COLLAGE Project
Intelligent System for Analysis and Diagnosis of Collagen-Based Artefacts
www.collage.com.ro

Mid term results

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Team Leader: Irina Petroviciu; Team members: Cristina Carsote

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Team Leader: Ovidiu Grigore; Team members: Valentin Velican, Ionut Bornoiu

P4 - Mira Telecom s.r.l., Bucharest

Team Leader: Silviu Ciobanu; Team members: Oana Miu
THE PREMISES

Historical and cultural objects made of collagen include; parchment, in the form of scrolls, documents and codices; leather, in a huge variety of items such as bindings, wall tapestry, storage vessels, musical instruments, luggage, objects of personal use such as shoes and garments, and mummified skins of animals or humans.

**Documents** made of parchment are the most important bearers of our recorded history from early times such as the *Dead Sea Scrolls* (408 BC - 318 AD) and the *Magna Carta* (1215) until the modern *U.S. Declaration, Constitution, and Bill of Rights* (1787), and present important state documents and parliamentary records.

**Leather objects** 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.

On the other hand, collagen is an integral part of the human body and the study of **mummies** can supply new informed directions for anthropological, paleopathological, genetic and medical research.

**All these objects and artefacts represent repositories of tangible-intangible cultural heritage which can offer answers on the state of health and beliefs of past civilisations.**
THE CHALLENGE OF THE COLLAGE PROJECT
FILLING THE GAP BETWEEN RESEARCH AND ITS APPLICATIONS FOR CULTURAL HERITAGE PRESERVATION

COLLAGE MAIN OBJECTIVE

aims to develop a unified kit of assessment tools for conservators, conservation scientists and scientists to evaluate the level of damage in collagen-based heritage and archaeological objects using a multi-disciplinary and multi-scale approach ranging from molecular, nano and mesoscale to macro scale visual assessment.

Additionally, the project

(i) takes advantage of previous results from national, international and EU projects and develop a parchment and leather damage database

(ii) critically reviews practices in the preparation of archival material and their conservation and restoration treatments in order to trace differences in traditions in different geographical areas and establish markers for identification and anti-counterfeiting purposes.

**Project Timeline**

- **I·D·A·P**
  - 2002 – 2005
  - EC FP5 Framework

- **OPERA**
  - 2006 – 2009
  - CIPE - Italy

- **PERGAMO (CEEX)**
  - 2006 - 2008

- **PELRESTAURO (PN I)**
  - 2007 – 2009

- **ETNOPEL (PN II)**
  - 2008 - 2011
THE CHALLENGE

COLLAGE – SPECIFIC OBJECTIVES

1. Development of a new measurement system for the automatic detection of shrinkage activity of collagen fibres in laboratory and in situ: **imageMHT system**

2. Development of an intelligent system for assisted damage diagnosis **CLEAR diagnostic software**

3. Development of a comprehensive parchment and leather **damage database**

4. Establishment of a **unified calibrated measurement protocol** enabling inter-laboratory comparison

5. Identification of analytical markers for **early damage identification** and anti-counterfeiting purposes

6. Definition of quantitative protocols for **damage quantification**
THE APPROACH

Accelerated Ageing / Exposure

Parchment
- New calf and goat parchment
- Historical parchment

Leather
- New calf and sheep leather
- (tannins: mimosa bark, quebracho wood, chestnut wood)
- Historical leather

temperature
humidity
UV and Vis light

8 - 64 days

air pollutants
(NO\textsubscript{x}, SO\textsubscript{2})

1-32 weeks
THE APPROACH

Multiscale analyses: Fibre level ↔ Molecular level

- Fibre bundles: 100-500 μm
- Fibre: ~10 μm
- Fibril: ~1 μm
- Microfibril: ~300 nm
- Triple-helix: ~1 nm
- α-chain

MHT method
fibres shrinkage

SEM, DSC
fibres morphology
thermal denaturation

NMR
water-collagen interaction

ATR/FTIR
collagen secondary structure

THE APPROACH

Translate analytical data into practically relevant measures

Shrinkage activity of collagen fibres
Parchment bindings, *Ordinati Collection* (1325 to 1499) Historical Archives of the City of Turin

DSC denaturation of collagen fibrils in parchment samples exposed to 80 °C and 40% and 80% RH in alternate days

NMR longitudinal relaxation time $T_1$ of historical parchments bindings, *Ordinati Collection* (1325 to 1499) Historical Archives of the City of Turin

ATR-IR spectra of parchments exposed to NO$_x$ (50 ppm) for 2 to 16 weeks

- microscopic scale
- mesoscopic scale
- nanoscopic scale
- molecular scale
Damage assessment: from macro to nanoscale

