3rd International Seminar & Workshop

# Emerging Technology and Innovation for Cultural Heritage

# BOOK of ABSTRACTS

edited by Elena Badea, Andrea Bernath and Irina Petroviciu

16–18 October 2014, Sibiu

*Advanced Technology for Diagnosis, Preservation and Management of Historical and Archaeological Parchment, Leather and Textile Artefacts*

ASTRA Centre for Heritage - CePCoR, ASTRA Museum, Sibiu, Romania

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**Emerging Technology and Innovation for Cultural Heritage (ETICH 2014)**
**16-18 October 2014**
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**Sibiu**
**Romania**

**Editors: Elena Badea, Andrea Bernath, Irina Petroviciu**



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# History and Scope

The International Seminar and Workshop on Emerging Technology and Innovation for Cultural Heritage (ETICH) is dedicated to the natural connection between ***science*** and ***conservation***. The main aim of ETICH is to bring together conservators, restorers, conservation scientists, chemists, physicians, engineers, teachers and show how interdisciplinary work across a broad range of discipline is contributing to the conservation and sustainable preservation of our cultural heritage. In the last decades the booming developments in chemical, physical and biological science, but also in the fields of electronics and computer sciences, nanomaterials and nanotechnologies has brought us new instruments and methods of great perfection, which present new horizons in the analysis, diagnosis and protection of historical and cultural objects and artefacts.

ETICH 2014 is the third edition after previous symposia organised in collaboration with the **National Museum of Romania History in 2012** and **Romanian Academy Library in 2013**, and focusses on advanced technologies for diagnosis, preservation and management of historical and archaeological parchment, leather and textile artefacts.

The need for full interdisciplinary participation of professionals in the conservation and restoration of cultural heritage has been universally recognised. We thus hope that the 2014 ETICH edition will particularly provide an international platform for presentation and discussion and on how to effectively integrate scientific research outcomes with preservation practice.

The 2014 Seminar and Workshop is jointly organized by the **National Research and Development Institute for Textile and Leather (INCDTP), ICPI Division, Bucharest**, **Romanian Association *Science and Cultural Heritage in Connection* (i-CON)** and **Training Centre for Conservators and Restorers (CePCoR), ASTRA National Museum Complex (CNM ASTRA), Sibiu**.

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# INVITED LECTURES

Invited Lecture

# INFLUENCE OF ETHYLENE OXIDE FUMIGATION AGAINST MOULD ON PARCHMENT AND LEATHER OF HISTORICAL BOOKS AND CHARTRES

Patricia Engel

*European Research Centre for Book and Paper Conservation-Restoration University for Continuing Education Krems, Austria*

The contribution reports on the EU project “Men and Books”, which dealt with written heritage of the Archives of the Protestant Parish of the Holy Trinity in Swidnica. This archive is one of the most valuable repositories for the history of Protestantism in Silesia, Bohemia, Moravia and Austria, however concerning material it represents an average archive in Europe, which allows to apply research results to other archives. Due to uncontrolled climate conditions in the past, many of the books were attacked by microorganisms. During the 1990's, the books of Swidnica were fumigated with ethylene oxide. The use of ethylene oxide for book-disinfection is considered highly controversial in the prevailing literature and whether or not ethylene oxide is a valid choice for book-fumigation still remained an open question. Several questions were put forward in the research, i.e. whether or not ethylene oxide harms material and/or the readers and if the fungi are killed.

So far no off-gassing ethylene oxide could be detected. GC was used. The original infestation with microorganism was killed, but new infestation exists. In the recent presentation the effect ethylene oxide does to leather and parchment is focused. Artificial aging, artificial infestation and fumigation and thereafter measurement of fibre length and $T$s revealed the decay potency the ethylene oxide has on collagen material.

Invited Lecture

# SIMULATION OF THE DEGRADATION PHENOMENA IN LEATHER AGEING

Anna Bacardit[1], Concepció Casas[1], Carmen Gaidau[2], Lucretia Miu[2], Luis Ollé[1]

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[2] *Leather Research Department, INCDTP-CPI, 93Ion Minulescu Str,031215, Bucharest, Romania*

**Abstract**

This work deals with the study of the effect of temperature, relative humidity, and UV radiation on leather ageing. Leathers with wet-white tannage and chrome tannage were exposed to weathering effects using a climatic chamber in order to identify the most important variables affecting this weathering process and to check for interactions. Both a multilevel centralized factorial experimental design and an analysis of variance (ANOVA) have been employed as statistical tools for estimating the effects of the parameters.

**Introduction**

As reported in previous studies, leather is strongly affected by three main environmental parameters: temperature, relative humidity and UV radiation[1-12].

When leather is exposed to sunlight or high temperatures, it absorbs energy which induces photochemical reactions by radical mechanisms. Firstly, chemical compounds split off and free radicals are formed. Secondly, these radicals react immediately with oxygen to form peroxide radicals. Peroxide radicals further react with the organic constituents of leather, and dyes, tanning agents and fat liquors, breaking some of the bonds between the said products and collagen[13-15]. It is known how unsaturated oils form free radicals when exposed to light[16-19]. Automotive industries and other sectors such as the building industries simulate the complex interactions of materials and weather by placing an entire automobile on exposure[20-22]. Most studies focused on weathering tests methods are performed on plastics, textile and coatings[23-27]. These industries focus material natural weathering exposure test on two major US locations: South Florida and Desert Arizona termed “Reference” or “Standard” Environments[28]. Desert Arizona reference environment provides arid exposures characterized by a large diurnal and seasonal temperature range, with high daytime temperatures (i.e. in summer up to 45ºC), and low night-time temperatures (i.e. in winter down to 0ºC) due to extremely low humidity. This local climate provides increased levels of two critical weathering variables: higher UV radiation and high temperatures. In contrast, South Floridareference provides subtropical exposures characterized by heavy rainfall, high humidity and high temperatures.

The interaction between temperature, UV radiation and relative humidity result in different environments and ecologies. The degradation mechanisms of materials should differ widely between these exposure environments. By exposure in both reference environments and analysis of empirical weathering data, it is possible to obtain and understanding of materials performance in worst case end use environments.

## Experimental

The tests were carried out on Spanish pickled cattle hides at pH = 3.2 – 3.5. Two types of tanned leather were tested: on the one hand, chrome tanned leather and on the other hand, wet-white tanned leather.

During a period of 7 days, the leathers were exposed to weathering effects using a climatic chamber 1000L/Dycometal model CCK 0/1000 with the aim to both identify the most important variables affecting this weathering process and to check for any possible interactions.

A multilevel centralized factorial experimental design and an analysis of variance (ANOVA) were employed as statistical tools for estimating the effects of the parameters.

In order to study the effect of temperature, relative humidity, and UV radiation on leather ageing, we carried out the following tests:

IUP 8. Measurement of tear load

IUP 9. Measurement of distension and strength of grain by the ball burst test

IUP 16. Measurement of shrinkage temperature

IUP 36. Measurement of leather softness

IUF 450. Color fastness of leather to dry and wet rubbing (1000 and 50 rubs)

IUC 4. Determination of matter soluble in dichloromethane

IUC 6. Determination of water soluble matter, water soluble inorganic matter, and water soluble organic matter

Color of the leathers was measured using a spectrophotometer (Datacolor International, Spectraflash SF300)

The infrared spectra of leather surface were recorded using an Infrared Spectrometer with Attenuated Total Reflectance (Perkin-Elmer Spectrum One FTIR with UATR accessory) and Spectrum v5.0.1. software for the visualization of changes among spectra.

To examine the changes in fibrous structure of the leather samples, we used the scanning electron microscopy JEOL JSM 6400.

## Results and discussion

***Effect of the weathering variables on physical and fastness properties of the leather***

The statistical analysis of the results obtained was carried out using the Statgraphics Plus Program. Wet-white leather and chrome-tanned leather show a different behaviour to leather ageing. Relative humidity was the factor in wet-white leather with the highest impact on most of the physical and fastness properties analysed, whereas in chrome-tanned leather it was UV radiation.

***Effect of the weathering variables in the modification of the leather composition***

UV radiation has again the largest effect on IR and on matter soluble in dichloromethane. Temperature also shows a significant effect on IR. The analysis also indicates the possibility of a two-way interaction between temperature and relative humidity, and between temperature and UV radiation.

The analysis confirms again that relative humidity was found significant on all of the properties analyzed in wet-white leathers. Temperature shows a significant effect on water soluble inorganic, IR, and fats.

***Changes in fibrous structure***

A slight loss in compactness can be observed in the fibers possibly as a result of the hydrolysis of collagen, since the protein chain of collagen has been exposed to high levels of humidity. However, this slight loss of compactness is almost negligible compared with that obtained in the wet-white leather.

## Conclusions

The aim of this study was to compare the effect of the temperature, relative humidity, and UV radiation on chrome-tanned leather and wet-white leather ageing. UV radiation was the factor with the highest impact on most of the properties analyzed on chrome-tanned leather. Therefore, it plays a key role in weathering and consequently in chrome-tanned leather ageing.

Chrome-tanned leather and wet-white leather show a different ageing behaviour. Whereas chrome-tanned leathers are strongly affected by UV radiation, wet-white leathers are strongly affected by relative humidity.

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Invited Lecture

# CONVENTIONAL METHODS AND MODERN APPROACHES IN CURATIVE CONSERVATION OF TEXTILES

Carmen Marian

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## General considerations

Textile heritage represent the testimony of the past, his main defining feature being to transmit information related to technology, aesthetics, fashion, thus reconstituting the unique aspects of the times of yesteryear. Conservation treatments must be applied to ensure the preservation and transmission of all information that we link to other eras and geographical areas and which, in fact, is the meaning and value of the textile objects.

Each textile object represents a heritage special case and should be diagnosed by specific methods. From this reason derived the complexity of curative conservation treatments and, as well as, most importantly, the option for a particular type of intervention.

## Curative conservation of textiles

Curative conservation aims chemical stabilization of objects by removing deposits (accumulated from outside environment or formed as a result of the degradation of the original material) that represents a potential source of damage. This is why cleaning is the most important stage of curative conservation treatment. On the choice and application of the method of cleaning depends the way in which the textile object will survive as well as the success of the subsequent restoration of the object cleaned. Any cleanup process is preceded by the physic-chemical and biological analyses to identify the nature of the contaminants and of the material support and the conservation status of the piece in question.

*Classical methods* of cleaning use as cleaning environment water in which various additives (detergents, soaps or solvents with water miscibility etc.) can be added to ensure the effectiveness of the cleaning process, while protecting the integrity of the subject textile.

Textile objects, most often have a composite structure, being made from both inorganic and organic materials (textile fibres, metal, ceramics, wood etc.) in various stages of decay. In such circumstances, the option for a particular treatment is established pending on the correlation between the properties of each material and the state of preservation.

Deposits are formed, whereas, on the surface of textile heritage objects, through the accumulation of foreign matter and does not have a uniform distribution, their adherence to the textile material being variable. Also the composition of these deposits is different, requiring, for their removal, the application of differentiated treatments. For this reason, the cleaning treatments of heritage textile are carried out using methods suited to the conservation status and to the nature of the materials, in successive stages, from time to time between cleaning phases, to ensure continued monitoring of the conservation status of the textile and the effectiveness of treatment. Deposits are removed initially by dry, mechanical methods and then by association with wet chemical processes.

As a result of cleaning treatments carried out in humid environment, textiles regains elasticity allowing their handling for the purposes of subsequent interventions of restoration. The improving of these characteristics as a result of *"deleted" physical aging"* of the textile in the wet environment constitutes an important argument when using the classical methods of cleanup.[1,2]

*The use of high-frequency cold plasma in the process of cleaning the textile heritage*

High-frequency cold plasma has been used in the textile industry, in the finishing field, for the modification of textiles surface in order to improve certain characteristics pertaining to the day-to-day functionality of these new textiles: to increase the ability of dyeing and watering of the fibres, to increase the adhesion of subsequent coatings for application with thin polymer films, to improve water repellence etc. The treatment in cold plasma of high-frequency causes significant changes in surface properties of new textiles due to the interaction between the particles with high energy and textile material surface.

In recent times have been carried out a series of experimental researches on the use of high-frequency cold plasma in the field of conservation of cultural heritage, with the aim of cleaning textile objects. Research has been completed by applying this method for cleaning of textile objects of heritage value.[3] Subsequent investigations have revealed that the application of cold plasma of high frequency, for a period of one to three hours, has generated irreversible degradation which, in turn, will initiate, through time, new slow degradation processes whose effects will be visible over the years.

In the vast majority of cases, textile heritage pieces are made up of materials whose structure is altered due to the degradation that has taken place in time. Thus, the decrease of molecular mass, the expansion of amorphous areas, lessening energy of chemical ties due to natural aging will result in amplification of the plasma effect over the old textile through the production of irreversible degradation. Subsequent experiments have shown that the heritage textile treated by the high-frequency cold plasma have undertaken the degradation of surface and of bulk properties of textile fibres as is clearly superior to the new textile materials, in the finishing processes. Also, research has highlighted the fact that the treatment by plasma has not achieved an optimal cleaning of treated materials and textile specific characteristics have not been improved.

For example, the paper presents some case studies concerning the application of curative conservation, by conventional methods and by the high-frequency cold plasma, in the case of some historical and archaeological textiles.

## Conclusions

Conservation treatments can be applied only when it is certain that they will not generate the physical-chemical changes in the intimate structure of objects that lead to their irreversible degradation. It should also to mention that repeated interventions are becoming dangerous, cumulating, each time, undesirable impact on the heritage textile.

The conservation process has assimilated, in recent times, new materials and techniques that have led to overrun the empiricism and to solve some important and difficult issues. However, from the multitude of discoveries, usually intended for other uses (processing industry, technological applications in the field of edicine etc.), only some can be included in the conservation process, adoption and adaptation of their being made with great caution.

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Invited Lecture

# EXAMINATION OF HISTORIC PARCHMENT MANUSCRIPTS BY NON-INVASIVE REFLECTION-FTIR. POSSIBILITIES AND LIMITATIONS

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## Introduction

Since ancient times, parchment has been used as support for manuscripts. As it shows a relatively high durability, many old parchment objects can be found in libraries and museums. Nevertheless, both religious and secular manuscripts often have been used extensively over centuries or were kept in suboptimal environmental conditions and hence signs of wear and degradation must be noticed in many cases. Among other methods, Fourier Transform Infrared Spectroscopy (FTIR) has been used for damage assessment of parchments by evaluation of the diagnostically relevant vibration bands of amide I (AI, C=O stretching at 1650 $cm^{-1}$) and amide II (AII, N-H bending and C-N stretching at 1550 $cm^{-1}$) as well as for the identification of inks, pigments and binding media on illuminated manuscripts. In particular, it has been reported[1] that degradation of parchment by denaturation can be evaluated from ATR-FTIR spectra by a shift of the amide II band to lower wavenumbers relative to amide I, whereas degradation by hydrolysis is characterized by an increase of the intensity of AI relative to AII, which is effected by additional O-H bending vibrations in the region of AI. However, only few studies utilized non-invasive approaches.

## Material and Methods

We used a portable reflection-FTIR instrument (Alpha, Bruker Optics) with DTGS-detector and a spot size of about 4 mm, which allowed non-invasive on-site examination of several manuscripts on parchment ($9^{th}$-$15^{th}$ centuries). Depending on the surface properties of the analyzed objects, 32-256 scans were collected for a spectrum in the range of 4000-375 $cm^{-1}$ with a resolution of 4 $cm^{-1}$. The spectra obtained were evaluated either using a self-built reflection-FTIR database or, the IRUG 2007 database (http://www.irug.org) after calculation of absorption index spectra by Kramers-Kronig transformation. According to the particular requirements of the objects analyzed, measurements were carried out either in vertical or horizontal position of the instrument, using several supports (studio stand, tripod, tetrapod or laboratory lifting platform). In addition, complementary XRF analysis was carried out at similar measuring points for the determination of the elemental, especially inorganic compounds in the inks and pigments.

**Results and Discussion**

As a result of the surface properties the obtained spectra showed relatively high noise levels and indications for contribution of diffuse reflection. The maxima of the amide bands were around 1660 $cm^{-1}$ (AI) and 1550 $cm^{-1}$ (AII) in the absorption index spectra, although an exact determination of AII often was impeded by interference of AII with bands from calcite ($CaCO_3$) and/or calcium soaps. Thus, no reliable assessment of degradation by denaturation and hydrolysis was possible. At several measuring points, a shoulder in the AI region at about 1700 $cm^{-1}$ indicated various degrees of oxidative degradation. The materials of the dark brown/black ink could not be identified. Although the results obtained by XRF indicated the use of iron gall ink (Fe contents), no evidence for gallotannic acid or $FeSO_4$ was found by reflection-FTIR. This might result from a contribution of uncovered parchment to the measuring signal, as the relatively large spot size of the instrument did not allow the analysis of areas completely covered with ink. Apart from that it should be considered that the inks additionally may contain carbon black, which cannot be detected by either FTIR or XRF. Calcium oxalate could be identified frequently at measuring points with ink, most probably deriving from mold fungi metabolism. The pigments identified in the manuscripts included cinnabar (HgS), red lead ($Pb_3O_4$) and orpiment (As2S3), all only detected by XRF as they do not show mid-infrared absorption. Lapis lazuli ($Na_{8}…10A_{l6}Si_6O_{24}S_{2}…4$), azurite ($Cu_3(CO_3)_2(OH)_2$) and green copper pigments, e.g. brochantite ($CuSO_4$*Cu3$(OH)_6$) could be identified clearly by both, FTIR and XRF. Furthermore, we were able to detect beeswax on the surface of several folia of a codex, most probably resulting from candle light illumination.

