[2] Dep. Conservação e Restauro, FCT, Univ. NOVA de Lisboa, 2829-516 Caparica, Portugal

[3] Museu Monográfico de Conímbriga — Museu Nacional, 3150-220 Condeixa-a-Nova, Portugal

[4] Dep. Arte, Conservação e Restauro, Inst. Politécnico de Tomar, 2300-313 Tomar, Portugal

Background of the study. In the recent past, hybrid materials based on polydimethylsiloxane (PDMS) and tetra-ethyl-ortho-silicate (TEOS) with addition of zirconium propoxide (ZPO), prepared by gamma irradiation, have been developed and studied mainly for biomedical applications at C2TN. Given their properties and composition, a different application is proposed in the conservation of roman mosaics as consolidants as well as biodeterioration preventers.

The case study presented here regards the mosaic of the *cubiculum* of the House of Trident and Sword in Conimbriga, Portugal. This house underwent its first excavation in 1936. Since then multiple campaigns took place to leave its full area in plain sight. All the found mosaics were documented and reburied for preservation purposes.

The mosaic of the *cubiculum* went through its last intervention this year in order to be subjected to state of preservation assessment, cleaning, graphical documentation recording, characterisation and sampling for the current study as well as for future ones.

Methodology. One of the major guidelines of this project is the characterisation of the mosaic's — mortars and *tesserae* — composition and preservation state. Based on these results, mock-ups of these constituents began to be produced in order to be used as testing supports for the hybrids that are being developed, taking into account the compatibility with original substrates as well as retreatability concerning future conservation interventions.

The polymeric based materials will be functionalised by adjusting experimental conditions like reactants' concentrations, irradiation method and atmosphere, dose rate and samples' absorbed dose, etc. This methodology allows tailoring the final material's properties and making them suitable for different applications.

After assessment of the behaviour of the hybrids on mock-ups and consequent readjustments and optimisation, the developed materials will also be tested on the original substrates, i.e. on the mosaic of the *cubiculum*.

Results. The previous studies reached a methodology that produces transparent, flexible and robust hybrid materials. They also present structural organisation at nano scale and high thermal, physico-chemical stability. Preliminary assay regarding their biocide properties against native microbiota seems to point at the decrease of the growth of micro-organisms when in contact with the referred hybrids. Zirconium appears to be the main responsible for this behaviour.

First results concerning the characterisation of the original roman substrates show that the mosaic of the *cubiculum* of the House of Trident and Sword are composed of bluish grey and white limestone *tesserae*, settled on a layered structure of lime-based mortars differing in the granulometry of each *stratum*. Main degradation phenomena found were concretions on the surface of the *tesselatum*, colour changes in some of the *tesserae* and loss of cohesion and adhesion among and between layers.

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DISINFECTION OF ARCHIVED MATERIAL BY RADIATION PROCESSING TECHNOLOGY KEEPING THE MATERIAL INTEGRITY

MD KHORSHED ALAM, MD. SOHEL RANA, ABDUL BATHEN MIAH AND MD KAMRUZZAMAN PRAMANIK

Institute of Food and Radiation Biology
Atomic Energy Research Establishment
Bangladesh Atomic Energy Commission
Dhaka, Bangladesh

Abstract

The aim of the study is to preserve paper-based archived material for a long period of time using ionizing radiation. To conduct this research, old book samples were selected as tentative archived material. Samples were prepared and irradiated at a series of radiation doses e.g. 0, 2.0, 4.0, 6.0, 8.0 and 10.0 kGy at a dose rate of 12.00 kGy/h from panaromic Batch type 75 kCi ^{60}Co source. After irradiation different quality parameters such as microbiological (Total Viable Bacterial Count, Total Fungal Count), mechanical (Tensile Strength, Percent of Elongation at Break and Elastic Modulus), color properties (L-, a- and b-value), Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) of samples were analyzed and assessed to observe the immediate and long term effect of ionizing radiation on paper quality. Irradiated samples were preserved for the study of above parameters at different intervals (e.g., 0 day and 60 days). Results showed that initial total bacterial count of control sample was $4.6x10^2$ cfu/g and radiation dose of 2.0 kGy was enough to eliminate the bacterial load completely for 0 and 60 day samples. Fungal count was found nil in both treated and non-treated samples. Among mechanical properties, tensile strength (TS) of unirradiated sample was 15.92 MPa and it was gradually increased as the dose increased and finally reached upto 19.03 MPa at a dose of 10 kGy causing the TS-change above significant level ($p < 0.05$). In the 60 day sample, TS was gradually increasing as the radiation dose increased and finally reached at 19.21 MPa at 10 kGy rendering the value above significant level. Percent of Elongation at Break (EB) was not changed significantly due to radiation treatment at any doses. Initial elongation module (EM) of the control sample was 325.21 N/m^2 and it was increased gradually as radiaton dose increased and changed significantly to 342.82N/m^2 in the sample treated with 6.0 kGy. Colour paramters with respect to L-, a-, and b-value changed very slightly and insignificantly at any doses of radiation. From these findings it can be inferred that a radiation dose of 4.0 kGy might be used to conserve the cultural heritage including valuable paper-based archived materials.