**Damage quantifying**  
Early damage detection  
Fake identification

### Collagen denaturation & gelatinisation

**Molecular manifestation**

- **ordered triple helix**
- **disordered triple helix**
- **conformational change**
- **3D packing**
- **peptide chains**
- **fragmentation**

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**Differential Scanning Calorimetry (micro DSC)**

- **ordered triple helix**
- **disordered triple helix**
- **gelatine**

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**Total Damage Ranking Equation**

\[ S_{tot} = 0.2 \ S[T_d] + 0.5 \ S[\Delta H] + 0.3 \ S[I_S] \]

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**Damage assessment: from macro to nanoscale**

**Damage quantifying by DSC and SEM**

Ranking of a group of archival bookbindings in 4 damage categories:

1. no damage; 2. minor damage; 3. medium damage and 4. heavy damage

**Sample no. 4 comprehensively displays increasing damage of its flap (F4), cover (C4) and spine (S4)**

Damage assessment: from macro to nanoscale

Damage quantifying

- **HYDROLYSIS**
- $I(A_1)/I(A_{II}) \sim 1$
- New parchment/leather
- Deteriorated sample

Early damage detection

- **GELATINIZATION**
- $\Delta \nu \sim 90 \text{ cm}^{-1}$
- New parchment/leather
- Deteriorated material

Fake identification

- **TRIPLE HELIX INTEGRITY**
- $I(A_1)/I(A_{II}) \sim 1$
- New parchment/leather
- Deteriorated material

P. Budruegeac, A. Cucos, L. Miu, Use of thermal analysis methods to assess the damage in the bookbindings of some religious books from XVIII century, stored in Romanian libraries, J Therm Anal Calorim (2014) 116:141–149.
Interdisciplinary approach

Unification of all these assessment methods to create a **reference toolkit for conservators and scientists** alike to assess the healthiness of objects / artefacts, the impact of past and future conservation treatments, and of climate change.

![Diagram](image)

**Applications Development**

**Image MHT system**
- image capturing device (ICD)
- precisely controlled heating block (HP)
- software commanding both heating element and image capturing

**CLEAR diagnostic system**
- analytical database
- software tool for evaluation and ranking damage, identifying main causes of deterioration, fingerprint the studied object
MHT method: thermal microscopy technique that measures the shrinkage activity of collagen fibres

Shrinkage is the macroscopic manifestation of thermal denaturation

In the first two intervals, A1 and B1, shrinkage discretely occurs in individual fibers and generally display higher activity in B1 interval. Fiber mass cooperatively shrinks in the C interval. The starting temperature of this interval is the shrinkage temperature, \( T_s \). Generally, shrinkage activity levels off through B2 and A2 intervals.

New collagen-based samples undergo the following changes as a function of temperature: no activity–A1–B1–C–B2–A2–complete shrinkage

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MHT method: a simple test for evaluating collagen deterioration

Shrinkage is visualised through a stereo microscope using reflected light as the motion of the fibres dispersed in water under constant heating rate (2 °C min\(^{-1}\)).

**MHT measurement system**

1: Caloris heating plate

1a: window slot for inserting the sample placed on a microscope slide with a concavity. Fibres are preliminary thoroughly wetted and separated in demineralised water for 10 min.

1b: window for viewing under the microscope

2: FP90 Central Processor for temperature programming

3: Steromicroscope equipped with a digital camera

4: PC
**Image MHT system and classic MHT method**

**imageMHT method**: automated system that measures the shrinkage activity of collagen fibres using image processing techniques

**Advantages**
- More reliable results secured by:
  - ALGORITHMS QUALITY, higher number of observed fibres, lower heating rate which enables to better discriminate between various motion types
  - AVOID HUMAN ERRORS (poor experience, fatigue, sight variability/problems, bad mood, etc.)
- Dramatic reduction of the operator time
- Portability and *in-situ* measurements
- Patentability

**imageMHT** – mainstream analytical technique for the primary evaluation of collagen-based artefacts, historical and archaeological objects

**Mid Term Results**
- **Hardware**: prototype of the precisely controlled heating block
- **Software**: experimental model for collagen fibres tracking and shrinkage intervals automatic detection
- **Testing of the experimental model**
**Improved features**

- **Heating/cooling interval**: $\Delta T = 15 \text{ – } 120 \degree C$
  
  *(Mettler Toledo heating plate: $\Delta T = 25 \text{ – } 100 \degree C$, but the system is stable only above 30 \degree C)*

- **Variable temperature increment**: 1, 2, 5 and 10 °C·min$^{-1}$
  
  *(Mettler Toledo heating plate: 2 °C·min$^{-1}$)*

**New functionalities**

- **Quick cooling to room temperature**

- **Miniaturized low-cost system**

**Gelatine and pre-gelatine fraction detection**

**MHT and DSC data comparison**

**Higher number of measurements**

**Increased portability: in situ measurements**
Automatic detection of shrinkage intervals using image algorithms for movement detection

Optical flow algorithms

Optical flow is the distribution of apparent velocities of movement of brightness patterns in an image.