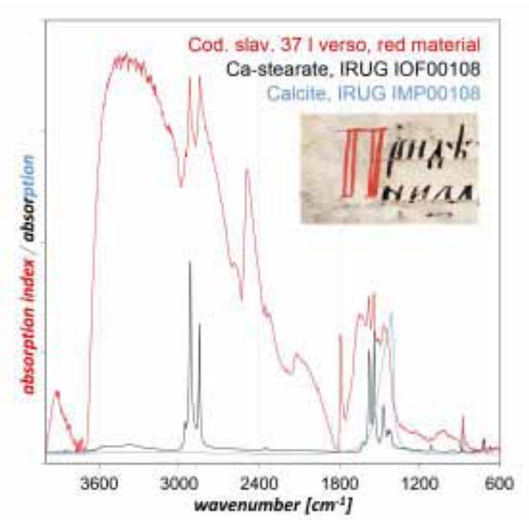


**Figure 1.** Calcite and calcium stearate could be identified by reflection-FTIR at a measuring point in a red area, whereas the red pigment (cinnabar) does not absorb mid-infrared radiation. The identification of cinnabar was achieved by XRF.

**Conclusion**

From our experiments we conclude that reflection-FTIR is a suitable method to identify pigments, inorganic and organic salts as well as certain other organic compounds (e.g. waxes) on the surface of parchments and illuminated manuscripts rather than for damage assessment of the parchment itself. Moreover, our experiments demonstrated that additional complementary methods (e.g. Raman spectroscopy) are required in order to characterize black ink materials.

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Invited Lecture

# LEATHER AND PARCHMENT ANALYSIS BY UV-VIS-NIR REFLECTANCE SPECTROSCOPY – FIRST RESULTS -

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As part of the bilateral collaboration between the Centre de Recherche sur la Conservation des Collections (CRCC) in France and the National Research & Development Institute for Textiles and Leather (INCDTP) in Romania, a research was initiated to quantitatively assess the impact of the environment on collagen-based materials. The objective of this work is to define, in fine, low-energy climate control in Archives and Museums.
Different leather and parchment samples were prepared at INCDTP using traditional recipes and part of these was aged artificially at the CRCC in controlled temperature, humidity and light conditions. A multi-scale analytical approach was developed focusing on non- and micro-destructive methods to monitor the changes and understand the alteration processes.
At the CRCC, the samples have been analysed by reflectance spectroscopy in the Ultraviolet-Visible (UV-Vis) and the Near-Infrared (NIR) domains. Reflectance spectroscopy is a non-invasive technique that can exist in a portable configuration, so that diagnosis measurements could be carried out in the storage or exhibition areas. This presentation will discuss the first results obtained for the different leather and parchments samples at four different stages of ageing using a lab-based spectrophotometer. It will show in particular that the UV-Vis and NIR regions provide complementary information regarding the nature and the degradation of the collagen molecule, specific amino acids, and tannins. The spectra gained from the lab-based instrument will also be compared to those collected using a portable equipment. Finally, based on the observations made on these first results, the future developments regarding data treatment and portable as well as imaging analytical techniques will be introduced.

Invited Lecture

# POSSIBLE METHODOLOGIES FOR IDENTIFING THE PROVENIENCE OF LITURGICAL EMBROIDERIES WORKED IN THE BYZANTINE TECHNIQUE

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Liturgical gold embroideries, despite unanimous scientific curiosity and appreciation, continue to unravel their manufacturing secrets. In spite of discovering some features of their technology, scholars consider that a lot of other characteristics are not yet completely understood. The main interest concerns the typology and functionality of embroidery supports, the nature and characteristics of silk and metal threads, the methodology of transferring pictorial image on the silk surface. Lots of artefacts travelled along the medieval civilized world, losing the memories of their origin. The cartons and craftsmanship evolved from one side to the other of the Christian world, in spite of historic events or liturgical limitations. The style, composition, iconography and comparisons with icons, frescoes or illuminated manuscripts are useful to identify the possible provenience of embroideries worked in the Byzantine style. The scientific research is not able to describe significant criteria for identifying particular patterns of workshop's production. The lack of comparative monographic studies about the Byzantine embroidery technique and limited access to collections, especially those from Mount Athos, Meteora, Israel, Ethiopia or Vatican introduces errors of assessment. Research on the original elements of working technique and materials may cover part of this approach, build methodologies and databases.

The liturgical Romanian medieval embroidery developed under the huge pressure of post-iconoclastic Ecumenical Conclaves, from the east and Catholic Church ideology from the west. The unifying process of the three feudal Romanian states have been interrupted by Slavic migration (6$^{th}$ c.) and Hungarians attacks from the Pannonia region (9$^{th}$-12$^{th}$ c.). The historic events have important impact in creating a new nation, the Romanians, having Latin origin and orthodox religion. The Assan's Brothers Wallach-Bulgarian Empire includes both parts of the Danube and dominates the Balkan Peninsula, being extremely important role in the development of this huge geographic area, until de middle of 13$^{th}$ c.

The embroideried sleeve fragment found at Dinogetia-Garvăn[1] (11$^{th}$c.) proves the contacts with Byzantium civilization and religion in, at least, one of the 35 fortify towns developed on

[1] Barnea, I& Ștefănescu. Ștefan - *Din istoria Dobrogei*, vol. III, Bizantini, Români si Bulgari la Dunarea de Jos, "Bibliotheca Historiae Romaniae", vol. 9, ed. Academiei RSR, Bucuresti, 1971. The fortified town is tutuated at

this Danube's shore. When the region was conquered by the Turks (13thc.-14thc), Wallachia and Moldavia developed as independent states, influenced by Byzantium social, cultural, religious and political systems. The Romanian liturgical workshops were established inside of important monastery centers or on the Voievod's domains. Their roots must be sought in the exodus of monks coming from Mount Athos, Meteora, Serbia or Bulgaria, trying to escape from Islamic persecution. They bought their own artistic and technique influence in the northern parts of the Danube: stylistically is rather difficult to be sure about the real provenience of objects, in the absence of inscriptions.

This paper is part of a comprehensive study dedicated to the specificity of Romanian embroidery technique. A preliminary study[2] included items from the Putna Monastery Museum, attested by inscriptions, mentioning the date, the workshop and the name of the donator. Working in interdisciplinary teams, it was intended to discover common characteristics of original technology: structure of the objects, the function of embroidered visible and invisible layers, constructing relief, the traditional types of working metal embroidery. The research dedicated to the provenience of natural dyes and the elemental composition of metal threads used in sacred embroideries and brocade valves is fundamental to confirm theoretic assessments, to understand and to select the main features of the genuine technique. This will be helpful to make the difference between the original parts of the object and the new ones, some of the artefacts being repaired using different materials. Romanian research is guided by comparison with the frescoes images from Romanian churches or in analogy with similar pieces from abroad. The previous studies regarding historical conservations show the possibility to use this data as temporal guide marks, by putting them in connection with information about the chemical nature of constitutive materials.

<u>First observations are of the research indicate (2013)</u>:

A. Identification of embroidery technical characteristics, similar with the Byzantine ones (13th-14thc.):

1. SPLIT CHAIN – used for embroideries worked before the 16th century.
2. The OUTLINE of the faces is GREEN, including the features of older portraits.
3. The MOUTH is very well marked and worked in red.
4. The HAIR is represented in detail (brown for young people and light blue for old ones).

B. A <u>*purple silk* layer</u> is specific to PUTNA MONASTERY, which almost have the rank of a dioceses. Similar Byzantine pieces are very rare (e.g. two "airs", Halberstadt Cathedral, 12thc).

C. A <u>*silk blue layer*</u> is specific to Stephan the Great embroidery workshops, probably in the last decade of his reign (1490-1504). Could this color be the "*signature*" of RADAUTI workshop?

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the confluence of Siret River with Danube, beeing an open door to imported or exported produts, including see routs.

[2] Cretu,I; Lupu, I.A.M – The Original Technique: A New Criteria to Identify a Liturgical Embroidery? in *Restitutio,* Buletin de Conservare-Restaurare, Muzeul National al Satului "Dimitrie Gusti"", nr.7/2013

D. *Red silk layer* coexist with the two, but it is not a local feature, coming probably from Italy.
E. *Silk green layer* appears only once on the epitrachelion 1496, with donor portraits and signature of donation "*Stephen and Alexander, the son of Stephen vv*", but with has atypical technical characteristics and materials.
F. The first half of the 16$^{th}$c. reflects the decreased interest for pictorial embroidery of the descendents of Stephen the Great, which donated only brocades with embroidered inscriptions in Byzantine technique, or finished the former items. The project (1996-2013) is the result of interdisciplinary collaboration between The National Museum of Art of Romania, the National Museum of Romanian History and Bucovina Museum, liturgical Museums from Putna and Sucevita Monasteries and well-known research centers and Universities from Belgium, Poland, USA and Hungary. The main goal is to build a methodology and a data-base to demonstrate identification of the liturgical embroideries provenience, by using scientific arguments and comparison with similar items. The research developed with the generous help of KIK/IRPA Bruxelles and of the *Cultural Heritage Advanced Research Infrastructures*, co-funded by the European Commission within the action “Research Infrastructures” of the Capacities Programme GA (No. FP7- 228330 CHARISMA ARCHLAB & FIXLAB 2011-2012).

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Invited Lecture

# MICROSCOPIC AND MOLECULAR NOVEL DISCOVERIES ON PARCHMENT BIODETERIORATION

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## Introduction

The defacement and destruction of parchment is due to the activity of microorganisms with extracellular proteolytic enzymes that make them metabolize collagen proteins through mechanisms of enzymatic hydrolysis of peptide bonds (Sterflinger and Pinzari, 2012). The structural proteins, not normally diffusible within the cells, are then converted into soluble peptides that can penetrate through the microbial cell wall. Microorganisms with these capacities are proteolytic bacteria and fungi that possess specific enzymes like collagenases, capable of cleaving the proteins of the parchment by hydrolysis. Fungi, however, can use as carbon sources also oils and waxes that can be constitutive of skins or be added during manufacturing processes. Recent studies conducted by Pinzari et al. (2012) and by Piñar et al. (2014a; 2014b) showed that microbial alterations on parchment are determined also by the salts present on the material surface, and that complex microbial communities more than single species have a role in the formation of the damage. These novel discoveries highlight a series of important issues from the conservation point of view. In fact, the environmental conditions that better preserve parchment from biodecomposition should be evaluated according also to the ecological peculiarities of the organisms that inhabit this material. Moreover, the disinfection of objects supporting the growth of a mixture of fungal and bacterial cells with different susceptibility to biocides could represent a thorny issue.

## Methods

Microbiological research carried out in the field of parchment biodeterioration was until recently based mainly on cultivation methods. Although these investigations were helpful to demonstrate the importance of microorganisms in deterioration processes, the results obtained covered only those few organisms that could be cultivated (1-5%). In addition, extensive cultivation strategies require more sample material than could be obtained from art objects. Combining microscopic (Scanning Electron Microscopy coupled with Electronic Dispersion Spectroscopy) and molecular analyses, proved to be a reliable tool to monitor the microbiota inhabiting different parchment samples and to establish a relationship between single species and the observed types of deterioration suffered by the parchments investigated (Piñar et al. 2014a; 2014b).

**Results and Discussion**

Members of the *Actinobacteria* and species of *Aspergillus* were detected as common microbial and fungal denominators in several investigated ancient parchment samples (Figure 1). The salty environment provided by parchment actually selected, in many of the studied samples, halophilic and halotolerant microorganisms. It was also highlighted a role of some salts used in parchment's manufacture in the creation of a particular environment, that can promote the occurrence and activity of some bacteria, capable of precipitating biogenic crystals while using collagen as carbon and nitrogen source (Hexiong *et al*., 2014). These halophilic microorganisms may be responsible for the purple stain discoloration frequently observed on ancient documents made of parchments (Piñar *et al*. 2014a; 2014b). In particular, *Saccharopolyspora* species was shown to be a constant presence on most of the samples recently examined. Among the fungi, *Aspergillus versicolor* appeared strongly associated with deteriorated parchment samples, suggesting a sort of co-occurrence or even an ecological relationship between its role and that of halophilic bacteria. A relationship between the phenomenon of purple spots on ancient parchments and that of the “red heat”, identified in leather and other salted products, was recently proposed (Piñar *et al*. 2014a).

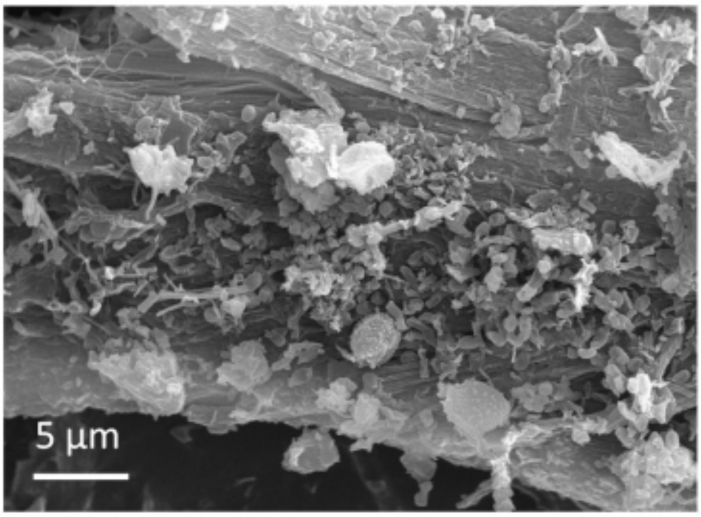


**Figure 1.** Damaged purple surface of an ancient parchment. The picture was obtained with High Vacuum Secondary Electrons SEM imaging on a gold sputtered sample obtained from an ancient parchment manuscript. The picture shows a collagen fibre covered with bacterial and fungal cells adhering on the surface of the fibre.

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Invited Lecture

# PARCHMENT: DAMAGE ASSESSMENT AND EVALUATION OF CONSERVATION TREATMENT AT THE COLLAGEN FIBRIL LEVEL USING ATOMIC FORCE MICROSCOPY AND AT THE MACRO LEVEL USING MECHANICAL TESTING

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The aim of this paper is to describe how atomic force microscopy (AFM) has been used to assess damage in parchment at the collagen fibril level on exposure to relative humidity (RH) fluctuations at a given temperature, and to pollutants. A method was developed for quantification of AFM images in the IDAP (Improved Damage Assessment of Parchment project EU FP5)[1] and data were found to correlate with the shrinkage temperature of parchment fibres. The effects of collagen denaturation were also observed at the macromolecular level by controlled-environment dynamic mechanical analysis[2]. The effect of internally generated volatile organic acids in storage enclosures was recently evaluated in the MEMORI project (EU FP6 (Grant Agreement no. 265132)[3]. This simulates damage that could occur under improper storage conditions. Exposure to the presence of volatile organic acids caused a lowering of pH, resulting in changes to the fibres, collagen denaturation, and surface gelatinisation. Localised regions where changes occurred have a different response to fluctuations in RH and temperature than intact regions and this promotes further damage. In the current NANOFORART project (EU FP7 ref. no 282816 http://www.nanoforart.eu) novel nanoparticle formulations have been developed and applied to model accelerated aged and historical parchment for adjustment of pH in selected regions. Application of alkaline nanoparticles [$Ca(OH)_2$ and calcium carbonate in selected solvents] showed an increase in pH

and also demonstrated, particularly in the case of calcium carbonate nanoparticles, a protective effect on the parchment with improved mechanical performance.

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# ORAL PRESENTATIONS

Oral Presentation

# EFFECTS OF AEROSOL PARTICLES ON COLLAGEN MATERIALS

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## Introduction

The research project "The methodology of evaluation of influence of air quality on book and archive collections" (2011-2015) should make more clear the relationship between environment quality and conditions of stored books and archive materials.

Solution of the project is divided into three topics complementing one another: a) development of advanced monitoring of gaseous pollutants and dust particles, b) evaluation of influence of individual pollutants on book and archive collections, and c) proposal of measures leading to improvement of indoor environment.

## Material and methods

Samples were prepared for testing the effects of aerosol particle on properties of collagen materials – squares of size 100 x 100 mm.

The following collagen materials were used: binding parchment, calf alum tawed leather, goat vegetable tanned binding leather, calf vegetable tanned binding leather, goat.

Thickness, area stability, weight, and color scheme were observed in the samples.

Samples were deposited in depositories, in which measurements were carried out of gaseous pollutants and dust particles. The selected depositories are situated in areas in the Czech Republic, which basically differ in air quality and in the quality of depositories: State Regional Archives in Trebon – a tourist region, Research Library of South Bohemia in Zlata Koruna - an agricultural region.

A set of control samples was deposited in laboratory conditions in the National Library in Prague. Originally planned one year´s exposure time of samples in depositories was extended to two years after visual estimation of extent of sample dustiness. After this time, characteristic optical, chemical and physical properties have been evaluated in samples and compared with those of control samples.

Mold infection of samples of collagen book materials was found during check of samples deposited in Trebon ca. one year after storage (as a result of increased air moisture owing to exceedingly rainy weather in summer season). Two sets of samples were repositioned from station in Trebon to National Library into laboratory temperature and relative humidity on

July 2013. One set of samples remained in Trebon, which was least affected by growth of microorganisms.

With respect to the fact that dust contamination of collagen materials deposited in selected depositories proved to be very small (0.1 weight per cent of settled dust), other samples of collagen materials were prepared, on which dust was applied by rubbing dust in by the help of a bag made of soft unwoven fabric. Real dust from depositories of the National Library Klementinum was used for application of dust, from which crudest particle

(splinters of paper, etc.) were removed by the help of a small sieve, which could mechanically damage surface of tested materials during rubbing in.

The following collagen materials were used: binding parchment, goat vegetable tanned binding leather.

Square shaped samples of side of 100 mm were conditioned at 23 °C and 50% RH and their weight and color schemes of flesh side and grain side of the sample were found out.

Samples of the right hand side of the materials were used as controls, dust was applied on the left hand side of the samples according to the schedule Table 1.