POSTERS

Branka Katušin-Ražem, Dušan Ražem, Mario Braun:
Irradiation treatment for the protection of cultural heritage objects - Croatian experience

Mario Braun, Nevena Krstulović, Lana Lalić:
Overview of the current state of wooden polychromed sculptures from Gora

Siniša Cvetković, Romana Jagić:
The altar of the St. Cross, Kamensko, church of the Blessed Virgin Mary of Snow

Romana Jagić:
Polyptich of the Virgin Mary from the church of St. Francis in Pula

Igor Kozjak, Tatjana Mušnjak:
Desinsection of book bindings by γ radiation

Bernarda Rundek Franić, Anamarija Franić:
Garments of Alka

Mihaela Grčević:
Ethnographic objects – preventive desinsection by irradiation

Radmila Iva Janković:
Project ''Atelier Kožarić''. Conservation of objects by irradiation desinsection

Tanja Jurkin, Branka Katušin Ražem, Dušan Ražem, Bernarda Rundek Franić, Anan Marija Franić, Maja Vrtulek, Venija Bubnjarić-Vučković:
Radiation desinsection method for the protection of textile cultural heritage artefacts

Katarina Marušić, Maja Šegvić Klarić, Ana Dumbović, Branka Mihaljević:
Protection of cultural heritage by ionizing radiation. A case study on an old canvas painting from the 18th century

Katarina Marušić, Irina Pucić, Vladan Desnica:
Color and UV-Vis spectral changes in irradiated nacres

Ana Božičević, Zvjezdana Jembrih:
The flood in the storeroom of the Diocesan Museum in Zagreb

Ana Božičević, Zvjezdana Jembrih:
Uncured saints

LIST OF PARTICIPANTS

Table 1. List of non-local Participants

	Country	Name and surname
1	**Argentina**	Ms **Celina HORAK** Radiation Technology and Application Management National Atomic Energy Commission Argentina e-mail: celina.horak@gmail.com
2	**Brazil**	Mr **Pablo Antonio VASQUEZ SALVADOR** Instituto de Pesquisas Energeticas e Nucleares (IPEN) Comissão Nacional de Energia Nuclear (CNEN) Av. Prof. Lineu Prestes, 2242; Cidade Universitaria 05508-000 São Paulo, Brazil e-mail: pavsalva@ipen.br
3	**Bulgaria**	Ms **Petya KOVACHEVA** Radiochemical Laboratory; Faculty of Chemistry; Sofia University St. Kliment Ohridski 1 James Bourchier Boulevard, 1164 Sofia, Bulgaria e-mail.: kovacheva.petya@gmail.com
4	**Egypt**	Mr **Hassan Ahmed Abd EL-REHIM** National Centre for Radiation Research and Technology (NCRRT), Egyptian Atomic Energy Authority (EAEA) P.O. Box 29, Nasr City, 3 Ahmed El-Zomor, Nasr City, CAIRO, El Zohoor, Egypt e-mail: ha_rehim@hotmail.com
5	**France**	Mr **Laurent CORTELLA** Atelier Régional de Conservation ARC-Nucléart CEA-Grenoble 17, Rue des martyrs 38 054 Grenoble Cedex, France e-mail: laurent.cortella@cea.fr
6	**Italy**	Ms **Stefania BACCARO** Ente per le Nuove Tecnologie L'Energia e L'Ambiente (ENEA) 301, Via Anguillarese; 00123 Rome, Italy e-mail: stefania.baccaro@enea.it
7	**Korea**	Mr **Hae Jun PARK** Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, Jeongeup 580-185, Republic of Korea e-mail: hjpark@kaeri.re.kr