Step 1: Finding the "good features to track"

As fibers are almost transparent and have thus the color of the background the best features to be tracked are their edges.

Step 2: Tracking the interest points in each sequence using the optical flow tracker.

ImageMHT test results

$T_s$ detected by optical flow algorithms (orange) compared with $T_s$ detected by the human eye (brown)

The mean absolute error of the estimated $T_s$ value was 1.1 °C for a series of 38 historical leather samples, less than the experimental accuracy of 2 °C determined for the classic MHT method by R. Larsen.

Features

• component of the diagnosis software
• elaborate and organise a huge amount of data (analytical and descriptive) on collagen artefacts of the Romanian patrimony with a common standard
• group the sub-samples from the same object and facilitate data correlation
• identify various deterioration patterns and suggest the most appropriate technique and procedure to detect such a pattern
• accounts for the animal species and age of each object

Advantage: support for monitoring and managing of the museum/library/archive environment and prioritization, and selection of the most appropriate methods for conservation to obtain the longest life for collection with the lowest resource employment
Related research: bilateral collaborations

• Assessment and mitigation of climate impact on library and archival heritage: experience, research, innovation (LIBER)
  Romania – Hungary bilateral collaboration PN II 671/2013

• Quantitative assessment of environmental impact on collagen-based materials for low-energy climate control in archives and museums (ENVICOLL)
  Romania – France, bilateral collaboration PN II 713/2013

• Advanced techniques and interdisciplinary studies for improved assessment of historical parchment documents (ParIS)
  Romania – Italy, bilateral collaboration PN II 638/2013
Young researchers career

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<th>Enrolment for PhD programmes related to the project topic</th>
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<tr>
<td>Cristina Carsote</td>
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<td>Thesis on <em>Damage assessment of historical parchment and leather</em></td>
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<tr>
<td>Claudiu Sendrea</td>
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<tr>
<td>Thesis on <em>Collagen based materials analysis using unilateral Nuclear Magnetic Resonance</em></td>
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<th>Participation in International Training Schools and Workshops</th>
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<tr>
<td>Cristina Carsote</td>
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<tr>
<td>Summer School on <em>Thermal Analysis and Calorimetry</em>, 11th Mediterranean Conference on Calorimetry and Thermal Analysis (MEDICTA 2013), Athens, Greece, 12 – 15 June 2013</td>
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<tr>
<td>Claudiu Sendrea</td>
</tr>
<tr>
<td>Ampere Summer School on <em>Analyzing Cultural Heritage using Portable Magnetic Resonance</em>, organised by the team of Prof Bernhard Blümich (Aachen University) which has been pioneering the field of mobile NMR and has developed MOUSE, Volterra, Italy, 12-15 June 2013</td>
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<tr>
<td>Oana Miu</td>
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<tr>
<td>Granted participation in the COST Action TD 1201 (COSCH) Training School on <em>Automated 3D documentation of CH artefacts with robotized structured light system</em>, Faculty of Mechatronics, Warsaw University of Technology, Warsaw, 25-27 November 2013</td>
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<th>Research stages within the Bilateral Collaboration Projects</th>
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<tr>
<td>Cristina Carsote</td>
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<td>Hungarian Academy of Sciences (August 2013), University of Turin (October 2013 and April 2014)</td>
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<tr>
<td>Irina Petrovici</td>
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<td>University of Turin (April 2014)</td>
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# Dissemination

## Publications (2012-2014)

- **ISI articles:** 5 published, 1 accepted, 2 submitted
- **Peer-reviewed articles:** 14 (2 indexed journals; 1 open-access journal; 2 indexed proceedings; 6 ISSN/ISBN conference proceedings; 3 conservation-restoration bulletins)
- **Books:** 1
- **Patents applications:** 1
- **Studies:** 1; software: 2; informatic services: 1

## Conference participation (2012-2014)

- **Invited lectures:** 8
- **Oral presentations:** 21
- **Poster presentations:** 20
Dissemination & Training

Seminar and Workshop organisation


**Media coverage**
TV: Omul si Timpul (6 oct 2012)
Radio Cultural (25 sept 2012)
Press release

http://www.e-conservationline.com/content/view/1093
Dissemination & Training

Seminar and Workshop organisation

Dissemination & Training

Seminar and Workshop organisation


You are warmly invited to attend this highly interesting event. Participation is free.

Contact: elena.badea@unito.it