Table 1. List of samples

| Sample | Dust application | Ageing |
|---|---|---|
| 1L | Flesh side | Laboratory conditions |
| 2L | Flesh side | Thermal - 120°C, 24 hours |
| 3L | Flesh side | Variation in moisture 20% and 70% RH, 40°C |
| 4L | Flesh side | (Thermal + variation in moisture) 2x |
| 5L | Flesh side | Thermal + variation in moisture |
| 6L | Flesh and grain side | (Thermal + variation in moisture) 2x |
| 7L | Flesh and grain side | Thermal + variation in moisture |
| 8L | Grain side | Thermal + variation in moisture |

**Results**

On samples of vegetable tanned leather, 3.8 - 4.3 weight % of dust was deposited in case of application on the flesh side of the sample, ca. 0.5 weight % of dust when applied on the grain side, and when applied on both flesh and grain sides, 4.9 and 5.9 weight % of dust, respectively.

In parchments, these values were similar, with larger scatter: 4.4 – 6.7 weight % in application on flesh side of the sample, 0.4 weight % in application on the grain side, and 5 - 6.6 weight % when applied on both sides.

Samples with deposited dust were subjected to artificial ageing according to the diagram, see Table 1. Effect of dust on condition of collagen materials was assessed according to variations of shrinkage temperature.

Shrinkage temperature of parchment with a layer of dust was less affected in artificial ageing, than shrinkage temperature of tanned leather.

Decrease of shrinkage temperature in vegetable tanned binding leather is higher in samples with dust applied only on the flesh side, in samples with dust both on the flesh and grain the decrease of shrinkage temperature is lower, although amount of applied dust on the sample is bigger. This tendency is not so distinct in parchment.

## Conclusions

Dust layer on vegetable tanned leather negatively affects its hydrothermal stability. Effect of dust on hydrothermal stability of parchment was not proved.

**Acknowledgements**: Presented results were obtained with the support of the research project no. DF11P01OOVV020 "Methodology of Evaluation of the Effect of Air Quality on Library and Archival Collections" - Ministry of Culture of the Czech Republic.

Oral Presentation

# THERMAL CHARACTERIZATION OF NEW, ARTIFICIALLY AND NATURALLY AGED LEATHER AND PARCHMENT SAMPLES

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## Introduction

Handwritten books, codices and letters stored or displayed in historic buildings are vulnerable to changes in the outdoor environment due to the limited climate control. Understanding the degradation mechanisms and changes in the structure of leather and parchment could help to find a proper way to protect these pieces from the aging and the environmental effects. In order to identify the aging mechanisms different analytical methods, among them thermoanalytical methods were used.[1,2]

In this work natural aging mechanisms were modeled by acid and alkaline pretreatments. Structural changes of the samples during the aging were explored using thermoanalytical methods, in order to understand the response of parchment and leather to the environmental effects.

## Materials

The new parchment was made from goat and the leather from calf skin. The leather was tanned by natural plant tanning agents. The aging modeling pretreatment conditions are given in Table 1. The historical parchment is from the Historical Archives of the University of Turin (Italy) from 1832. The historical leather sample originated from an old gospel Blaj (Romania) dated 1765.

## Methods

*Thermogravimetry-Mass spectrometry (TG/MS)*

About 3 mg sample was measured in argon atmosphere at a flow rate of 140 ml min$^{-1}$ using the TG/MS system. The samples were heated at a rate of 20°C min$^{-1}$ from 25 to 1000°C in a platinum sample pan. The evolved products were introduced through a glass lined metal capillary heated at 300°C into the ion source of the mass spectrometer.

*Pyrolysis-Gas chromatography/Mass spectrometry (Py-GC/MS)*

Approximately 0.8 mg samples were pyrolyzed at 600°C for 20 s in helium atmosphere using the pyrolyzer interfaced to the GC/MS. The pyrolysis products were separated on a DB-1701 capillary column. The GC oven was programmed to hold at 40°C for 2 min then increase the temperature to 280°C (hold for 5 min) at a rate of 6°C min$^{-1}$.

**Table 1.** Pretreatment types and conditions of new leather and parchment

| Pretreatment type | Conditions | Neutralizing | Drying |
|---|---|---|---|
| Alkaline | $Ca(OH)_2$+NaOH 25°C, 48 h | 1 % $(NH_4)_2SO_4$ | 120°C 96 h |
| Acid | 0.5 M acetic acid 4°C, 48 h | 0.7 M NaCl | 120°C 96 h |

**Results and discussion**

*TG/MS experiments*

Leather and parchment behave differentially during the linear heating in TG/MS. More char yield was observed from leather samples then parchments, due to the cross-linked collagen structure of the tanned leather. Figure 1 shows the TG and DTG curves of new, artificially and naturally aged leather and parchment samples. The main decomposition process starts at the same temperature of all four examined parchment samples, however their maximum rate of decomposition are slightly different. The DTG curve of alkaline treated parchment is more similar to the naturally aged historical sample. There is a peak on the DTG curve of the alkaline pretreated parchment samples at about 690°C, indicating the decomposition of inorganic carbonate content.

*Py-GC/MS experiments*

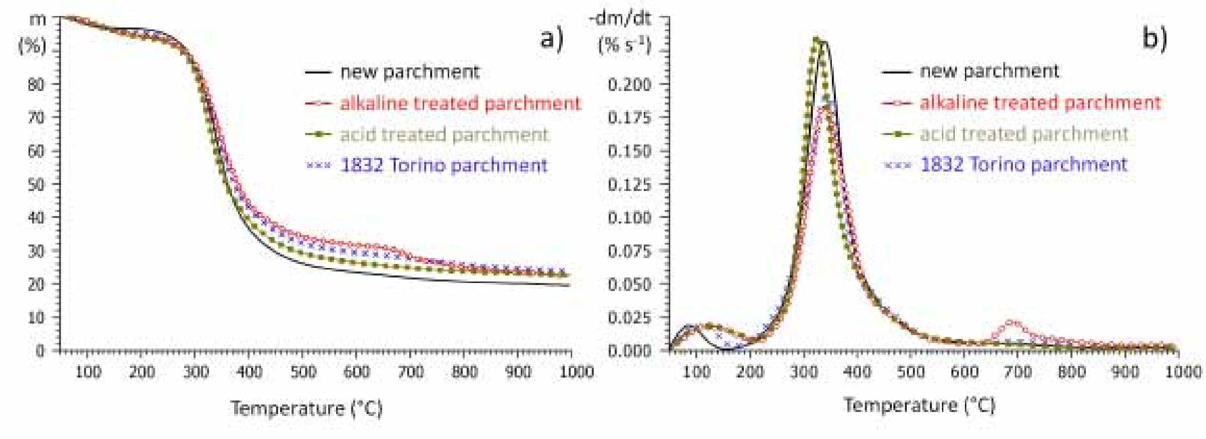


**Figure 1.** Thermogravimetric (a) and derivative thermogravimetric (b) curves of new, artificially treated and naturally aged parchment samples

Pyrolysis-gas chromatography/mass spectrometry has been applied to reveal the changes in the pyrolysis product distribution of leather and parchment samples after the pretreatment and after the natural aging. The peaks at lower retention time correspond to the lower molecular mass products of the collagen. $SO_2$ was formed mainly from the $CH_3$-S- and $CH_2$-SH- groups of the sulfur containing amino acids. The main decomposition products of the leather and parchment samples are the aromatic compounds and the diketopiperazines (DKP), which are cyclic dipeptides formed from the amino acids (Figure 2).[3,4]

According to the results, the evolution of the aromatic compounds decreased after the artificial aging as well as the natural aging. The yield of DKP's did not change. 1H-pyrrole-2-carboxamide (retention time: 26 min) can be seen on the pyrolysis gas chromatograms of new, acid and alkaline treated leathers as well as the parchments. The small peak disappears from the pyrograms of the historical samples so the amount of the peptide bonds decreased under the aging process. At lower retention time (5 min) can be found the 1-vinylaziridine, which was only formed during the pyrolysis of the alkaline treated and historical sample.[2]

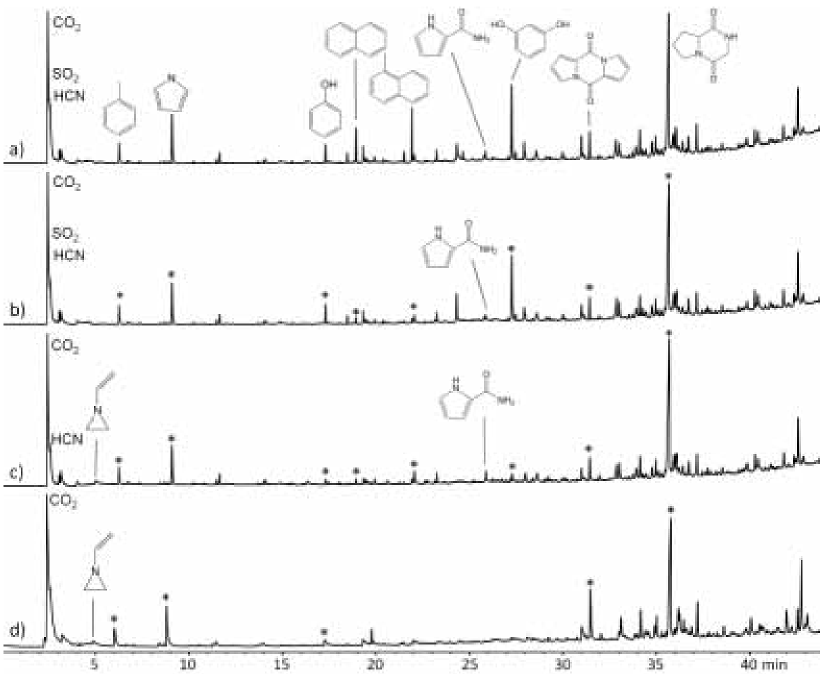


**Figure 2.** Pyrolysis chromatograms of new (a), acid treated (b), alkaline treated (c) and historical leather (d) samples. Some of the main decomposition products are represented.

**Conclusions**

The decomposition of the naturally aged leather starts at lower temperature than that of the new sample. The thermal stability of parchment samples did not change after the treatments.

The main decomposition products are aromatic compounds and diketopiperazines (DKP), which are cyclic dipeptides formed from the amino acid content of the samples. According to the TG/MS and Py-GC/MS, the evolution of the aromatic compounds decreased after the artificially aging as well as the natural aging. The yield of the DKP's did not change. The results show that after the alkaline treatment the thermal behavior of the leather is very similar to the naturally aged leather's. Modeling of the aging process using organic acids was not effective. The alkaline treated leather can model the 300 years old leathers and parchments during the thermal experiments, thus avoiding the application of the destructive analytical methods on the precious samples.

**Acknowledgement**

This paper is based on some of the outcomes of the Bilateral Cooperation between Hungary and Romania Assessment and mitigation of impact of climate on library and archival heritage: experience, research, innovation (LIBER, CB 671/2013). The authors are grateful to the TÉT_12_RO and OTKA K 81959 projects for the financial support.

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Oral Presentation

# MULTISPECTRAL IMAGING AND IDENTIFICATION OF WRITERS OF HISTORICAL DOCUMENTS

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## Introduction

This work presents investigation methods for degraded and historical manuscripts. Due to the bad condition of the manuscripts, the ancient writings have been imaged with a portable MultiSpectral Imaging (MSI) system in order to enhance the legibility of the degraded writings. Additionally, three different post-processing techniques have been applied on the multispectral images: These methods are based on dimension reduction and allow for a further contrast enhancement. Additionally, a method for the automated identification of writers of ancient Slavic manuscripts has been developed. This paper provides an overview on the manuscript investigation techniques mentioned.

## Methodology

The objects of investigation have been created starting from the 10th century and are partly in a poor condition, including faded out script or mold infestations on the parchment and may even contain palimpsests, i.e. manuscripts that contain an initial text that had been erased and overwritten by a younger text in order to save costly material. MSI has proven to be capable of enhancing the contrast of such degraded writings, since it can be used to recover image details that are not visible to the human eye.[1]

Therefore, the objects investigated have been captured with a portable MSI system. Our portable MSI system employs two sets of LED panels, which provide 11 different narrowband spectral ranges, ranging from UltraViolet (UV) (at 365nm) to Near Infra Red (NIR) (at 940nm). Compared to an MSI setup that applies optical filters, the LED illumination has two major advantages: First, the heat put on the manuscripts is reduced since broadband illumination is not required. Second, geometrical distortions stemming from optical filters are avoided and an image registration step is not necessary since the optical characteristics are not changed during acquisition. The images are acquired by two cameras, namely a Hamamatsu NIR greyscale camera and a Nikon D4 SLR camera. As a result the multispectral images provided already improved contrast and readability of the ancient writings in several spectral ranges, such as the UV range - compared to ordinary white light illumination.

Nevertheless, due to their bad condition, some manuscript portions still remain unreadable. Hence, we have implemented three different enhancement techniques, all of which are based on dimension reduction. The dimension reduction techniques are used to lower the third dimension of the multispectral scan in order to extract the relevant information, which is in our case the handwriting. Thus, for manuscripts containing only one writing, the MSI scans are reduced to just one image to emphasize the ancient text. For palimpsests, on the other hand, the third dimension of the MS scan is reduced to two images emphasizing the two different layers of texts. The dimension reduction techniques investigated are: Principal Component Analysis (PCA), Independent Component Analysis (ICA) and Linear Discriminant Analysis (LDA).

PCA and ICA are unsupervised dimension reduction techniques, meaning that they find the relevant information within the MS scans by themselves. Contrary, LDA is a supervised dimension reduction technique and hence it is required to label a subset of the multispectral samples as belonging to different classes. The classes considered are in our case: Foreground (the writing) and background (the unwritten parchment). In the case of palimpsests the younger writing is considered as a third class. In order to avoid a time-intense labelling by a human investigator, we have proposed an automated labelling technique in[2] that is based on document analysis techniques. The resulting images were subjected to qualitative comparison. It was found by scholars that the images produced by the LDA based approach are partially superior to images produced by the remaining techniques. Additionally, it was found that the enhancement results are often superior compared to unprocessed multispectral images. One exemplar resulting image of the method and the corresponding PCA and ICA results are given in Figure 1.

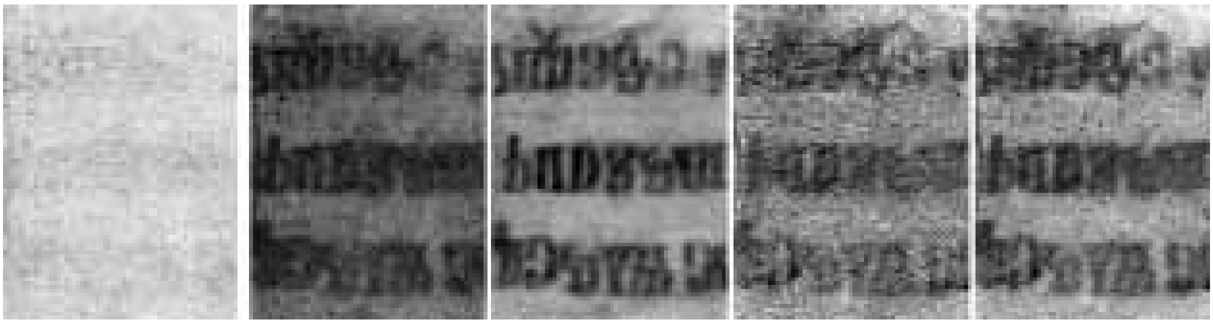

**Figure 1.** Portion of an ancient manuscript imaged with our MSI system. From left to right: White light image. UV fluorescence image. LDA based result. PCA based result. ICA based result.

The images of the ancient manuscripts are used to facilitate the work of philologists. These scholars are also concerned with the identification of scribes. By automating the task of writer identification, this method can be applied to a vast amount of historical documents and thus become a valuable tool for paleographers. For this purpose, we have recently proposed a writer identification method in reference 3: The method makes use of a text region segmentation method as well as a binarization technique in order to remove background regions and clutter.

It was experimentally found, that such regions containing no text worsen the performance of the algorithm. The writer identification algorithm itself is based on Fisher Kernels[4] which are calculated on Visual Vocabularies. The algorithm has been tested on 361 images of ancient Slavic writings and experimental results showed that the method is capable of correctly identifying the majority of the scribes.

## Conclusion

This work presents efforts taken to support the work of philologists, which are analysing ancient writings. These manuscripts are often in a poor condition and hence they have been imaged with a portable MSI system. This non-invasive investigation technique proved to be capable of enhancing the contrast of the faded-out writings. In order to further increase the legibility of the text, three different dimension reduction techniques have been applied on the multispectral scan, namely PCA, ICA and LDA. It was found that the techniques are capable of enhancing the contrast of the degraded writings, compared to unprocessed multispectral images.

Additionally, a method for the automated identification of scribes of ancient writings has been developed. The method has been tested on historical Slavic writings, which have been imaged during the course of our project. The technique proved to be useful for the identification of scribes of historical writings.

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Oral Presentation

# DIFFERENTIAL SCANNING CALORIMETRY. A VALUABLE TECHNIQUE FOR CHARACTERISING VEGETABLE TANNED LEATHER

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## Introduction

The chemical degradation of vegetable tanned leather is mainly caused by acid hydrolysis and oxidation due to environmental deteriorative factors like air pollutants, heat and light. In addition, the type of tannin material influences the rate of deterioration of leather. Recently Differential Scanning Calorimetry (DSC) has been successfully used to characterise and evaluate deterioration patterns in new, artificially aged and historical leathers[1-4].