8	**Romania**	Mr **Constantin Daniel NEGUT** HORIA HULUBEI National Institute for R&D in Physics and Nuclear Engeneering (IFIN-HH) IRASM Radiation Processing Department 30 Reactorului St., MAGURELE – Ilfov, RO 077125, Romania e-mail: dnegut@nipne.ro
9	**Poland**	Ms **Dagmara CHMIELEWSKA SMIETANKO** Institute of Nuclear Chemistry and Technology ul. Dorodna 16, 03-195 Warsaw, Poland e-mail: d.chmielewska@ichtj.waw.pl
10	**Portugal**	Ms **Maria Helena CASIMIRO** C2TN, Instituto Superior Técnico, Univ. de Lisboa, 2695-066 Bobadela LRS, Portugal e-mail: casimiro@ctn.tecnico.ulisboa.pt
11	**Portugal**	Mr **Luis Miguel MOTA FERREIRA** Centro de Ciências e Tecnologias Nucleares Instituto Superior Técnico Estrada Nacional 10, Km 139,7 2695-066 Bobadela, Portugal e-mail: ferreira@ctn.tecnico.ulisboa.pt
12	**Portugal**	Ms **Paula Alexandra PINTO RODRIGUES** C2TN, Instituto Superior Técnico, Univ. de Lisboa, 2695-066 Bobadela, Portugal 2 Dep. Conservação e Restauro, FCT, Univ. NOVA de Lisboa, 2829-516 Caparica, Portugal e-mail: alexandra.rodrigues@ctn.ist.utl.pt
13	**Serbia**	Mr **Slobodan MAŠIĆ** Vinča Institute of Nuclear Sciences PO Box 522, 11001 Belgrade, Serbia e-mail: Slobodan.Masic@gmail.com
14	**Serbia**	Mr **Ivica VUJČIĆ** Vinča Institute of Nuclear Sciences PO Box 522, 11001 Belgrade, Serbia e-mail: ivica@vin.bg.ac.rs
15	**Sri Lanka**	Mr **Kumarawadu Ruwan Chandima De SILVA** Sri Lanka Atomic Energy Board e-mail: ruwan@aeb.gov.lk

16	**Syrian Arab Republic**	Mr **Zaki AJJI** Department of Chemistry, Atomic Energy Commission, P. O. Box 6091, Damascus, Syria e-mail: zajji@aec.org.sy
17	**Tunisia**	Mr **Arbi MEJRI** High dose dosimetry Laboratory . National Center for Nuclear Sciences and Technologies. Sidi Thabet, 2020 Ariana, Tunisia. e-mail: arbi.mejri@cnstn.rnrt.tn
18	**Ukraine**	Mr **Volodymyr Victorovich MORGUNOV** Ukrainian Engineering Pedagogical Academy Universitetskaya str. 16, 61003 Kharkiv, Ukraine e-mail: volodymyr.morgunov@gmail.com
19	**Ukraine**	Mr **Oleksandr BUHAY** Institute of Applied Physics NAS of Ukraine, Sumy, Ukraine e-mail: alex.buhay@gmail.com
20	**IAEA**	Mr **Sunil SABHARWAL** International Atomic Energy Agency Department of Nuclear Sciences and Applications Division of Physical and Chemical Sciences Physics Section P.O. Box 100, Vienna International Centre Wagramer Straße 5, 1400 Vienna, Austria Tel.: +43 1 2600 21744 Fax: +43 1 26007 e-mail: S.Sabharwal@iaea.org Internet: http://www.iaea.org

Table 2. List of local Participants

	Country	Name and surname
1	**Croatia**	Mr **Joško BOGDANOVIĆ**, mag.art./assistant lecturer University of Dubrovnik Department for Art and Restoration/ Restoration of Wood Branitelja Dubrovnika 41 20 000 Dubrovnik, Croatia T: +385 20 446 038 M: +385 91 151 6924 E: jbogdanovic@unidu.hr
2		Ms **Ana BOŽIČEVIĆ**, mag.art./ assistant lecturer Academy of Fine Arts, University of Zagreb Conservation-Restoration Department Ilica 85, 10000 Zagreb, Croatia tel.: 01/4824307 mob: 098 787 379 e-mail: bozicevic.ana@gmail.com
3		Mr **Mario BRAUN** Restaurator advisor (retired) Croatian Conservation Institute e-mail: mbraun52@yahoo.com
4		Ms **Vanja BRDAR MUSTAPIĆ**, Museum advisor, Head of furniture collection and *varia* collection Museum of Arts and Crafts Trg Republike Hrvatske 10 10000 Zagreb Tel.:+ 385 1/4882 111; 4882 140 e-mail: vanja.brdar.mustapic@muo.hr
5		Ms **Ivona ČIPOR** City Museum Sisak Ulica Kralja Tomislava 10 44000 Sisak
6		Ms Suzana **DAMIANI** Department of Conservation and Restoration Artworks Academy of Fine Arts, University of Zagreb Zamenhofova 14 10000 Zagreb, CROATIA
7		Mr **Vladan DESNICA**, as.prof. Academy of Fine Arts, University of Zagreb Conservation-Restoration Department Ilica 85, 10000 Zagreb, Croatia GSM +385 91 573 7623 tel. +385 1 482 4305 e-mail: vdesnica@irb.hr