## Materials

This paper reports some of the results obtained for:

- New leather from calf and sheep hides tanned with condensed (e.g. mimosa bark and quebracho wood extracts) and hydrolysable (e.g. chestnut wood extract) tannins. Leather samples were prepared by traditional methods at the National R&D Institute for Textile and Leather, ICPI Division, Bucharest.
- Artificially aged leather obtained by exposing new leather to accelerated ageing by heating at 70 °C in controlled atmosphere at 30% RH for 8, 16, 32 and 64 days using a Binder APT Line KBF-ICH test chamber.
- To study the synergistic effect of light, another series of samples was also exposed to visible light (4000 lx illuminance) during ageing. Irradiation corresponds to 60, 120, 250 and 500 year – dose, respectively.
- Historical leather objects (XVII-XIX century) from various Romanian Museums.

## Method

DSC measurements were performed both in water excess (samples of ~ 2 mg were suspended in 0.5 M acetate buffer solution, pH = 5.0, kept for 2h at 5° C in the calorimetric cell before measurement to assure reproducible hydration conditions and heated at 0.5 $C{\cdot}min^{-1}$ in the temperature range 20-100 $^{o}C$) and under nitrogen flow (samples of 3–5 mg were placed in open aluminum pan, heated at 10 $C{\cdot}min^{-1}$ in the temperature range 25-280 $^{o}C$).

## Results and discussions

Results for new leather showed that (i) hides tanned with condensed tannins were more stable than those tanned with hydrolysable tannins, independently of the animal species, i.e. the hydrothermal stability decreased as follows quebracho> mimosa > chestnut; (ii) mimosa and quebracho tanned calf leather was more thermostable than mimosa and quebracho tanned sheep leather.

For the artificially aged leather we observed that (i) hydrothermal stability linearly decreased on ageing time for both leather series analysed, whereas their structural heterogeneity increased; (ii) visible light irradiation induced a slight thermal stabilisation and altered the number and distribution of collagen populations with different thermal stability; (iii) softening temperature of collagen crystalline fraction did not significantly change during ageing.

For the historical samples micro DSC in excess water conditions provides both quantitative and qualitative parameters which enable us to (i) classify leather in two classes depending on their environmental stability, i.e. ability to withstand temperature and relative humidity values and fluctuations higher than those recommended by the current standards and guidelines; (ii) evaluation of de–tanning process which evolves in parallel with deterioration; (iii) distinguish between vegetable tanned leather and fat/ enzymatic tanned leather; (iv) discriminate between new and old artefacts, between an original artefact and a forgery.

## Acknowledgements

This paper is based on some of the outcomes of the Romanian ANCS project *Intelligent System for Analysis and Diagnosis of Collagen-Based Artefacts* (COLLAGE, PNII 224/2012) and Bilateral Cooperation between Romania and Italy *Advanced Techniques and Interdisciplinary Studies for Improved Assessment of Historical Parchment Documents* (ParIS, CB 638/2013).

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Oral Presentation

# PRELIMINARY STUDIES ON GAMMA RADIATION INFLUENCE ON THE PHYSICAL-MECHANICAL CHARACTERISTICS OF TEXTILE

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**Introduction**:

In this paper are presented the results of stage II of the project TEXLECONS: ’’Preliminary characterization tests before and after irradiation of textiles and leather cultural goods from cultural heritage deposits’’.

As part of the project, were analysed cotton and wool yarns before and after gamma irradiation at different intensities, in order to study the influence of radiation on yarn structure. We selected these two types of fibres because people used wool and cotton yarns for everyday clothing and decorative objects for the home. Our country is recognized for the production of high quality wool, while cotton yarns were predominantly brought from Asia.

**Contents**

For the cotton and wool yarns physical-mechanical analysis and SEM observations were performed before and after irradiation. The same analyses were repeated after a 6-month period.

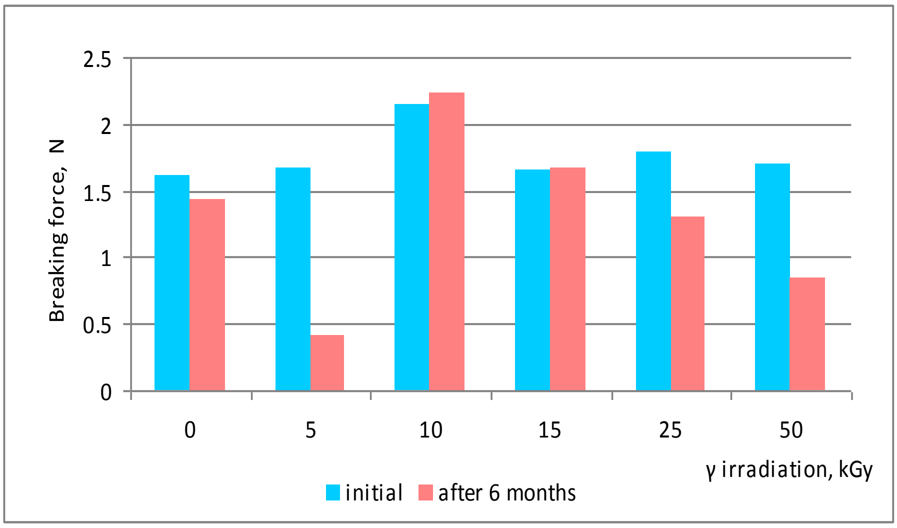


**Figure 1.** Breaking force for the irradiated wool yarns samples: initially (turquoise) and after a 6-month period (pink).

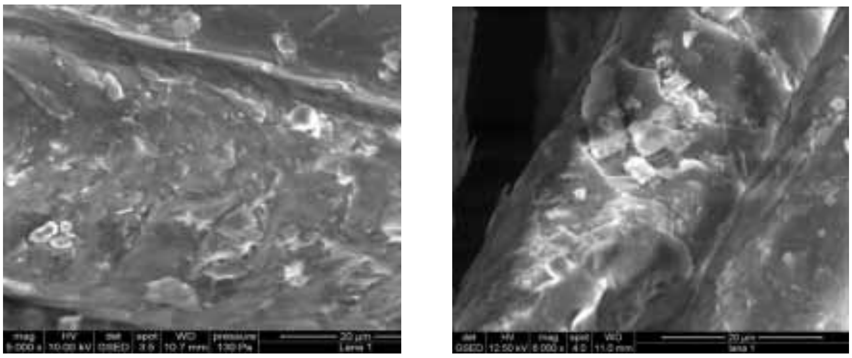

**Figure 2.** Wool sample before irradiation and after a 6-month period following the irradiation with 5 kGy

## Conclusions

It has been noticed that both for cotton and for wool yarns irradiation with a 5 and 10 kGy doses of gamma radiation does not induce significant changes of the yarn properties, a slight increase of the measured parameters values being observed.

SEM images indicate a slight modification of the yarn cuticular layer when the irradiation dose is 5 kGy and 10 kGy, thus confirming the physical-mechanical properties. A significant degradation is noticed for the yarn irradiated with 25 kGy, and this explains a decrease of breaking forces' values.

After six months for wool yarns irradiated with 5, 25 and 50 kGy a significantly decreased of breaking strength is notice, while the yarns irradiated with 10 and 15 kGy a slight increases of values being observed.

Breaking force does not decrease significantly for intensities of 5 and 10 kGy, but increases slightly for the cotton yarn irradiated at 25 kGy, after 6 months storage.

Oral Presentation

# NON-DESTRUCTIVE INVESTIGATION OF 11-12TH CENTURY PARCHMENT DOCUMENTS PRESERVED IN THE STATE ARCHIVES OF TURIN

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**Introduction**

Two groups of 11th-12th c. parchment documents from the *Novalesa* and *Rivalta* monasteries in Italy were investigated by optical microscopy (OM) and infrared spectroscopy (FTIR/ATR), within a cooperation bilateral agreement between Italy and Romania.[1]

Based on a large amount of data acquired on new and artificially aged collagen based materials in the last years [1], the work aimed to identify materials added to parchment during the manufacturing process and evaluate damage assessment in parchment. Analytical data obtained by FTIR/ATR was processed as indicated in literature.[2,3] Taking the opportunity to investigate such old parchment documents, experiments also aimed to understand the advantages and limitations of FTIR/ATR in this approach.

**Results and discussion**

About 330 measurements were performed on both sides of the 52 documents studied. More than 85 % of the documents contain calcium carbonate, which is present on both sides, in different amounts. On most of the documents the presence of aluminosilicates was also observed. About 10 documents presented areas of intervention, mostly on the edges. Measurements performed on such areas showed the presence of a carbohydrate compound (probably starch and Japanese paper) and a synthetic polymer, polyvinyl acetate (PVA). As this compound was first prepared at the beginning of the 20th c., the interventions should be placed after this date.

Measurements performed on different areas of the same parchment were in many cases very different, which confirm the parchment heterogeneity. In what damage assessment is concerned, the experiments showed that, with some exceptions, parchments are not degraded by denaturation (present a difference of the amide I and amide II peak positions around 90).

Some of the documents present higher values which mostly correspond to visual gelatinized areas, where a signal around 1574 $cm^{-1}$ was also observed. According to our knowledge, this signal was never mentioned in literature. Based on experiments performed on parchments exposed to high temperature, its presence may be connected with gelatinization.

## Conclusion

FTIR/ATR may be used for non-destructive investigation of parchment documents. It could offer information regarding the parchment manufacturing technique based on the compounds identified on the surface and could reveal the restoration areas and the compounds used for restoration. The latter could further suggest the moment when the intervention took place. The level of degradation at the molecular level may be also estimated. FTIR could also offer information about past aggressive conditions the parchment document supported, as for example its exposure to high temperature.

Ideally, for a more detailed approach on degradation observed at different levels, from macroscopic to molecular, the information should be correlated with that provided by other analytical techniques. However, the more detailed the information is, the larger sample size is required. The high “pro” on the use of FTIR/ATR is non-destructiveness (no sample is required) but the amount of information

## Acknowledgements

The present work was developed within the Romanian-Italian bilateral agreement *Advanced techniques and interdisciplinary studies for improved assessment of historical parchment documents* (CB 638/2013) and COLLAGE project (*Intelligent System for Analysis and Diagnosis of Collagen-Based Artefacts*”, PNII 224/2012, www.collage.com.ro. The authors are grateful to the Italian Ministry of Foreign Affairs and International Collaboration (MAE), Directorate General for the Country Promotion and to UEFISCDI Romania for the financial support.

## References and notes

1.The work mentioned was carried out within the following projects: Intelligent System for Analysis and Diagnosis of Collagen-Based Artefacts (COLLAGE, PNII 224/2012, in progress); The influence of environmental factors in the conservation of collagen based museum objects (Bilateral Agreement RO-AT, CB 227/2009, 2009-2010) and Experiments aiming to establish the optimum microclimate conditions for historical parchments preservation (Bilateral Agreement RO-AT, CB 549/2012, 2012-2013), the last two projects having as partner Institute of Science and Technology in Art – Academy of Fine Arts, Vienna

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Oral Presentation

# EVALUATION OF SOME CONSERVATION TREATMENTS FOR PARCHMENT ARTEFACTS

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## Introduction

The present study aims to identify a protocol for the validation of analytical procedures for the restoration of parchment, which sees the joint action of conservators, restorers and researchers. The method adopted consists of a multiscale examination based on non-invasive and micro-invasive methods to characterize the morphological, structural and physical-chemical properties of the new parchment and that subjected to artificial aging treatments followed by restoration operations such as direct humidification with hydroalcoholic solutions of different concentrations; softening with polyethylene glycol and with aqueous solution of ethyl alcohol, urea and sodium chloride, with cream-based protective lanolin and bibliobalsamo®crema Frati&Livi, etc.

## Materials and methods

The new scrolls obtained from INCDTP-ICPI of Bucharest have been previously subjected to heat treatment by radiation (heat flux: 20 $kW/m^2$ and 80 $kW/m^2$) and convection (fan oven at 200 °C). The parchments damaged by heat were examined before and after the treatments mentioned above by means of non-invasive spectroscopy, FTIR/ATR and differential scanning calorimetry DSC.

## Results

It was observed in this work that the use of alcohol and/or substances that may affect the ability of the collagen molecules to establish hydrogen bonds, may interfere with the peptide bonds along the collagen triple helix causing structural alterations at the molecular level. Also, substances such as isopropyl alcohol, PEG 200, acetone and urea can induce a change in the structural parameters of collagen causing changes in the physical-chemical and mechanical properties of collagenous tissue.

It was noted that the use of alcoholic solution of urea and sodium chloride is more effective when followed by drying under tension by means of the magnets. It seems that the drying under tension generally has a stabilizing effect. It was found that if necessary, isopropyl alcohol should be used in its pure state and followed by drying under tension. Finally, based on our results, the use of PEG 200 in any formulation and concentration and bibliobalsamo®crema Frati&Livi is discouraged. The reported results have important implications for the work of conservation and restoration of parchment.

**Acknowledgement**

The present work was developed within the Romanian-Italian bilateral agreement *Advanced techniques and interdisciplinary studies for improved assessment of historical parchment documents* (CB 638/2013) and COLLAGE project (*Intelligent System for Analysis and Diagnosis of Collagen-Based Artefacts*", PNII 224/2012, www.collage.com.ro. The authors are grateful to the Italian Ministry of Foreign Affairs and International Collaboration (MAE), Directorate General for the Country Promotion and to UEFISCDI Romania for the financial support.

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Oral Presentation

# DECONTAMINATION OF TEXTILE, LEATHER AND PARCHMENT ARTEFACTS BY GAMMA IRRADIATION

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**Introduction**

Cultural heritage (CH) artefacts made of organic materials such as textile, wood, paper, leather, parchment are attacked by insects, fungi, yeasts, moulds and bacteria that feed with them. These biological agents affect the CH artefacts causing changes in appearance, loss of strength, partial or total destruction of the material. All of these biological threats will affect not only the cultural heritage artefacts but also the health of the people working with them. Due to the specific contamination of old items (especially of those recovered from archaeological sites and graves), the problems related to the work environment may be considerable different from the usual workplaces that are dealing with biological threats such as health care facilities. This is the reason for uncovering new sanitizing methods and agents to be applied for cultural heritage storages and workplaces.[1]

The fungicidal and bactericidal effect of the ionizing radiation is indubitable. Radiation sterilization is currently one of the few existing industrial sterilization methods used in the field of the manufacturing of medical devices and pharmaceutics.

After the irradiation treatment, both bioburden (microbial load of the items) and degradation effects (chain scission, oxidation, etc.) depend on the absorbed dose.[2,3] High radiation doses will highly decrease the bioburden (exponential decay), while low doses will lead to a lesser degradation on the irradiated materials.

The purpose of this work is to identify the maximum irradiation dose that does not affect the materials exposed to gamma rays for decontamination purposes.

Material and methods

Experimental models of leather, parchment and textile -wool, silk, cotton, hemp and linen - and archaeological samples of textile form different sites were exposed to several doses of gamma radiations. To simulate the effects of natural physical chemical aging some textile samples (Figure 1) were artificially degraded at 80 °C and 65% relative humidity to check possible differences of gamma irradiation post effects.

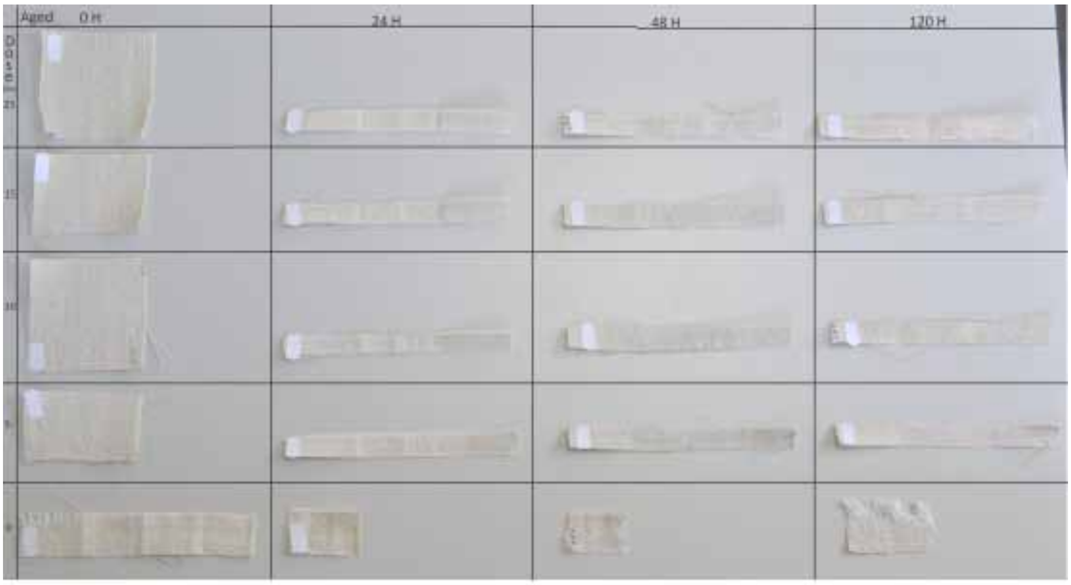


**Figure1.** Textile experimental models of flax gamma irradiated and artificially aged

Several techniques, infrared, visible and electron paramagnetic resonance spectroscopy, thermogravimetry and mechanical tests were used for investigation of the physical chemical properties of the studied samples but only the results obtained by infrared spectroscopic methods are reported in this work. Microspectrometric and non destructive macroscopic, Attenuated Total Reflectance (ATR) and Diffuse Reflectance Spectroscopy (DRS) techniques were used for investigation.

**Results and discussion**

The infrared spectra pre and post gamma irradiation are very similar. As an example, the ATR spectra of a quebracho tanned goat leather unirradiated and irradiated with 10 and 25 kGy are shown in Figure 2.

The difference between the frequency of vibration of amide I and amide II bands was calculated from the spectra and is shown in Figure 3.

The small decrease in the amide I-amide II frequency of vibration shift indicates cross linking of collagen and stabilization of the tridimensional structure of leather. The influence of this effect on the preservation of leather has to be evaluated by specific tests.

**Conclusions**

Very small spectral changes observed after gamma irradiation of textile, leather and parchment up to 10 kGy for cellulose based artefacts and up to 20 kGy for protein based artefacts recommend the use of the treatment for biological decontamination.

The study will continue with the aim to obtain the safe maximum irradiation dose admitted for decontamination using in correlation the results obtained by other physical chemical methods.

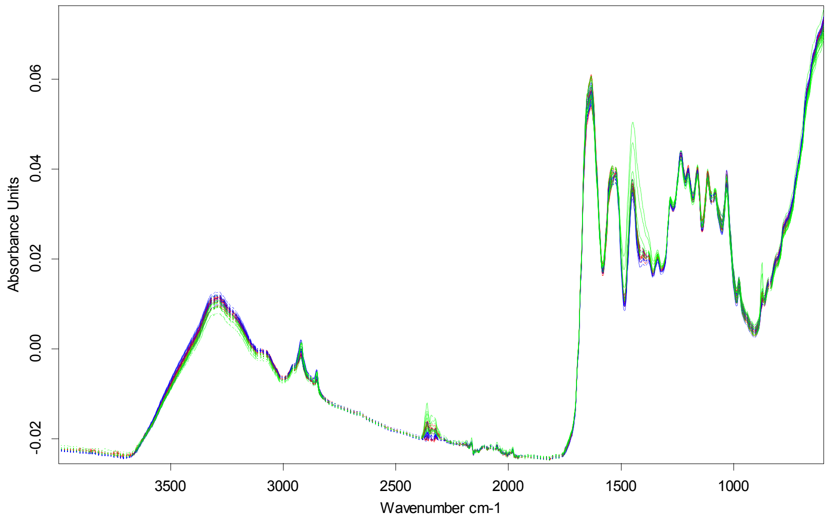


**Figure 2.** ATR spectra of quebracho tanned goat leather pre and post irradiation

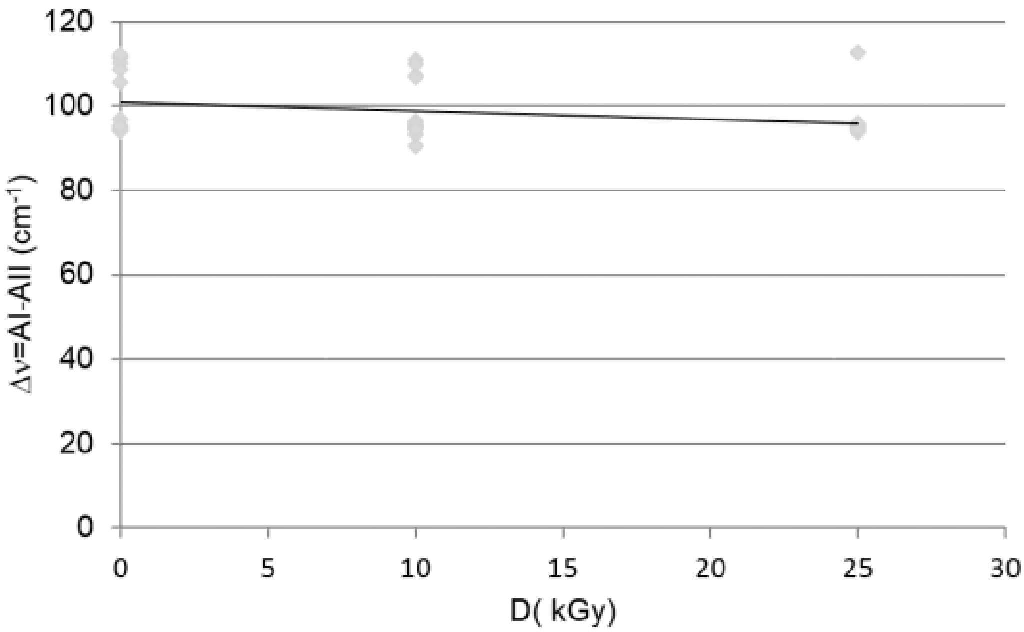


**Figure 3.** Variation of amideI-amide II frequency of vibration shift with the irradiation dose


**Acknowldgements**

Experimental models of textile, leather and parchment and archaeological artefacts were kindly provided by colleagues from the National Museum Complex “Moldova” of Iasi and National Institute of Research and Development for Textiles and Leather of Bucharest. This study was partially supported by the Romanian National Authority for Scientific Research, Executive Unit for Financing Higher Education, Research, Development and Innovation (UEFISCDI), project TEXLECONS, Contract No. 213/2012 and project ETCOG, Contr. C3-05 IFA-CEA/2012.

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# POSTER PRESENTATIONS

Poster Presentation

# ILLUMINATED MANUSCRIPTS ON PARCHMENT AN ANALYTICAL STUDY ON THE MATERIALS FROM TEXTS AND DECORATIONS

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The conservation of illuminated manuscripts on parchment is a very challenging task. Highly valued for its imagery, the written or painted layers within a book or a document can be very problematic for the physical survival of the object. The pigments and their attachment to the parchment can be threatened by the environment or even by pigments themselves. Significant deteriorations can be determined by unbalanced chemical compositions of gall inks, leading to the formation of degradation products under the action of the environment.

In these circumstances, a non-invasive analytical survey at detailed level is needed in order to make key observations that will uncover not only technical details, but also structural and qualitative information on parchment and decoration materials, that can be essential for their preservation. The present study includes microscopic (SEM and OM) observations on inks and pigments, along with spectroscopic techniques (micro-Raman, FTIR, XRF) for pigments identification and characterisation.

Poster Presentation

# A UNIQUELY EMBROIDERED TRADITIONAL ROMANIAN BLOUSE. DEGRADATION AND CONSERVATION ISSUES

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## Introduction

A typical folk blouse, embroidered with symbolic ornamental motifs (winged horses, the tree of life), in silk and golden metal threads, the object described bellow is part of Bucovina Museum's ethnographic textiles collection. Several decades ago, in order to stop a devastating biological attach, a chemical treatment was applied to, which, however, in the long run, had negative effects, as it triggered the corrosion of the alloys in the metal threads, and, subsequently, a series of other degradations.

Dating from late 19th century, the blouse (Figure 1), embroidered with silk, cotton and metal threads on homespun cotton fabric, was made in the household, to be worn on holidays.

The blouse was made out of one fabric bolt in front, and two on the back, while the sleeves were made from one length of cloth, with a rectangular part, cut and embroidered separately, "altiţa", joining the upper part of the sleeves. The rectangular pieces of cloth were cut and embroidered separately, and assembled using a blanket stitch, in tile-colour yarn; the blouse is gathered round the neck using a cotton string, "brezărău".

*The decorum* is organized in ornamental registers, on the shoulders, arms and chest. The chest and the back are decorated with vertical, narrow rows of floral motifs, embroidered in coloured silk.

**Figure 1.** The blouse

The most representative decoration, however, is the embroidery on the sleeves, following the three parts ornamental motifs pattern: „altiţă - încreţ - râuri". *Altiţa*, (Figure 2) cut and embroidered beforehand, is decorated with rare zoomorphic motifs, depicting winged horses, worked in coloured silk and black cotton yarns. The motifs are organized in four horizontal, parallel, repeating ornamental registers, separated by a border of decorative stitches, namely two rows of oblique stitches, in black cotton, the space within filled with four rows of golden metal threads stitches (chain stitches, worked from left to right).

The *încreţ* (Figure 3) is decorated with repeating geometrical motifs (the rhombus and the cross, typical, traditional ornamental motifs, are predominant), worked in kaki-green silk, using the straight and half a straight stitch. The rest of the sleeve is decorated with vertical rows of floral motifs (*râuri late*). The ornamental motifs represent another traditional, symbolic, decoration, namely the “tree of life”, depicting vegetal (stylized body, branches, leaves and flowers) and zoomorphic (stylized birds) elements; the “tree of life” (Figure 4.) is bordered on each side by narrow rows of floral motifs. The ornamental motifs, for both *altiţa* and *încreţ* are worked in coloured silk and black cotton, using the cross stitch, the straight and half a straight stitch, the vertical, oblique and horizontal stitch, and the chain stitch.

**Figure 2.** The *altiţa*

**Figure 3.** The *încreţ*

**Figure 4.** The tree of life

The object underwent a series of *investigations*, in order to identify the nature of the fabric and threads, and the embroidery technique; the analysis of the object, the micro and macro photographic documentation, the physical and microscopic investigations, all were performed in order to determine the nature of the degradations and their causes, and to make an informed decision regarding the restoration methodology.

The *condition* of the textile object was characterized by deteriorations of the fabric and silk, cotton and metal threads embroidery (Figure 5): dehydration, traces of dye stains, rust marks and corrosion deposits, formed due to the corrosion of the metal alloy (copper-zinc) in the metal threads (golden metal threads- coiled metal strip, wrapped around a textile core), heavy corrosion of the alloy, lacunas in the fabric and in the silk, cotton and metal threads embroidery.

**Figure 5.** Degradations of the metal threads

The *causes for the degradations* of the museum object were as follows: the original usage of the textile (stains, dye stains, lacunas); the storage conditions (rust marks, corrosion deposits, lacunas in the silk, cotton and metal threads embroidery, caused by the corrosion (Figure 6) of the alloy); the fluctuating temperature and humidity accelerated the corrosion process of the metal threads (which inevitably deteriorated the textile core as well - Figure 7), already affected by the use of a powerful insecticide[3] (the treatment was initiated in order to stop a devastating moths attack; however, it had negative consequences, as it accelerated the corrosion of the metal alloy, the metal threads themselves becoming a constant source of degradation, Figure 8).

**Figure 6.** Details: degradations in the metal threads embroidery, neighbouring silk and cotton embroidery and cloth – stereomicroscope

[3] According to the chemical investigations undergone by Bucovina Museum's investigator, while in contact with the humidity in the atmosphere, the hydrogen phosphate in the insecticide, Delicia, reacted with the copper in the metal alloy

According to the restoration methodology approved by Bucovina Museum's Restoration Commission following the Study Regarding the Degradation of Metal Threads, 2009, in order to save the textile objects severely damaged by the corrosion of the metal threads –source for a continuous degradation- the metal threads would be removed and replaced with mercerized cotton yarn, in a patinated gold colour, for the golden metal threads, following the original embroidery technique. Thus, considering the condition of the blouse, and the continuous degradation of the metal threads, the approved restoration methodology would be the best solution to save the museum object and, at the same time, to restore its original aspect.

**Figure 7.** Details: degradations of the coiled metal strip and textile core by stereomicroscope

**Figure 8.** Details: degradations caused by the continuous corrosion of the alloys in the metal threads

**Figure 9.** Previous restorations

**Figure 10.** The restoration of the embroidery in the original technique

Prior to 2009, similar objects, with similar degradations, were restored by consolidating the damaged parts on a new support fabric, and restoring the metal threads embroidery using khaki-green cotton yarns (as the metal threads turned khaki in colour, due to corrosion). The blouse under discussion was previously restored using the later methods (Figure 9); however, following the 2009 Study, the Restoration Committee agreed on removing previous repairs and restoring the object to its original aspect, by removing the deteriorated golden metal threads and restoring the embroidery using mercerized cotton yarn, in a patinated gold colour, following the original embroidery technique (Figure 10).

## Conclusions

The restoration methodology approved upon by Bucovina Museum’s Restoration Committee was considered to be the optimum solution to save the textile object and, at the same time, to restore it to its original aspect; although invasive, the restoration methods are, nonetheless, intended to save the blouse from further degradation by removing the deterioration source.

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Poster Presentation

# REWIVING ANCIENT CRAFTS WITH NEW TECHNOLOGIES AND IDEAS. EVALUATION OF FURSKINS BIODEGRADABILITY AS AN ECOLOGICAL TOOL FOR NATURAL PRODUCTS VALORIZATION

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## Introduction

Natural furskins are probably the oldest material used for body protection, which along the history played an important social role in marking the social position.

Restoring natural values is a weapon in the confusion of synthetic materials that mimic well the natural ones that are cheap but highly polluting. The furskins biodegradability labeling represents an important tool for the consumer awareness regarding the end life of their garments as compared to the synthetic ones.

The aim of our research was the development of a new technology for furskins processing in order to reach the maximum level of biodegradability and to preserve the genuine durability. For this aim we turned back to the technologies based on aluminum salts and organic materials and we have developed a quick method for biodegradability assessment.

The natural furskins manufactured as ecological prototype for biodegradable labeled products showed highest level of biodegradability and natural features.

## Experimental part

Goat furskins were processed with aluminum salts as alternative to chromium salt based technologies and were evaluated from the biodegradability point of view. The method for biodegradability was developed in the frame of BIOFUR project and is based on selected microorganisms which were grown on specific substrate. The biodegradability tests were carried out in OxiTop device on finished furskin samples by measurement of biochemical oxygen demand for 20 days as compare to a control sample (Figure 1).

The most biodegradabl  ere tested for the resistance to sewing and garment confection in industrial he wearing tests of prototype furskin garments are in progress and will show t f biodegradable furskins (Figure 2).

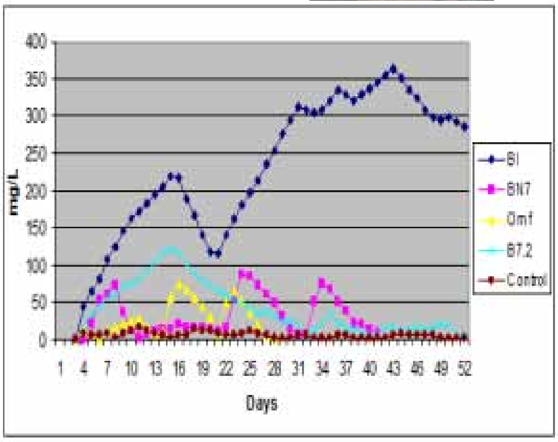


**Figure 1.** Furs biodegradability assessment

**Figure 2.** Biodegradable furskins coats prototypes

## Conclusions

- A new method for quick evaluation of natural furskins biodegradability was elaborated as a market tool for consumer awareness on natural products as compare to synthetic ones.
- Return to old methods of processing furs is an exercise to appreciate the durability and ecological values of traditional products.

**Acknowledgement**

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Poster Presentation

# "*PROCOVĂȚ*" FROM THE 13$^{TH}$ CENTURY, FROM THE COTROCENI MONASTERY

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Serban Cantacuzino, the ruler of Wallachia (1678-1688), raised the Cotroceni Monastery between 1679 and 1680. The church was designed as a royal necropolis. In 1821, Tudor Vladimirescu established his residence there and in 1852, during the time of Barbu Ştirbei, a part of the garden was organized. Life in the monastery was almost over through secularization of the monasteries fortunes in 1863. In 1866, Prince Carol I established his residence here, and in 1888 the former monastery cells were transformed in a palace of King Ferdinand I and Queen Maria. The present church is dedicated to Saints Sergius and Vah.

The *procovăț* (Romanian word for a textile which covers the bowl during the Orthodox religious service) presented in this paper is an 18$^{th}$ century liturgical embroidery from Wallachia and had belonged to the old church of Cotroceni Monastery. The *procovăț* was recovered before the monastery demolition in 1984. The object, which was made betwwen 1725 and 1750, is in the custody of the National Museum Cotroceni since 2012. In the central part of the *procovăț* there is a fabric made of red-burgundy satin, decorated with flowers embroidered with gold and silver threads. The green satin frame is decorated with floral and vegetal motifs, embroidered with metallic thread. Before restoration, the satin support had a dehydrated aspect, presented wrinkles, swelling, abrasions, tears, marks stitches, wax stains, oxidation of metal threads in embroidery and stains of dirt clogged. During the restoration in 1988-1989, performed at the National Museum of Art of Romania, mechanical cleaning operations were made and the piece was reinforced on the back with ochre-brown cotton satin.

Although time was extremely short, the present restoration included all phases: dismantling the piece, mechanical cleaning, textile softening with solution of ethyl alcohol, glycerine and distilled water, wet cleaning with a solution from the decoction of the *Radix Saponariae*, ethanol and distilled water followed by rinsing with distilled water to remove the impurities detached from the piece and from the trimmings and the fabric. Restoration also included drying with filter paper and then drying on the glass table, impregnation of the silk with CMC solution. Consolidation was performed on a textile support (cotton fabric), dyed in a neutral colour, on the frame, through many points of consolidation, the silk area between the motives being fixed by zigzag point, network reunification in areas with material lacks. For the surface protection, tulle dyed in the existing colours was used, outlining the patterns and embroidery through brush paintings with textile pigment, the tulle was fixed to the rest of the piece with dyed silk thread, surrounding the embroideries. The chromatic integration respected two fundamental principles of restoration: intervention readability as aesthetic attitude and reversibility, as work technique. After strengthening the silk on the cotton canvas and sizing the piece, netex was added on the back, fixed in point furrier, in order to equally take over the embroidery weight. The process was followed by reassembling parts of the piece by needle hand sewing, leaving a corner for verification.

On the silk fabric surface, realised in fundamental diagonal bounding, the system effects ordering in oblique lines was observed. Warp threads density is higher, so the oblique line has a slope sideways and the aspect on the front is different from that on the reverse, which results in an unbalanced density fabric. In terms of technical execution, in order to give the embroidery a more pronounced roundness, over the silk an uncombed cotton thick cord was use to outline the model on which the embroidery trimmings field was created. The metallic threads which form the frame are attached with double cross stitch, revealing the cross wires on the silk back. The metallic threads are not sewn but laid on given trail and caught almost invisible, from place to place. Typical for the embroidery of the 17$^{th}$-18$^{th}$ centuries, the number of colours is reduced to: red, green, yellow, rarely blue, the silk background is free and the ornaments form a frame to the embroidered piece.