8		Ms **Andreja DRAGOJEVIĆ** Head of the Central Laboratory for Conservation and Restoration Croatian State Archives Marulićev trg 21; 10 000 Zagreb; Croatia Tel .: 01 4801968 e-mail: adragojevic@arhiv.hr
9		Ms **Iva DŽEBA** Ruđer Bošković Institute Division of Materials Chemistry Radiation Chemistry and Dosimetry Laboratory Bijenicka c. 54, 10000 Zagreb, Croatia Tel.: +385 1 456 1070 e-mail: idzeba@irb.hr
10		Ms **Mihaela GRČEVIĆ**, restaurator Ethnographic museum Trg Mažuranića 14, 10000 Zagreb mgrcevic@emz.hr
11		Ms **Zvjezdana JEMBRIH** Associate Professor, mr. art. Senior conservator-restorer of polychrome wooden sculpture Department of Conservation and Restoration Artworks Academy of Fine Arts, University of Zagreb Zamenhofova 14 10000 Zagreb, CROATIA GSM: +385 91 1856322 e-mail: zjembrih@yahoo.com
12		Ms **Jasna JAKŠIĆ,** librarian curator, Museum of Contemporary Art Habdelićeva 2 10000 Zagreb e-mail: Jasna.Jaksic@msu.hr
13		Ms **Tanja JURKIN** Ruđer Bošković Institute Division of Materials Chemistry Radiation Chemistry and Dosimetry Laboratory Bijenicka c. 54, 10000 Zagreb, Croatia Tel.: +385 1 457 1255 e-mail: tanja.jurkin@irb.hr
14		Ms **Iskra KARNIŠ VIDOVIČ** Head of the Section for Training, Professional Development and International Cooperation CROATIAN CONSERVATION INSTITUTE Nike Grškovića 23, 10000 Zagreb, Tel. +385 1 4693870, Mob. 00385 91 4683620, e-mail: ikarnis@h-r-z.hr

15		Ms **Branka KATUŠIN-RAŽEM** (retired) Ruđer Bošković Institute Division of Materials Chemistry Radiation Chemistry and Dosimetry Laboratory Bijenicka c. 54, 10000 Zagreb, Croatia e-mail: brazem@irb.hr
16		Ms **Željka KNEŽEVIĆ** Ruđer Bošković Institute Division of Materials Chemistry Radiation Chemistry and Dosimetry Laboratory Bijenicka c. 54, 10000 Zagreb, Croatia Tel.: +385 1 456 1098 e-mail: zeljka.knezevic@irb.hr
17		Mr **Igor KOZJAK** Central Laboratory for Conservation and Restoration Croatian State Archives Marulićev trg 21; 10 000 Zagreb; Croatia Tel .: 01 4801968 e-mail: ikozjak@arhiv.hr
18		Ms **Dragica KRSTIĆ** Head of the NSK Preservation and Storage Department National and University Library in Zagreb, Hrvatske bratske zajednice 4 10 000 Zagreb, Croatia Tel: +385 616 4077 e-mail: drkrstic@nsk.hr
19		Ms **Marija MAJER** Ruđer Bošković Institute Division of Materials Chemistry Radiation Chemistry and Dosimetry Laboratory Bijenicka c. 54, 10000 Zagreb, Croatia Tel.: +385 1 456 1051 e-mail: marija.majer@irb.hr
20		Ms **Katarina MARUŠIĆ** Ruđer Bošković Institute Division of Materials Chemistry Radiation Chemistry and Dosimetry Laboratory Bijenicka c. 54, 10000 Zagreb, Croatia Tel.: +385 1 456 1154 e-mail: kmarusic@irb.hr
21		Ms **Branka MIHALJEVIĆ** Ruđer Bošković Institute Division of Materials Chemistry Radiation Chemistry and Dosimetry Laboratory Bijenicka c. 54, 10000 Zagreb, Croatia Tel.: +385 1 456 1071 e-mail: branka.mihaljević@irb.hr