Metallic threads were characterised by X-Ray Fluorescence (XRF) at the National Museum of Romanian History, Centre of Research and Scientific Investigation. The presence of silver in a silk thread was explained by the fact that silver is one of the most reactive metals and, in a humidified and polluted atmosphere, oxides as well as sulphur and chloride salts are formed, which react rapidly with amino acids in silk.

**Figure 1.** Details before restoration (upper) and image after restoration (bottom)

The various problems encountered during the restoration process, the manufacturing technique "decoding", collaboration with colleagues and support of the specialists in order to choose the best method of treatment, complete a picture of the teamwork that made the effort look easier, in a very short period of time. The embroidery execution beauty, with floral patterns in technical trimmings, post Brancovenian style with influences from Russian embroidery school, the accuracy of the ensemble, place the *procovăț* among the most valuable 18$^{th}$ c. works in our country.

**Acknowledgements**

The author is grateful to specialists in the National Museum of Romanian History, Centre of Research and Scientific Investigation for the XRF analysis and microscopy.

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Poster Presentation

# RESTORATION OF A FLAG BELONGING TO THE TOWN HALL OF RÂŞNOV, BRAŞOV

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## Introduction

According to the embroidery, the flag was dated at the beginning of the 19th century and belonged to the Society of Reading from Râşnov. This artefact was purchased by the Town Hall of Râşnov with the purpose of preserving the past. Professional restoration was demanded from ASTRA Museum.

## Short description of the object

The flag consists of two parts (flag and pennon) which combine various materials, such as: industrial fabrics, textile and metal threads, braids and tassels made of metal threads, decorative ribbons with textile and metal thread, metallic rings, wooden pole. The textile parts were assembled by manual and mechanical sewing.

Biological investigations had confirmed the nature of the textile fibres as being cotton and natural silk, while the chemical analysis had revealed the composition of the metals. The metal thread is a strip of copper based alloy, containing also gold, zinc and nickel, which was wrapped over a cotton textile core, coloured in yellow (the section of the stripe is between 0.35-0.02 mm). On the surface of the metal alloy, locally, there were identified brick-red corrosion products of copper (cuprous oxide).

## Assessment of the textile object and the interventions of conservation-restoration

The conservation state of the flag was very unstable, with degradations having affected the aesthetical aspect, the structure and the integrity of the materials. The following degradations were identified:

- dust and depositions of dirt over the entire surface;
- strong discoloration of the green silk;
- stains of unknown origin;
- crumpled fabrics and distended areas;
- a 70% loss of metal fringes, losses of tassels and braids of metal, which were attached through sewing;
- losses of textile fragments (red silk fabric);
- wear and tear;

- corrosion of metal components;
- deformation of the metallic rings, some of which were attached temporarily with safety pins because the original textile ears had been broken;
- inappropriate and rough sewing at the level of the wooden pole.

The intervention of conservation and restoration had imposed disassembling the object into pieces for a thorough and differentiated access to all layers of fabrics and for the treatment of the metal components.

Stages:

- the textile material was dry cleaned by vacuuming and wet treated by immersion in neophaline, then it was selectively pressured with weights of flat glass;
- the metal parts were cleaned mechanically to eliminate the corrosion products and complexing treatments were applied (immersion in aqueous solution containing EDTA; neutralization with demineralised water);
- protection of the metal components was assured with a 3% solution of Paraloid in ethyl acetate (immersion or brushing);
- delicate consolidation of the metal braids, with a synthetic textile thread of the same colour as the original ones;
- cleaning the pennon on the torn edges of the red silk and vacuum cleaning the other parts;
- dying the fabrics needed for the consolidations – the cotton in yellow and the natural silk - intense red;
- consolidation of broken fragments, worn and torn edges, or missing areas with additional material and by using the ‘Byzantine point’ technique;
- filling in the lacunae with red silk, sized according to gaps;
- filling in the missing braid with a similar one, which was obtained out of twisting textile threads;
- replacing the silk from the reverse of the pennon with new material, but keeping an original sample which was mounted below the pole;
- re-assembling the flag and the pennon by manual sewing.

**Conclusions**

Following the conservation and restoration interventions, the aesthetic aspect of the object was recovered, since this had been severely affected by functional wear and inappropriate storage conditions. The deposits of dirt were removed through dry cleaning, avoiding this way that the organic remains favours the development of mould and contribute to the acceleration of the textile fibres degradation. The treatment of metal elements had included removal of the corrosion products and applying a coating layer which ensures protection and restores the specific brightness. The fillings and the consolidations were made with compatible materials which were chromatically integrated to resemble with the original colours, in order to establish a pleasant visual effect. The remaining metal fringes were redistributed, as it was not possible to add any other new ones. Where the marks of the original pieces were visible, the imitation of the metal braids with textile ones allowed filling in the missing elements. The whole process was undertaken according to the restoration principles in museums and the interventions took into consideration both aesthetic criteria and durability aspects.

Poster Presentation

# THE ISSUE OF CONSERVING THE MEDALLIONS OF HISTORICAL FLAGS

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## Introduction

People's spiritual aspirations and their artistic vision and found their expression in wonderful creations, among which a special place is occupied by flags, banners and other heraldic symbols, representing the quintessential reflection of place and time civilization "*spiritus loci*".

In this perspective, flags are some of the most expressive marks of the human creative impulse, sanctified by history and legends.

In the European culture, for example, the chromatic and practical symbolism of flags, highlight the ethnic, state, regional, professional, religious, military, etc. differences, it has a universal value, and cannot become absolute.

In the composition structure of historical flags, central medallions are an identification and customization element.

As a result of our research, undertaken in Banat, between 2004 and 2014, we discovered a major deficiency in the preservation of historical flags and hence a significant series of damaged medallions.

## Content

The more than 150 heritage pieces, that we have researched and described, allow us to make a comparative study of the degradation, damage and destruction phenomena of historical flags.

The places where flags have been found are: museums and museum-like places, parishes, churches, town halls, fire stations, individuals, associations, community centers, building attics etc. In all cases, including in museums, historical flags have not been stored, preserved and handled according to the proper standards and requirements specified in the literature.

In fact, flags were wrapped around the pole, stored in inappropriate, vulnerable, dusty, places, exposed to light, bad weather and unsuitable biological conservation conditions.

When exposed, they were mounted directly on the wall, nailed, with no show cases, within visitors' reach.

For these reasons, central medallions and representations of the flags have different types of damages. The issue of damage and physical, chemical and biological degradations of the medallions is extremely complex and diverse. From the point of view of conservation and restoration, this generates specific challenges that need to be addressed, representing as many case studies as their actual number.

On the flags, the unique textile pieces, with a large specific size and weight, fixed or removable medallions are made in different techniques:

1- Painted, in tempera and oil, usually without primer, on a single canvas layer, both on the obverse and on the reverse.

2- Painted on a single canvas layer, on one side.

3- Painted directly on the textile surface of the flag.

4- Embroidered in the alto-relief technique, with metallic thread and decorative string, with or without a textile core, sequins, beads, stones, different metallic buttons, coloured embroidery thread, elements that are also used in the technical e execution of the inscriptions.

5- Embroidered in the flat technique (without a cardboard support) with coloured embroidery thread and applied metallic thread.

6- Textile collage made by putting together different textile fabrics (silk, velvet, cotton) on a textile support, in most cases, natural silk.

Degradations may also have been caused due to the technical execution, along with the state of conservation. For example, the different techniques, and the incompatibility of the different materials favours medallion degradations.

For the painted ones, the fact that no primer was used, that they were not protected by lacquer, that the support canvas (banner) is mobile, that they were wrapped around the pole, that the flag was folded and waved, resulted into a partial or general breaking of the paint layer, into the presence of numerous crackles, micro-cracks, cuts and tensioning traces. The excessive functional wear also leaves damaging traces caused by repeatedly touching the textile canvas, and, implicitly, the central medallion, by the pole, and the ornamental nails, as well as by the mechanical destruction of the fabric (lack of warp and weft).

For the embroidered ones, in a high relief, most of the time we discovered that the metal wires were oxidized and they detached from the cardboard relief. Between the decorative elements, usually the support canvas is cut and torn, empty areas appeared due to the tensioning of the bordering areas. The thread used for fastening the metallic wires, strings and ornaments degrades over time faster than metal threads.

In the case of flat embroidery, the most common degradations are caused by the fading of the embroidery thread, by the oxidation and non-fixation of its colouring agents and by the detachment and rupture of the threads.

The textile collages are damaged due to the combination of various material structures, sometimes coloured, incorrectly fastened, causing numerous dye migrations to the bordering areas.

The medallion image aesthetics is also affected by the gaps, stitches, cutting, tearing and detachment of part of them or of the entire medallion. Repairs, "restorations" made by the unadvised persons, changing the size of the flag, cutting and mounting again parts of the primary central composition on other types of textile support, etc., contribute to the loss of authenticity of historical flags.

## Conclusions

The fact that it was possible for us to see and research the flags is due to the kindness of some people, of the owners, but who, lacking the knowledge required for the conservation of the textile movable heritage and not being interested in specific conservation activities, necessary for the long term preservation of these objects, have become mere spectators of the degradation and slow destruction phenomena. In sporadic cases, we found an unjustified reserve to the flag research program, due to their expressed fear of not taking away the object in question. The lack of financial resources also contributes to the causation of this phenomenon. Such research programs are compulsory before starting the conservation and restoration procedure of historic flags.

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Poster Presentation

# X-RAY FLUORESCENCE (XRF) - COMPOSITIONAL ANALYSIS METHOD APPLIED FOR TEXTILE AND LEATHER OBJECTS AT ASTRA NATIONAL MUSEUM COMPLEX, SIBIU

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## Introduction

ASTRA National Museum Complex from Sibiu cares for a rich collection of textile and leather objects which determined us to focus on studying their composition in order to improve our knowledge from a documentary perspective, but also to get more scientific details to be used for restoration and conservation strategies.

For the study of the constitutive materials the following investigation methods have been employed: micro-chemical and burning tests, macro and microscopic visual examinations, digital micro-photographing, micro-metric measurements, all of which being carried out in the laboratory of chemical investigations at ASTRA Museum in Sibiu. The scientific and logistic support for applying the X-Ray Fluorescence Spectroscopy (XRF), (*portable) [InnovX Systems Alpha Series type with Wolfram anticathode, 35 kV, 40 µA, acquisition time 30 seconds, Si-PIN detector, cooling through the Peltier effect]*[1] was provided by Gheorghe Niculescu, physicist at the National Research Centre for Scientific Investigation (MNIR/CCIS) within the National Museum of Romanian History. The S1 TRACER Spectrometer, with applications in art history and art conservation, anthropology, archaeology, geo-chemistry, chemistry, and material science, was also used at ASTRA Museum through the scientific support granted by the Total Spectrum Company within the "Bruker X-Ray Fluorescence Workshop".

## X-Ray Fluorescence and other examination methods

X-Ray Fluorescence (XRF) is a non-destructive analytical method, the most often used in the investigation of cultural heritage.

A bed embroidery (Inv. No. 1967 T) belonging to the collections of The "Emil Sigerus" Museum of Ethnography and Saxon Folk Art from the ASTRA National Museum Complex was examined through this method, as well as by optical microscopy. The latter confirmed that for the structure of the basis fabric natural undyed vegetal threads were used, which presented the characteristics of the hemp fibres. Natural protein threads of a yellow-brownish colour were used for the embroidery. Their structure consisting in fascicles of fibres *twisted in S-shape* is specific for wool fibres coloured with organic dyes. Dyes were attached to the fibre by a mixture of mineral mordants. The mordants are chemical compounds which facilitate the formation of dye-fibre bonds, a phenomenon called mordant dyeing which supposes a certain number of reactions depending both on the nature of the dyes and on the nature of the support material.[2] Information regarding the methods applied for dyeing threads, known from ethnographic studies based on the research of rural areas (for example *Cromatica Poporului Roman/'Chromatics of the Romanian People'* by Simion Florea Marian, Tudor Pamfile, and Mihai Lupescu), were correlated to the outcomes obtained at the level of our laboratory, determining us to establish that the mineral mordants which had been used were probably alum $KAl(SO_4)_2 \cdot 12H_2O$ and copperas (green vitriol) $FeSO_4 \cdot 7H_2O$. The mineral mordants compose through the salt metal (aluminium-Al, iron-Fe) coordinative compounds which most often have a different colour than the initial dying material.[2] We can say that the dye which was used had probably vegetal origin, belonging to the class of non-nitrogen dyes. The X-Ray Fluorescence (XRF) method was useful in the analysis of the mordant found in the object. XRF has also facilitated analysing the elements, respectively determining the composition of the materials. The elements identified in a reduced or average concentration represent the impurities from the fibre, while the elements which appear in a larger amount (like Ca) derive from the washing water.

Another studied object was a flag with pennon belonging to the Town Hall of Râşnov, Braşov county, dated 1896-1909. Metal threads based on copper and gilded copper were used for the manufacture of this object. For a minimum invasiveness, a thorough research of the entire fabric has been carried out, in order to find the most relevant samples detached from the smallest fallen pieces which could not be reintegrated during the restoration process of the object. The metal threads were studied at the microscope and some micro-chemical tests were undertaken for identifying the basic elements. On the surface of the sample was dropped a solution of 1:1 nitric acid and distilled water. The colour of the solution obtained in combination with the nitric acid had put into evidence the presence of copper as the basic element.[3,4] Out of all constitutive materials that have a higher sensitivity and are more complicated from a technical point of view, metal threads mostly used for the decoration of textile objects. Copper, which is more vulnerable to corrosion than other elements, was mainly used for their manufacturing. Because of their complex stratigraphy, copper-based metallic threads are less resistant to the effects of the environmental agents than the ones made of precious metals. In moist conditions, copper corrosion products can appear on the surface.[5]

**Conclusions**

A thorough examination of the items decorated with metal threads can give us a series of useful information related to the colour of the surface, the basic metal and the corrosion products. Classical micro-chemical methods or optical microscopy methods are not able to exactly identify the qualitative and the quantitative elementary composition, but they are appropriate for the identification of the basic-type of the main materials. Chemical investigations combined with physical analyses such as X-Ray Fluorescence can provide clearer data regarding the nature and composition of the constituting materials for each object individually.

Scientific examination offers an important help in choosing the appropriate treatment and gives us information related to the dating and authenticity of the object. In the case of textile objects, the work technique, the dyes, the identification of the metal thread type (copper-based, gilded or silvered copper), all can be decisive features in establishing the age, the origin, and the authenticity of an object.

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Poster Presentation

# ASSESSMENT AND INVESTIGATION TECHNIQUES FOR BUILT HERITAGE CONSERVATION

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**Introduction**

The present paper aims to evaluate the characteristics of masonry, based on the characteristics of bricks and mortars used in old clay brick masonry, when performing the simple tests.
According to the Romanian regulations the inspection of the construction must be realized by an experienced construction inspector.
It is of utmost importance to know all the characteristics of the site and, at the same time, the characteristics of the building, namely the quality of the materials.
In the case of the *Stirbey* family chapel, simple tests have been performed, in order to preserve the historical pictures and the architectural elements.

**Short history**

The chapel is situated in the North-western side of the *Stirbey* estate, at the end of the only straight alley of the park. In spite of the fact that the building has been deserted a long time ago, elements that are characteristic to different architectural styles can still be observed. The dome is inspired from the byzantine style, the decorations present classical elements, while the towers resemble the Gothic style.
The exact construction date, as well as the name of the architect who built the chapel, are still unknown, due to the fact that until present time, documents confirming these details have not been discovered. However, it is believed that the chapel was built between 1885 and 1893.
In a picture taken in the first decade of the 20$^{th}$ century, the original aspect of the Chapel can be observed. It had a tall pedestal, and the masonry was characterized by a chess-like colour scheme. The terracotta arm, brought from Vienna, represented the connection with the upper part of the building, while eight imposing towers were surrounding the dome. Being situated in the lateral corner, they played the role of buttresses.

As a result of the decision to restore the Chapel, an expertise of the building is necessary, in order to establish its current state, as well as the measures to be taken for the restoration of structure and for ensuring its stability and resistance

Given the importance of the building and the fact that it is part of the national cultural heritage, it was decided to better analyze the characteristics resistance and to evaluate its properties by performing destructives tests, so as to determine the characteristics of masonry components; the bricks on one side, and the masonry mortar, on the other.

For a more exact evaluation of the materials, a documentary analysis was made, as well as a visual one, thus choosing (with the help of an expert evaluator) the areas from which sample preservation was possible.

**Experimental programme**

It should be mentioned the fact that several major earthquakes have affected the structural frame, which is why the stress should be laid on the restoration and consolidation process of the building. The main focus was on the retrofit of masonry and on the restoration of the dome. The result of the evaluation consisted in the analysis of brick samples from 4 different zones:

- two areas of masonry from the basement (the crypt area)
- two areas from the body of structure (the dome area) .

The brick specimens were labelled and packed individually, in order to avoid potential disturbance during the tests (photo 1).

The grout samples were taken from the two areas of the suprastructure, shaped as massive elements (photo 2).

Processing interventions were made in the laboratory, which helped obtain a testing process as close to the standard conditions as possible. The sample bricks were processed in the laboratory by cleaning the lime mortar off the sides, in order for plain surfaces to be obtained. The resulted samples were then tested with the purpose of revealing their physico-mechanical properties. The physico-mechanical properties are the following:

- Determining the bricks sizes;
- Determining the relative density and the dry strength density of the bricks;

- Determining the bricks water absorbability;
- Determining the compression strength of clay brick


Photo 1 Photo 2

Determination of compressive strength of the bricks was performed on specimens made by adjusting surfaces by grinding them with mortar. Standard specimens for manufacturing bricks were cut into two halves.

The specimens prepared for tests are left to cure for three days in normal medium, covered with plastic wrap to provide moisture to 90% percent. After drying, the specimens were acclimatized by drying at 100 °C for 36 hours, and then let them cool.

The determination of the compression resistance of the grout used for the masonry was made by sampling grout specimens from areas P I and P II. The samples were processed in the laboratory, being cut with a thin diamond canvas, so as to obtain samples according to the standard dimensions required for the tests - ½ of the standard (40x40x160) mm.

**Conclusion**

As resulted from the documentary research, the construction has suffered various interventions, at both aesthetic and stability and endurance levels. The damages resulted from the major effects of the important seismic action, and partial reconditioning works of the building were necessary. Apart from the seismic effects, another important factor that provoked damage was the high humidity registered at the infrastructure level (in the crypt area), where the lack of ventilation systems led to a degradation of the masonry.

The destruction of the original terracotta base of the building was a result of the excessive humidity, together with the freeze-thaw effects.

While restoring the plinth, during the 1958-1959 intervention, air drains were introduced, with the aim of reducing the humidity produced by the capillarity. The excess water in the soil is a result of the direct connection with the lake from the *Stirbey* domain. More recently, it was decided to protect the plinth by using a stone veneer, while the original ventilation system was kept.

Compression tests revealed a lower endurance of the bricks from the infrastructure area, compared to the ones from the supra-structure.

The sampling process from the supra-structure area revealed the layered character of the structure. The endurance characteristics of the bricks are superior to the ones in the infrastructure, but a higher variability can be observed at this level.

The values that have been obtained are used to access the database and obtain the design characteristics for old structural masonry:

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Poster Presentation

# BIODEGRADATION OF OLD BOOK COVERS FROM CHURCH COLLECTIONS

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## Introduction

Degradation of the old books' cover is the most frequent result of microorganism and insects' attacks over entire book. The diversity of species identified like biodegradation agents for books is in perfect connection with the variety of materials present in the structure of one book: wood, paper, but also textiles and adhesives. The biodegradation agents produce aesthetic (spots in different colours, exit halls, galleries, deformations, superficial erosions) and functional damages (loose materials, fractures, ph-changes with consequences over the durability of the material). The paper presents the danger represented by biological agents, such as insects and microorganisms, to ecclesiastical collections and analyses the conditions of books' preservation, which favour the occurrence and development of the biological attack.

## Work methods

Research was done in 13 locations (libraries, churches) from the counties of Bacău, Iaşi, Neamţ, Suceava. Insects were taken (alive or dead, larvae exuviae, excrements etc.) from collections of books. 385 books were studied, having covers made by wood or carton, covered by leather and having the back from leather. The microbiological samples have been seeded in aseptic condition on culture media Sabouraud agar for fungal grow.

The frequency of insect species identified was calculated using the formula: $F = p/P \times 100$, where: p – the number of old books covers in where a species was found, P – the total number of books.

## Results and conclusion

We found 11 species and genera included into 6 families belonging to 3 orders of insects. From the Coleoptera group, the insects related to the *Anobiidae* family were most frequently, followed by the *Ptinidae* (7,5%) and the *Demerstidae* (2,8%). This significant presence of the *Anobiidae* is due to the large number of wooden objects or its derivatives. The *Stegobium paniceum* appears far more frequently from the all recorded species (in 70% old book covers), being followed by the *Xestobium rufovillosum* (16,8%) and the *Anobium punctatum* (13,1%).

Quite the opposite is the case of the *Curculionidae* - the species *Ptilinus pectinicornis*, *Niptus hololeucus* were found only in one location. The dermestids appear very frequently in collections of natural history, fur, leather and old books. As they are mainly keratophagus species they get into the books in the second group, after the *Anobiidae* and the *Ptinidae*.

*Ptilinus pectinicornis*
„Sf. Evanghelie" (Holy Gospel), 1742

*Stegobium paniceum*
Biblia" (Bible), 1795

Species of acari, booklice, lepismatids were also identified in the book deposits, their presence being associated with the superficial erosions from the numerous covers. The rodents produce mechanical and chemical damages on the book, but can be also responsible for incidental fires. As microbiological agents, species like *Penicillium sp, Aspergillus niger and Trichoderma viridae,* well known as leather biodegradation agents were identified.

Poster Presentation

# THE RESTORATION OF A WIDE LEATHER BELT FROM THE COLLECTION OF ASTRA MUSEUM, SIBIU

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## Introduction

The 20th century wide leather belt (with the inventory number 4444-P) from Hunedoara County is made of leather, brass, pewter, gemstones and coloured glass. The technics used for manufacturing the object included casting, punching, perforating, riveting and application of various materials.

The wide belt consisting of three layers of leather was decorated, on the middle, with rectangular plates hemstitched with brass, on the two sides, with three rows of rivets and, in the front, with glass stones of various colours, which were attached in the riveted boxes. The lock applied recently is not authentic.

From a conservation point of view we could note the following observations. The strap was generally fragile and it was severely affected by functional wear, presenting chemical and biological degradations. The object was also damaged by the action of the mechanical agents which had worked in time through the deposits of corrosion products resulted from the metal elements on the leather and the fat deposits on the aged and dehydrated leather. In addition, on some areas, the fractured material fragments had losses of metal pieces and, also, chromatic changes of leather and metal had been put into evidence. There were identified significant stone losses, of which: five were missing including their metal mountings, two others were lost from their frames, while another two were just fallen out. Corrosion products were more visible on the inner side and on the hobnails, where deformations of the material and white stains on the inside were also noticed.

## Investigation

After general visual investigations using magnifiers, dimensional and pH measurements of the wide leather belt we could gather more information regarding the following aspects: the colour, the technical degradations and the thickness of the leather. We could also establish the type of the animal by studying the grain of the leather.

Further, through scientific investigations (microscopy and micro-chemical tests), there was revealed that the metal stripe was made of an alloy based on copper, which had explained the presence on the surface of the green corrosion products of copper (basic copper carbonate, malachite).

## Restoration

Considering the complexity of the interventions needed for the restoration of such a problematic object there was established a plan of general and local treatments to apply.

At the beginning, the dusty and dirty surfaces had been cleaned by using fine brushes, after which the object was covered with a gauze material and it was vacuum cleaned. Dry mechanical cleaning was performed for removing not so adherent dirt with the help of ‘wilbra’ (a sponge for cleaning leather). This was followed by other differentiated investigations. Glass rocks had been cleaned mechanically with cotton swabs on wood sticks and soft brushes. Mechanical cleaning for metals had been performed with a glass fibre pen, steel wool and brushes. There was applied a 1% solution of ‘Paraloid’ B73 (ethyl acetate) in a single protecting layer for the preservation of metal elements. Direct contact between the leather and the metal was prevented through the use of acid-free Melinex transparent sheet.

After thoroughly cleaning the object, a composition of lanolin, neat's-foot oil, thymol and alcohol, mixed until homogenization, was applied in moderate concentrations for softening the leather, by using cotton wool pads on the surface, until the cream was totally absorbed. Following a couple of day the belt was polished with a soft cloth.

Considering the important role of the ornaments, the next step was represented by the manufacturing of two glass stones which were fixed in the place of the missing ones by using of a ‘BiComponent’ adhesive. The new stones were shaped according to the original ones by using a grinder. Before gluing the stones, the old adhesive was detached with pincers and scalpel under magnifying glass in order to remove the unnecessary remains. Then the adhesive was applied on the specific areas in thin layers. Pressure was assured through the positioning of flat glass weights on the top of the stones.

In the end a textile covering was made for the protection of the object during its storage.

## Conclusions

After the restoration the leather belt can be exhibited if conditions are adequate. Display was suggested to be in showcases, which are externally illuminated. Exposing the object under physical tensions is undesirable. Appropriate microclimate values were recommended to include temperature between 10-18°C and relative humidity between 45-65%. Good ventilation and keeping the relative humidity below 70% are the first measures that are imposed in order to prevent fungal attack.

Poster Presentation

# "DIFFERENT" RESTORATION OF A 18$^{th}$ CENTURY LEATHER BOOKBINDING

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The book is part of the Romanian Academy Library collection, being printed in Greek language, in two volumes: VIVLION ISTORICHON PERIECHON EN SYNOPSEI DIAPHOROYS KAI EXOCHOYS ISTORIAS DOROTHEOY-1798 (Venice-Nikolao Glykei), author: Dorothei al Monembasiei. It has wood covers protected with leather. The wood presents multiple gaps. In the leather cover multiple perforations caused by a massive Xylophage attack, currently inactive, are observed. The cover also presents fractures, incomplete portions in the corners, leather darkening, blunting especially in the ribs. Only traces of the original locks were preserved.
The calf leather presents multiple gaps, tears, embrittlements. For restoration, operations aiming to remove the old canvas and capital-band were performed, as well as wood and leather cleaning. In order to fill in all the holes and the multiple traces left behind by the xylophage attack, a leather paste was used, which was a demand to the National Research and Development Institute for Leather and Textiles. This paste was prepared with the purpose to complete all traces and holes in a uniform manner, in an intervention as less visible on the front cover as possible.

Images of the leather bookbinding before restoration

In order to maintain the authenticity and accuracy of the volume as it was worked originally, it was sewn using the frame, the book block being initially sewn on two profiled ribs. The canvas spine was lined between the ribs, a capital-band as close to the original as possible was sewn. The book block was then inserted into the restored covers. The book is now preserved in a box made of non-acidic cardboard.

Images of the leather bookbinding after restoration

Poster Presentation

# SYNERGETIC EFFECT OF TEMPERATURE, RELATIVE HUMIDITY AND LIGHT IRRADIATION ON VEGETABLE TANNED LEATHER BY NMR MOUSE AND MHT METHOD

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## Introduction

Historical and archaeological leather objects and artefacts are an infinite source of information of historical and cultural interest. They illustrate the evolution of social customs, habits, aesthetics and technology, but also the perpetuation of popular and religious traditions. It is vital therefore that these materials and artefacts remain well preserved. The aim of our study is to bring together non- and minimal invasive investigation techniques for collagen fibre characterisation as practiced by conservators, i.e. shrinkage activity measurement, with the current nanoscale measuring systems, i.e. unilateral NMR, to relate information at the fibre level to that at the collagen fibril level. Early detection and identification of deterioration by using qualitative tests as unilateral NMR and MHT method can highly extend the life of the historical objects and artefacts.

Unilateral NMR has been developed after 1990, when the first portable equipment NMR MOUSE (Mobile Universal Surface Explorer) was built.[1] NMR MOUSE is a relatively small and compact device design to perform noninvasive and nondestructive analyses, highly valued in the field of cultural heritage. Objects like mummies,[2] paintings,[3] frescoes[4] and parchments[5,6] were successful analysed using NMR-MOUSE.

The hydrothermal stability of collagen fibres is currently evaluated by a micro-destructive diagnostic technique based on the combined use of optical microscopy and thermal analysis and called MHT method. The shrinkage temperature $T_s$ of collagen fibres characterises the collagen fibres structural collapse and hence the loss of mechanical stability and strength. This parameter is widely used to evaluate degradation level of collagen-based historical materials.

This work concerns with the investigation of the synergetic high temperature, low RH and visible light irradiation effect on the deterioration of calf and sheep leather tanned using various vegetal tanning extracts by correlating $T_1$ (longitudinal relaxation time) and $T_s$ (shrinkage temperature) values.

**Experimental part**

New leather from calf and sheep hides was obtained through traditional using different tannin extracts such as mimosa bark, quebracho and chestnut wood at the National Research and Development Institute for Textile and Leather, Leather and Footwear Research Institute Division (INCDTP-ICPI), Bucharest.

A first series of leather samples were exposed to accelerated ageing treatments inside a test chamber Binder APT Line KBF-ICH, at 70 °C, 30% RH and 4000 lx illuminance (visible light region) for 8, 16, 32 and 64 days. The visible light exposure corresponds to 60, 120, 250 and 500-year dose, respectively.

Unilateral NMR measurements were performed with a portable Magritek NMR MOUSE, model PM 25, at 13 Mhz frequency. Longitudinal relaxation time $T_1$ was measured using a saturation recovery sequence combined with Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence. $T_1$ values were measured by directly placing the leather samples on the measurement window of the instrument.

Shrinkage temperature $T_s$ was measured with the home-made MHT equipment available at INCDT-ICPI using the procedure previously described.[7] For the $Ts$ evaluation a few fibres (~0.3 mg) from the corium side were immersed in demineralised water, covered with a cover glass placed inside the thermostatic cell of the hot table and heated at 2 °C $min^{-1}$. Collagen fibres' shrinkage activity was recorded with the camera connected to the stereomicroscope and then visually evaluated by the operator.

**Conclusions**

- Shrinkage temperature $T_s$ significantly decreased with ageing time independently of animal species and tannin type. Chestnut tanned leathers were the most sensitive to the ageing treatment.
- $T_1$ values showed to depend on both animal species and tannin type. Moreover, sheep leather was sensitive to the ageing treatment, while calf leather does not show significant changes during accelerated ageing treatment.
- $T_1$ and $T_s$ parameters are potential indicators for characterising tannin – collagen interactions as well as for assessing conformational, structural and stability changes during ageing and deteriorating of leather.

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This paper is based on some of the outcomes of the Romanian ANCS project *Intelligent System for Analysis and Diagnosis of Collagen-Based Artefacts* (COLLAGE, PNII 224/2012) and Bilateral Cooperation between Romania and Hungary *Assessment and mitigation of impact of climate on library and archival heritage: experience, research, innovation* (LIBER, CB 671/2013).

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# Workshop Presentations

Workshop Presentation

# USE OF ADAPTIVE BACKGROUND ESTIMATION ALGORITHM FOR THE AUTOMATIC DAMAGE ASSESSMENT OF COLLAGEN BASED HISTORICAL OBJECTS

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## Introduction

An adaptive background estimation technique was used for the automatic detection of the shrinkage temperature obtained from the Micro Hot Table analysis of the collagen fibres.

The properties of collagen fibres and their structure determine the physical-chemical and mechanical properties of both parchment and leather and hence their response to degradation by a wealth of external factors as temperature, relative humidity, airborne pollution, visible light and UV radiation, mechanical damage and bacterial/fungal growth. Ageing and deterioration lead to discoloration, structural and mechanical weakening, dimensional variations and other alterations less visible to the naked eye that, in the absence of intervention to stop or slow down degradation, may result in a multitude of consequences ranging from the difficulties in reading of a document to its partial or total loss. This has created a strong need to conserve parchment and leather artefacts and prevent their irreversible quality loss and/or physical degradation. It follows that detailed knowledge of the behavioural properties of these materials is a fundamental component of the successful and durable conservation and restoration methods. This includes knowledge of the collagen structure in parchment and leather and its hydrothermal and structural stability.

The Micro Hot Table (MHT) method is currently used for evaluating shrinkage temperature $T_s$ and shrinkage intervals of collagen fibres from heritage objects. This method was refined and included in the damage assessment protocol of historical parchments established by the EU Project IDAP[4] and criteria for grouping of historical parchment and leather into four damage categories were established.[1,2] Moreover, the analysis of shrinkage intervals

[4] European Commission project *Improved Damage Assessment of Parchments* EVK4-CT-2001-00061

supplement the information given by the $T_s$ value alone and enable us to evaluate the heterogeneity and degree of deterioration of collagen based objects.[3]

The success of MHT method lies in the simplicity of the equipment and micro-destructiveness (about 0.05 mg of fibres is required). The measurement is time-consuming and requires a good experience from the operator. The automatic estimation of damage level would lead to a dramatic improvement of MHT method and facilitate a routinely spread in small conservation and restoration laboratories with limited financial and human resources.

The MHT method principle consists in heating collagen fibres in demineralised water at $2°C·min^{-1}$ and registering their motion called shrinkage activity. This phenomenon is the macroscopic manifestation of the conversion of collagen triple helical structure to a random coil disordered structures over a defined temperature interval. The term shrinkage activity is used to denote any observable shrinkage motion going on in a fibre. The shrinkage activity of parchment/leather/skin is described in three temperature intervals with the following characteristics[4]:

Intervals A1–A2: Distinct shrinkage activity in individual fibres.

Intervals B1–B2: Shrinkage activity in one fibre is followed by shrinkage activity in another fibre.

Interval C: At least two fibres show simultaneous and continuous shrinkage activity. The starting temperature of this interval has been assumed as the shrinkage temperature $T_s$. $T_l$ (last) is the temperature of the very last observed motion and $T_f$ (first) is the temperature at which the very first motion is observed.

Based on these two parameters both historical parchment (Table 1) and leather (Table 2) can be ranked in four damage categories as follows:

- Level 1: no visible changes or very little changes
- Level 2: Minor changes (some collagen fibres contract at room temperature)
- Level 3: Significant changes (some fibres turn into gelatine at room temperature and/or shrink)
- Level 4: Major changes (partial or total „melting" of the fibres)

**Table 1.** MHT protocol for parchment classification [Ref.1]

| Damage category | ***T*f / °C** | ***T*s / °C** |
|---|---|---|
| **1** | > 45 °C | > 50 °C |
| **2** | > 40 °C to ≤ 45 °C | > 45 °C to ≤ 50 °C |
| **3** | > 35 °C to ≤ 40 °C | > 40 °C to ≤ 45 °C |
| **4** | ≤ 35 °C | ≤ 40 °C |

**Table 2.** MHT protocol for vegetable tanned leathers [Ref.2]

| Damage category | $T_s$ / °C |
|---|---|
| **1** | > 70 °C to ≤ 90 °C |
| **2** | > 60 °C to ≤ 70 °C |
| **3** | > 50 °C to ≤ 60 °C |
| **4** | > 40 °C to ≤ 50 °C |
| **5** | < 40 °C |

The aim of this work was to develop an algorithm for the automatically estimation of $T_f$ and $T_s$. An adaptive background estimation algorithm was chosen. Most background estimation techniques use only the difference between grey scale values for considering changes in the illumination.[5] Among the different background estimation algorithms, the Σ-Δ background estimation was selected. It is a simple method to detect pixels that substantially change in the static scene, considering variation of grey levels. It is a temporal processing that can only offer detection at pixel level.