22		Ms **Svjetlana MIHELIĆ**, teacher School for wood processing Savska cesta 86, 10000 Zagreb 01 61 77 502 e-mail: drvoskolazg@gmail.com
23		Ms **Marijana MIMICA TKALČEC** Central Laboratory for Conservation and Restoration Croatian State Archives Marulićev trg 21; 10 000 Zagreb; Croatia Tel .: 01 4801968 e-mail: mmimica@arhiv.hr
24		Ms **Marijana NODILO** Ruđer Bošković Institute Division of Materials Chemistry Radiation Chemistry and Dosimetry Laboratory Bijenicka c. 54, 10000 Zagreb, Croatia Tel.: +385 1 456 1156 e-mail: mnodilo@irb.hr
25		Mr **Anđelko PEDIŠIĆ**/ MA Consultant conservator-restorer/Head of Division for Branch Departments I CROATIAN CONSERVATION INSTITUTE Division for Branch Departments I Zmajevac 8, 10000 ZAGREB tel: +385 /1/4683 515 gsm: +385 91 617 0244 vpn: 277 email: apedisic@h-r-z.hr
26		Mr **Neven PEKO**, conservator - restaurator City Museum Sisak Ulica Kralja Tomislava 10, 44000 Sisak Tel: +385 91 649 7322 e-mail: neven.peko@gmail.com
27		Ms **Vesna PLANINC**, restaurator Mimara Museum Rooseveltov trg 5, 10000 Zagreb Tel: +385 1 48 28 100 e-mail: mailto:vesna.planinc@mimara.hr
28		Ms **Jasminka PODGORSKI** Museum of Arts and Crafts Trg Republike Hrvatske 10 10000 Zagreb Tel.:+ 385 1/4882 111; 4882 140 e-mail: jasminka.podgorski@net.hr

29		Ms **Irina PUCIĆ** Ruđer Bošković Institute Division of Materials Chemistry Radiation Chemistry and Dosimetry Laboratory Bijenicka c. 54, 10000 Zagreb, Croatia Tel.: +385 1 456 1166 e-mail: irina.pucic@irb.hr
30		Ms **Lada RATKOVIĆ BUKOVČAN**, museum advisor Mimara Museum Rooseveltov trg 5, 10000 Zagreb Tel: +385 1 48 28 100 e-mail: lada.ratkovic@mimara.hr
31		Mr **Duško RAŽEM** (retired) Ruđer Bošković Institute Division of Materials Chemistry Radiation Chemistry and Dosimetry Laboratory Bijenicka c. 54, 10000 Zagreb, Croatia e-mail: razem@irb.hr
32		Ms **Antonina SRŠA**, restaurator advisor Museum of Arts and Crafts Trg Republike Hrvatske 10 10000 Zagreb Tel.:+ 385 1/4882 111; 4882 140 e-mail: antonina.srsa@muo.hr
33		Mr **Domagoj ŠATOVIĆ** Head of the Conservation-Restoration Department Academy of Fine Arts, University of Zagreb Zamenhofova 14, 10000 Zagreb GSM: +385 91 1856322 e-mail: domagoj.satovic@alu.hr
34		Ms Maja **ŠEGVIĆ KLARIĆ** Department of Microbiology, Faculty of Pharmacy and Biochemistry, University of Zagreb, 10000 Zagreb, Croatia e-mail: msegvic@pharma.hr
35		Ms **Ivana TARTARO BUJAK** Ruđer Bošković Institute Division of Materials Chemistry Radiation Chemistry and Dosimetry Laboratory Bijenicka c. 54, 10000 Zagreb, Croatia e-mail: ivana.tartaro@irb.hr

36		Ms **Tijana-Annar TRPUTEC STRČIĆ** Senior Furniture Conservator CROATIAN CONSERVATION INSTITUTE Nike Grškovića 23, 10000 Zagreb, Tel. +385 1 4693870 e-mail: tannar@h-r-z.hr
37		Ms **Ljiljana VILUS JAPEC**, senior conserver Ethnographic museum Trg Mažuranića 14, 10000 Zagreb Tel: +385 1 48 26 220 e-mail: Ljiljana.Vilus.Japec@emz.hr