## Results

The Σ-Δ background estimation was applied for the automatic detection of the $T_f$ and $T_s$ temperatures. The $T_S$ and $T_f$ evaluation was tested on the image sequences obtained for 80 historical leather and parchment samples. The mean absolute error of $T_S$ and $T_f$ values evaluated through the Σ-Δ background estimation was 1.6 °C and 2.1 °C, respectively, in very good agreement with the accepted error of the visual microscopic analysis (2 °C).

## Conclusions

The developed application can be used especially in institutions (libraries, archives) that have limited personnel who do not have specific competences of this type of analysis.

## Aknowledgements

This research has been carried out within the ADAS project E!5837 within the Eureka Network.

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# NEW HOTPLATE PROTOTYPE FOR AUTOMATIC MEASUREMENT OF SHRINKAGE ACTIVITY

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## Introduction

Current research performed in the cultural heritage area that involves the measurement of collagen fibres' shrinkage activity through the Micro Hot Table (MHT) method for leather and parchment materials and objects requires a hotplate for samples heating at a fixed temperature rate. Generally, the hotplates currently used in the conservation-restoration laboratories heat at 2 $°C·min^{-1}$, only. Using one heating rate is however limitative for analytical purposes. This article reports the progress of the development of a new hotplate prototype designed to solve most of the problems encountered by both conservators and scientist using the commercially available hotplates.

## Material and methods

The new prototype was designed so as to answer the requirements of users and improve the analytical potential of the MHT method. It thus provides:

- multiple temperature gradients (0.2, 0.5, 2, 10 $°C·min^{-1}$) to allow comparison of results with other thermal analysis methods
- rapid cooling capabilities for reducing time between measurements
- truly portable and *in situ* use due its lightweight and small dimensions

The system consist in an aluminium case fitted with a 10 mm isoprene layer for thermal insulation, a heating element, an absolute temperature sensor and a Peltier cell with a small heat sink for the cold side and a large heat sink cooled by a fan for the hot side.

The heating element is formed by two nichrome coils encased in quartz tubes for electrical insulation. The dissipated heat is monitored by a LM135 absolute temperature sensor[1] which provides a linear temperature output for the microcontroller.

Both the sample and hotplate case cooling is performed by a 77.1 W multicomp thermoelectric module[2] also known as a Peltier cell or a heat pump. The Peltier cell has two sides, hot side and cold side, and as long as a current is applied to its two electrodes the cell maintains a 30 ºC temperature difference between its hot and cold sides, e.g. when the hot side is maintained at 25 ºC the cold side will reach –5 ºC. Since the hot side should dissipate at least 77.1 W power, a very efficient cooling system is required to maintain 25 ºC at the hot side surface. The cooling system used for this application, widely available on the market, is a CPU cooler which is able to dissipate 140 W power. It consists of heat transferring tubes, a heatsink and a fan.

Temperature control and USB communication with the computer used for image processing and data analysis is performed by a Microchip PIC18F1330.[3] Temperature is acquired from the LM135 absolute temperature sensor via a 10 bit analog-to-digital converter which provides a resolution of 0.1 ºC/bit.

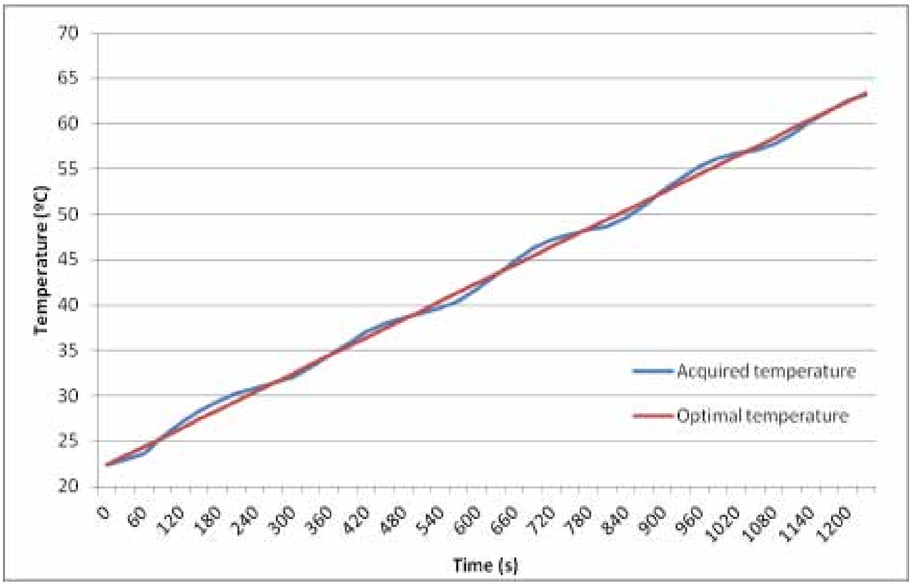


**Figure 1.** Acquired temperature evolution in the range (22 to 63) ºC

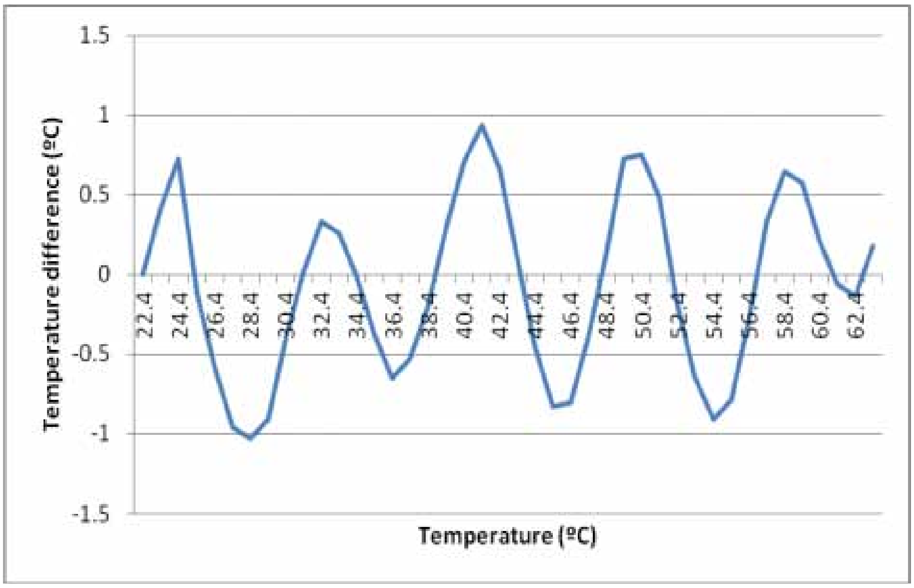


**Figure 2.** Temperature difference between the case temperature and optimal temperature

## Results and discussion

The temperature is acquired from the sensor at 2 ms periods and analyzed by the microcontroller to evaluate its trend and compare it with the selected temperature gradient. This information is used to control the power output from the two heating elements. In Figure 1 the obtained temperature evolution for a 2 ºC·min$^{-1}$ gradient (blue line) is displayed together with the 2 ºC·min$^{-1}$ gradient.

By using the graph in Figure1 an error graph to illustrate the prototype performance is obtained by plotting the difference between each data point and its corresponding optimal value, as shown in Figure 2.

## Conclusions

From Figures1 and 2 it can be observed that the prototype provides a ± 1 ºC gradient error on heating. A better heating control is being implemented to reduce this gradient error to 0.1 ºC, the temperature sensor resolution.

For a number of test measurements performed at room temperature the cooling interval from 100 ºC to 25 ºC was about 16 minutes. This cooling interval can be further improved by minimizing the case footprint.

## Acknowledgement

This research is being carried out within the Romanian ANCS project Intelligent System for Analysis and Diagnosis of Collagen-Based Artefacts (COLLAGE, PNII 224/2012).

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2. Part datasheet (Thermoelectric module): http://www.farnell.com/datasheets/1662217.pdf
3. Part datasheet (PIC18F1330): http://ww1.microchip.com/downloads/en/DeviceDoc/39758D.pdf

## Support Projects

***The 3rd International Seminar and Workshop is organised within the Joint Applied Research Projects INHerit (PNII 325/2014) and COLLAGE (PNII 224/2012), and in collaboration with the bilateral collaboration projects between Romania and Italy (PNII 638/2013), France (PNII 713/2013) and Hungary (PNII 671/2013). All these projects are financed by the Romanian National Authority for Scientific Research (CNDI – UEFISCDI).***

**Romania - Italy (PNII 638/2013): Advanced Techniques and Interdisciplinary Studies for Improved Assessment of Historical Parchment Documents (ParIS)**

**Romania - France (PNII 713/2013): Quantitative Assessment of Environmental Impact on Collagen-Based Materials for Low-Energy Climate Control in Archives and Museums (EnviColl)**

**Romania – Hungary (PNII 671/2013): Assessment and Mitigation of Impact of Climate on Library and Archival Heritage: Experience, Research, Innovation (LIBER)**

### COLLAGE

### Intelligent System for the Analysis and Diagnosis of Collagen-based Artefacts

**Total Cost:** 737.155 EUR
**Duration:** 2012 - 2016
**Start Date:** 01/09/2012
**Project Coordinator:** INCDTP-ICPI, Bucharest
**Consortium:**
Mira Telecom SRL, Bucharest
National Museum of Romanian History, Bucharest
ICPE-CA, Bucharest
University Politehnica, Bucharest
**Project Web Site:** www.collage.com.ro
**Key Words:**

- assisted analysis and diagnosis
- portable tools
- damage quantification
- damage database
- historical parchment and leather

## INHerit

### Intelligent Strategy for Movable Cultural Heritage Monitoring in Changing Climate

**Total Cost:** 318.345 EUR
**Duration:** 2014 - 2016
**Start Date:** 01/07/2014
**Project Coordinator:** INCDTP-ICPI, Bucharest
**Consortium:**
Mira Telecom SRL, Bucharest
ICPE-CA, Bucharest
ASTRA National Museum, Sibiu
Romanian Academy Library, Bucharest
Bucovina Complex Museum, Suceava
National Museum of Village *Dimitrie Gusti*, Bucharest
**Project Web Site:** www.inherit.ro
**Key Words:**

- wireless sensors
- low-cost climate control
- indoor air quality
- web-based environmental management

MEMORI

# The MEMORI technology

## *Innovation for Conservation*

*Deteriorating parchments, cracking varnishes, degraded textiles: airborne pollutants cause severe problems in collections all over the world, in exhibitions, and in storage rooms. They are invisible, mostly odourless, destructive and endanger cultural heritage objects; no matter whether paper, wood, textiles, paintings or metal objects.*

MEMORI

MEMORI
Dosimeter (front and back side)

MEMORI
Dosimeter Reader

Analysis of MEMORI
Web Pages

### Damaging environments threaten heritage objects

Museums, art collections, conservation enterprises, insurance companies and art transport companies have to face the same problem: Heritage objects on exhibition, in storage or in transit may come into contact with a degrading environment. Indoor climate (temperature, humidity and air flow conditions) and light (visible and UV) are often measured in heritage institutions, however, air pollution is seldom measured. Air pollution can be aggressive trace gases such as sulfur dioxide and nitrogen dioxide, ozone and organic acids, or particles of various sizes and chemical composition. These environmental factors can vary greatly and combine to degrade our most sensitive historical objects. Having a technology which mimics the total impact is vital if we want to safeguard these artefacts.

### MEMORI – the early warning system

The MEMORI solution is a new early warning system sensitive to the main degradation factors of indoor environments, which behave in a synergistic manner. It integrates the latest knowledge on the impact of pollutants on cultural assets with technology that can identify the environments which will create a negative impact BEFORE any effect can be seen on the artefacts. The MEMORI dosimeter is sensitive to indoor climate and light, photo-oxidizing gases and organic acidic gases. Subtle changes on the dosimeter are used to indicate and forecast the impact on sensitive cultural assets. The MEMORI reader is designed for on-site measurements and web based solutions provide evaluation of the dosimeter readings. The handheld reader improves the functionality of the dosimeter, reduces the time needed for evaluation of results and makes the system flexible and convenient. It allows the end user to collect and analyze data on-site simplifying and streamlining the process of identifying problem areas. The MEMORI dosimeter and reader can be connected to a web based system designed to visualize and interpret the results from the reader. This MEMORI web site will provide info on air quality risks, related preventive conservation measures and guidelines on how to improve air quality indoors.


Microclimate frame
(SIT Grupo Empresarial , S.L)


Mounting a microclimate frame
(SIT Grupo Empresarial , S.L)


Storage of organic objects
(Museum of Cultural History, Oslo, Norway)

MEMORI

## MEMORI – European knowledge for heritage institutions and the conservation market

MEMORI involves scientists, conservators and cultural heritage specialists from various institutions in ten European countries collaborating to develop new knowledge and technology in order to protect our historic artefacts. The team wants to provide the conservation market with an innovative measurement technology. The goal is to take the current state of affairs one step further. MEMORI focuses on the impact that gaseous pollutants have on cultural assets and how various assets respond to this impact when placed in different locations such as storage, protective enclosures, transportation and on public display.

## Benefits for cultural heritage institutions

The MEMORI technology offers a tool for preventive conservation with the aim of reducing costs for restoration, to provide long term benefits for cultural heritage collections and to give a head start in coping with airborne pollutants. The MEMORI approach offers clear benefits for preventive conservation and a market advantage for conservation companies, for art transportation services and insurance companies. The key aspect of the MEMORI solution is that it will provide conservators with a tool which allows them to make more informed decisions.

- Designed for use by both new and experienced conservators
- Easy to understand and detailed information
- Full inventory of air quality as it pertains to organic materials
- Better management of artefact care
- Reduce restoration costs
- Ensure best quality environment for visiting pieces

MEMORI


Placement of the MEMORI dosimeter in a showcase of the Museum of Cultural History, Oslo / Norway

## How does the MEMORI technology work?

The MEMORI product will be the first of its kind on the market which provides not only the tools required for measuring, which themselves are innovations, but the software interface to a database which enables conservators and curators to make well informed decisions when it comes to air quality and the impacts on their collections.

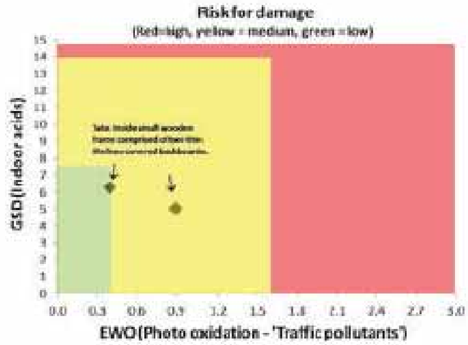
MEMORI dosimeters were tested and data analyzed at

- The Tate, London/United Kingdom
- National Museum of Krakow/Poland
- Museum of Cultural History, Oslo/Norway
- Rangers House and Apsley House, English Heritage, London/United Kingdom
- Putna's monastery textile collection, Putna/Romania
- Istanbul University – Municipality of Istanbul/Turkey
- Lithuanian Theatre, Music and Cinema Museum, Vilnius/Lithuania
- Old Palace in Stuttgart/Germany
- National Research Center of Cultural Properties, Tokyo/Japan
- Musée National Picasso, Paris/France
- Austrian National Library, Vienna/Austria
- Picasso Guernica Gallery in the National Museum and Art Center Reina Sofía, Madrid/Spain
- Royal Academy of Fine Arts, Madrid/Spain
- Stibbert Museum, Florence/Italy
- The Royal Library, Copenhagen/Denmark

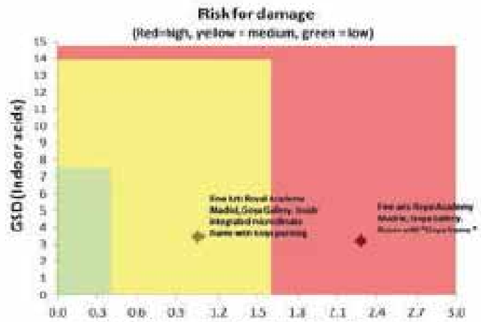
MEMORI

## Two examples

MEMORI dosimeters were tested e.g. at **Tate (London/United Kingdom)**. The dosimeter was placed inside a frame construction, designed to replicate the conditions created by current frame backboards. The results show that the frame design provides good protection against external pollution but also raise the question whether museums should now look more closely at the materials used to enclose works of art and the implications for air-conditioning filtration.




Two other dosimeters were tested in the **Goya Gallery at the Fine Arts Royal Academy in Madrid/Spain**. One dosimeter was positioned in a microclimate frame with a Goya painting, another in the Goya Gallery with a "Goya frame". The results clearly show that the open room has a higher rate of airborne pollutants and that preventive action is recommended.

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MEMORI

**The MEMORI technology was developed in the MEMORI project**

**"Measurement, Effect Assessment and Mitigation of Pollutant Impact on Movable Cultural Assets. Innovative Research for Market Transfer"**

**supported by the European Commission under the 7th Framework Programme (Grant Agreement No 265132).**

SEVENTH FRAMEWORK PROGRAMME

NILU
Norwegian Institute for Air Research

Fraunhofer
Fraunhofer-Gesellschaft zur Foerderung der Angewandten Forschung

Kultur und Arbeit e.V.
Kultur und Arbeit

University of Pisa

UNIVERSITEIT GENT
University of Ghent

Royal Danish Academy of Fine Arts, School of Architecture, Design and Conservation

BOKU
University of Natural Resources and Life Sciences

University of Arts "George Enescu" Iasi

ENGLISH HERITAGE
English Heritage

Birkbeck UNIVERSITY OF LONDON
Birkbeck University of London

SIT
SIT Grupo Empresarial, S.L.

TATE
Tate

DCU
Dublin City University

NILU INNOVATION
NILU Innovation

Photos are provided by partners of the project.

## Photo Gallery

# INDEX